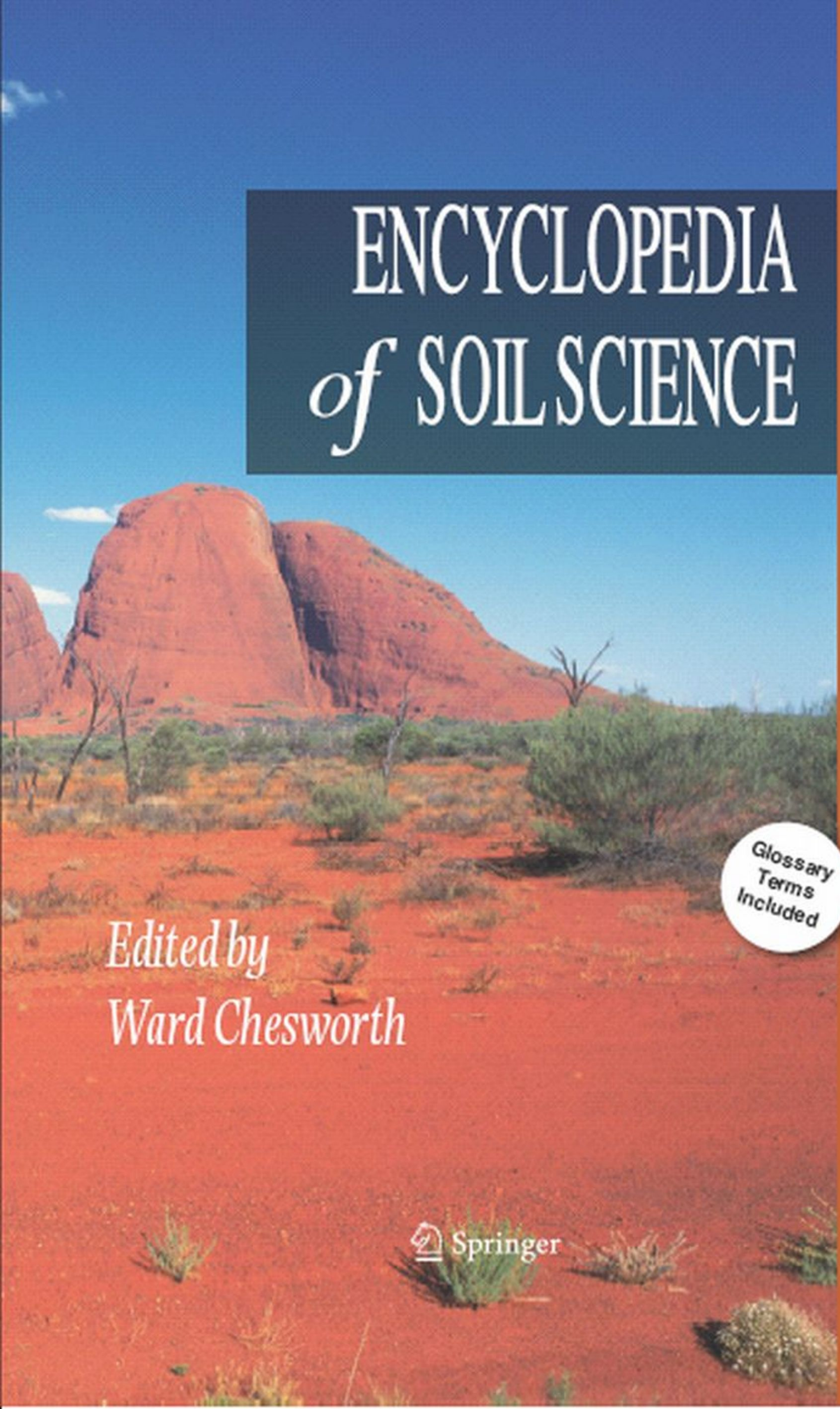


ENCYCLOPEDIA *of* SOIL SCIENCE

Glossary Terms Included

Edited by
Ward Chesworth

Springer

ENCYCLOPEDIA *of* EARTH SCIENCES SERIES

ENCYCLOPEDIA OF EARTH SCIENCES SERIES

ENCYCLOPEDIA *of* SOIL SCIENCE

edited by

WARD CHESWORTH
University of Guelph
Canada

Springer

ENCYCLOPEDIA *of*
SOIL SCIENCE

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN: 978-1-4020-3994-2 Springer Dordrecht, Berlin, Heidelberg, New York
This publication is available also as:
Electronic publication under ISBN 978-1-4020-3995-9 and
Print and electronic bundle under ISBN 978-1-4020-5127-2

Published by Springer
PO Box 17, 3300 AA Dordrecht, The Netherlands

Printed on acid-free paper

Cover photo: Mount Olga (Katatjula), 25 km west of Ayers Rock (reproduced courtesy of Getty Images, image 55862814, photographer: DAJ).

Encyclopedia of Earth Sciences Series

ENCYCLOPEDIA OF SOIL SCIENCE

Volume Editor

Ward Chesworth is Professor Emeritus of Geochemistry at the University of Guelph, Ontario, Canada. He co-edited Weathering, Soils and Paleosols, and three volumes of the annual Hammond Lecture Series broadcast in part by the Canadian Broadcasting Corporation: Malthus and the Third Millennium, Sustainable Development, and The Human Ecological Footprint. He co-wrote Perspectives on Canadian Geology. In 2003 he received the Halbouty Prize of the Geological Society of America, of which he is a Fellow.

Advisory Board

Aims of the Series

The *Encyclopedia of Earth Sciences Series* provides comprehensive and authoritative coverage of all the main areas in the Earth Sciences. Each volume comprises a focused and carefully chosen collection of contributions from leading names in the subject, with copious illustrations and reference lists.

These books represent one of the world's leading resources for the Earth Sciences community. Previous volumes are being updated and new works published so that the volumes will continue to be essential reading for all professional earth scientists, geologists, geophysicists, climatologists, and oceanographers as well as for teachers and students. See the back of this volume for a current list of titles in the *Encyclopedia of Earth Sciences Series*. Go to http://www.springerlink.com/reference-works/ to visit the "Earth Sciences Series" on-line.

About the Editors

Professor Charles W. Finkl has edited and/or contributed to more than 8 volumes in the *Encyclopedia of Earth Sciences Series*. For the past 25 years he has been the Executive Director of the Coastal Education & Research Foundation and Editor-in-Chief of the international *Journal of Coastal Research*. In addition to these duties, he is Principal Marine Geologist with Coastal Planning & Engineering, Inc. and Research Professor at Florida Atlantic University in Boca Raton, Florida, USA. He is a graduate of the University of Western Australia (Perth) and previously worked for a wholly owned Australian subsidiary of the International Nickel Company of Canada (INCO). During his career, he acquired field experience in Australia; the Caribbean; South America; SW Pacific islands; southern Africa; Western Europe; and the Pacific Northwest, Midwest, and Southeast USA.

Professor Michael Rampino has published more than 100 papers in professional journals including *Science*, *Nature*, and *Scientific American*. He has worked in such diverse fields as volcanology, planetary science, sedimentology, and climate studies, and has done field work on six continents. He is currently Associate Professor of Earth and Environmental Sciences at New York University and a consultant at NASA's Goddard Institute for Space Studies.

Founding Series Editor

Professor Rhodes W. Fairbridge† has edited more than 24 Encyclopedias in the Earth Sciences Series. During his career he has worked as a petroleum geologist in the Middle East, been a WW II intelligence officer in the SW Pacific and led expeditions to the Sahara, Arctic Canada, Arctic Scandinavia, Brazil and New Guinea. He was Emeritus Professor of Geology at Columbia University and was affiliated with the Goddard Institute for Space Studies.

Contents

Entries without author names are glossary terms

Entries without author names are glossary terms

Entries without author names are glossary terms

Entries without author names are glossary terms

Entries without author names are glossary terms

Entries without author names are glossary terms

Contributors

I. P. Abrol
Centre for the Advancement of Sustainable Agriculture
National Agricultural Science Centre (NASC) Complex
DPS Marg, Pusa
New Delhi 110 012, India
email: Iabrol@vsnl.com

Christine Alewell
Environmental Geosciences
University of Basel
Bernoullistr. 32
CH-4056 Basel, Switzerland
email: christine.alewell@unibas.ch

Gonzalo Almendros Martín
Center of Environmental Sciences
Soils Dept./Soil Biochemistry Lab.
c/ Serrano 115 dpdo
28006 Madrid, Spain
email: humus@ccma.csic.es

Olafur Arnalds
Keldnaholt
Reykjavik 112, Iceland
email: oa@lbhi.is

Emmanuelle Arnaud
(no address)

Richard W. Arnold
1145 Glenway
West Lafayette, IN 47906-2203, USA
email: CT9311@aol.com

M. A. Arshad
Agriculture Canada Research Station
Box 29
Beaverlodge, AB T0H 0C0, Canada
email: charlie.arshad@ualberta.ca

K. Auerswald
Lehrstuhl für Grünlandlehre, TU München
Am Hochanger 1
85354 Freising-Weihenstephan, Germany
email: auerswald@wzw.tum.de

Bryon W. Bache
The Chestnuts
The Green
Lolworth
Cambridge, CB3 8HF, UK

N. J. Barrow
22 Townsend Dale
Mt. Claremont
Western Australia 6010, Australia
email: nbarrow@bigpond.net.au

Valerie M. Behan-Pelletier
Agriculture and Agri-Food Canada
K.W. Neatby Bldg.
960 Carling Avenue
Ottawa, ON K1A 0C6, Canada
email: behanpv@agr.gc.ca

Friedrich H. Beinroth
Departamento de Agronomia y Suelos
Universidad de Puerto Rico
P.O. Box 9030
Mayaguez, PR 00681-9030, Puerto Rico
email: fred_beinroth@cca.uprm.edu

George R. Blake
2215 N 1400 E St
Provo, UT 84604, USA
email: blake001@umn.edu

Johannes Bouma
(no address)

Herman Bouwer
(no address)

Michael Brookfield
Department of Land Resource Science
University of Guelph
Guelph, ON N1G 2W1, Canada
email: mbrookfi@lrs.uoguelph.ca

Gaylon S. Campbell
Decagon Devices, Inc.
2365 NE Hopkins Court
Pullman, WA 99163, USA
email: gaylon@decagon.com

Marta Camps Arbestain
NEIKER
c/ Berreaga, 1
48160 Derio (Bizkaia), Spain
email: mcamps@neiker.net

G. E. Cardon
Department of Plants, Soils & Biometeorology
Utah State University, Ag. Science Building
4820 Old Main Hall
Logan, UT 84322-4820, USA
email: grantc@ext.usu.edu

Keith D. Cassel
Department of Soil Science
North Carolina State University
100 Derieux Street, Williams Hall
Raleigh, NC 27695-7619, USA
email: keith_cassel@ncsu.edu

Ward Chesworth
Department of Land Resource Science
University of Guelph
Guelph, ON N1G 2W1, Canada
email: wcheswor@uoguelph.ca

Brent E. Clothier
HortResearch Palmerston North
Private Bag 11030, Manawatu Mail Centre
Palmerston North 4442, New Zealand
email: bclothier@hortresearch.co.nz

Maurice G. Cook
Ecologistics Limited
Consultants in Environmental Management
3458 Leonard Street
Raleigh, NC 27607, USA
email: mgcook@mindspring.com

Miguel Cooper
Depto de Solos e Nutrição de Plantas, University of São Paulo
Avenida Pádua Dias, 11
13418-900 Piracicaba, Brazil
email: mcooper@esalq.usp.br

Randy A. Dahlgren
Land, Air and Water Resources, University of California
One Shields Avenue
Davis, CA 95616-8627, USA
email: radahlgren@ucdavis.edu

John W. Doran
School of Natural Resouces
University of Nebraska
119 Keim Hall
Lincoln, NE 68583-0934, USA
email: jdoran1@unl.edu

S. A. Ebelhar
University of Illinois
Dixon Springs Agricultural Center
Crop Sciences Division
RR1, Box 256, Simpson, IL 62985, USA
email: sebelhar@uiuc.edu

William Joseph Edmonds
1610 Kennedy Avenue
Blacksburg, VA 24060, USA

W. W. Emerson
(no address)

Hari Eswaran
USDA Natural Resources Conservation Service
1400 Independence Avenue (Room S-4836)
Washington, DC 20250, USA
email: hari.eswaran@wdc.usda.gov

L. J. Evans
Department of Land Resource Science
University of Guelph
Guelph, ON N1G 2W1, Canada
email: levans@lrs.uoguelph.ca

Rhodes W. Fairbridge
(deceased)

Steven B. Feldman
Consulting Mineralogist
238 West Main St.
Millbury, MA 01527, USA
email: zoeeko@verizon.net

Yucheng Feng
Department of Agronomy and Soils
University of Alabama
202 Funchess Hall
Auburn, AL 36849, USA
email: fengyuc@auburn.edu

Tiago O. Ferreira
Dep. de Ciências do Solo
CCA/UFC
Fortaleza, Brazil

Charles W. Finkl
Coastal Planning & Engineering, Inc.
CPE Coastal Geology & Geomatics
2481 Boca Raton Boulevard
Boca Raton, FL 33431, USA
email: cfinkl@coastalplanning.net

P. W. Ford
CSIRO Land & Water
GPO Box 1666
Canberra, ACT 2601, Australia
email: philip.ford@csiro.au

Carlota Garcia Paz
Departamento de Edafologia y Quimica Agricola
Facultad de Biologia
Universidade de Santiago de Compostela
Campus Universitario Sur s/n
15782 Santiago de Compostela, Spain
email: edcmgp@usc.es

Walter H. Gardner
1160 Telegraph Road #10
Washington, UT 84780, USA

Robert G. Gast
(no address)

James J. Germida
Department of Soil Science, University Saskatchewan
51 Campus Drive
Saskatoon, SK S7N 5A8, Canada
email: germida@sask.usask.ca

Carlo Gessa
Dipartimento di Scienze e Technologie Agroambientali
Universita di Bologna
Via Fanin, 40
40100 Bologna, Italy
email: carloemanuele.gessa@unibo.it

Jan Gliński
Institute of Agrophysics, Polish Academy of Sciences
Doświadczalna 4
20290 Lublin 27, Poland
email: jglinski@demeter.ipan.lublin.pl

Pieter H. Groenevelt
Department of Land Resource Science
University of Guelph
Guelph, ON N1G 2W1, Canada
email: pgroenev@uoguelph.ca

Paul R. Grossl
Department of Plants, Soils, and Biometeorology
Utah State University
4820 Old Main Hill, AGS 348
Logan, UT 84322-4820, USA
email: grossl@cc.usu.edu

Raj K. Gupta
ICARDA – CAC Regional Office
P.O. Box 4564, Tashkent
Uzbekistan

Amos Hadas
Institute of Soils, Water and Environmental Sciences
The Volcani Center, A.R.O.
P.O. Box 6
Bet Dagan 50250, Israel
email: ahadas@volcani.agri.gov.il

R. David Hammer
National Leader, Soil Survey Investigations
USDA-NRCS-NSSC
Federal Building, Room 152
100 Centennial Mall North
Lincoln, NE 68508-3866, USA
phone: 402-437-5321
email: david.hammer@lin.usda.gov

R. J. Hanks
1305 E. 2050 N.
Logan, UT 84341, USA
email: jhanks@cc.usu.edu

Roger Hartmann
Agr Sci, Coupre Links 65
State University of Ghent
Ghent 9000, Belgium
email: roger.hartmann@ugent.be

Richard J. Heck
Department of Land Resource Science
University of Guelph
Guelph, ON N1G 2W1, Canada
email: rheck@uoguelph.ca

Michael Herlihy
(no address)

Stuart B. Hill
School of Education, University of Western Sydney
Locked Bag 1797
Penrith South DC
NSW 1797, Australia
email: s.hill@uws.edu.au

William R. Horwath
3226 Plant and Environmental Science Building
University of California
One Shields Avenue
Davis, CA 95616-8627, USA
email: wrhorwath@ucdavis.edu

L. R. Hossner
Department of Soils & Crop Sciences, Texas A&M University
370 Olsen Blvd
College Station, TX 7784-2474, USA
email: lhossner@ag.tamu.edu

P. M. Huang
Department of Soil Science, University Saskatchewan
51 Campus Drive
Saskatoon, SK S7N 5A8, Canada
email: Pan.Huang@usask.ca

William F. Jaynes
Plant and Soil Science, MS 2122
Texas Tech University
Lubbock, TX 79409, USA
email: william.jaynes@ttu.edu

M. B. Kirkham
Department of Agronomy
Kansas State University
2004 Throckmorton Hall
Manhattan, KS 66506, USA
email: mbk@ksu.edu

Krystyna Konstankiewicz
Institute of Agrophysics
Polish Academy of Science
ul. Doświadczalna 4
20-290 Lublin 27, Poland
email: konst@demeter.ipan.lublin.pl

Nikola Kostic
Faculty of Agriculture, University of Belgrade
Nemanjina 6
11080 Belgrade, Yugoslavia
email: nkostic@agrifaculty.bg.ac.yu

J. Lag
(deceased)

David M. Lavigne
International Fund for Animal Welfare
40 Norwich Street East
Guelph, ON N1H 2G6, Canada
email: dlavigne@ifaw.org

David T. Lewis
2520 Penny Lane
Rogers, AR 72758, USA

Jerzy Lipiec
Institute of Agrophysics, Polish Academy of Sciences
ul. Doświadczalna 4
20-290 Lublin 27, Poland
email: lipiec@demeter.ipan.lublin.pl

Richard H. Loeppert
Department of Soil and Crop Sciences, Texas A&M University
370 Olsen Bldv
College Station, TX 77843-2474, USA
email: r-loeppert@tamu.edu

Felipe Macías Vázquez
Departamento de Edafologia y Quimica Agricola
Facultad de Biologia, Universidade de Santiago de Compostela
Campus Universitario Sur s/n
15782 Santiago de Compostela, Spain
email: edfmac@usc.es

Antonio Martínez Cortizas
Departamento de Edafologia y Quimica Agricola
Facultad de Biologia, Universidade de Santiago de Compostela
Campus Universiatario Sur s/n
15782 Santiago de Compostela, Spain
email: edantxon@usc.es

Burl D. Meek
(no address)

Konrad Mengel
Institut für Pflanzenernährung, IFZ, Justus Liebig Universität
Heinrich-Buff-Ring 26-32
35392 Gießen, Germany
email: konrad.mengel@ernaehrung.uni-giessen.de

Erika Micheli
Soil Science and Agrochemistry Department
Szent Istvan University
Páter Károly u. 1
2100 Godollo, Hungary
email: Micheli.Erika@mkk.szie.hu

Lloyd N. Mielke
P.O. Box 98
Gallatin Gateway, MT 59730, USA
email: ajjones@littleappletech.com

Fred P. Miller
(deceased)

Myron J. Mitchell
Environmental Sciences and Forest Biology
SUNY, 210 Illick Hall
1 Forestry Drive
Syracuse, NY 13210-2788, USA
email: mitchell@syr.edu

Carmela Monterroso Martinez
Departamento de Edafologia y Quimica Agricola
Facultad de Biologia, Universidad de Santiago de Compostela
Campus Sur, 15782 Santiago de Compostela, Spain
email: edcarmel@lugo.usc.es

H. J. Morel-Seytoux
57 Selby Lane
Atherton, CA 94027-3926, USA
email: hydroprose@batnet.com

Y. Mualem
Hebrew University of Jerusalem
Department of Soil and Water Sciences
P.O. Box 12
Rehovot 76100, Israel

J. C. Nóvoa Muñoz
Departamento Bioloxía Vexetal e Ciencias do Solo
Facultade de Ciencias, Universidade de Vigo
As Lagoas s/n
32004 Ourense, Spain
email: edjuanca@uvigo.es

Jnakwa O. A. Odeh
Faculty of Agriculture
A05-JRA McMillan, The University of Sydney
NSW 2006, Australia
email: i.odeh@usyd.edu.au

J. J. Oertli
Schaienweg 25
4107 Ettingen, Switzerland
email: jakob_oertli@yahoo.de

D. S. Orlov
(no address)

Xose L. Otero
Departamento de Edafologia y Quimica Agricola
Facultad de Biologia, Campus Sur s/n
15782 Santiago de Compostela, Spain
email: edajax@usc.es

Marcello Pagliai
Istituto Sperimentale per lo Studio e la Difesa del Suolo
CRA-ISSDS
Piazza D'Azeglio, 30
50121 Firenze, Italy
email: marcello.pagliai@entecra.it

Quirino Paris
Department of Agricultural and Resource Economics
3105 Social Science and Humanities Bldg.
University of California
One Shields Avenue
Davis, CA 95616, USA
email: paris@primal.ucdavis.edu

Gary W. Parkin
Department of Land Resource Science, University of Guelph
Guelph, ON N1G 2W1, Canada
email: gparkin@uoguelph.ca

J.-Y. Parlange
Department of Biological and Environmental Engineering
Cornell University
Ithaca, NY 14853-5701, USA
email: jp58@cornell.edu

Keith Paustian
Natural Resources Ecology Lab
Colorado State University
Ft. Collins, CO 80523, USA
email: keithp@nrel.colostate.edu

Augusto Perez-Alberti
Departamento de Geografia
Universidad de Santiago
Plaza de la Universidad
15703 Santiago de Compostela, Spain
email: xepalber@usc.es

X. Pontevedra Pombal
Departamento Edafologia y Quimica Agricola
Facultad de Biologia, Universidade de Santiago de Compostela
Campus Universitario Sur s/n
15782 Santiago de Compostela, Spain
email: edpombal@usc.es

Jarosław Pytka
Institute of Agrophysics PAS
ul. Doświadczalna 4, P.O. Box 201
20-290 Lublin 27, Poland
email: j.pytka@demeter.ipan.lublin.pl

Hervé Quiquampoix
UMR Rhizosphère et Symbiose, INRA-ENSAM
2 Place Pierre Viala
34060 Montpellier Cedex 1, France
email: quiquamp@ensam.inra.fr

William O. Rasmussen
Department of Agricultural and Biosystems Engineering
The University of Arizona
Tucson, AZ 85721, USA
email: rasmussw@email.arizona.edu

Ernest Rawitz
(deceased)

Paul F. Reich
Soil Survey Division
USDA-Natural Resources Conservation Service
Room 4250 South Building, 14th & Independence Ave, SW
Washington, DC 20250, USA
email: paul.reich@wdc.usda.gov

Wayne P. Robarge
Department of Soil Science, North Carolina State University
P.O. Box 7619
Raleigh, NC 27695-7619, USA
email: wayne_robarge@ncsu.edu

Pedro A. Sanchez
(no address)

Randall J. Schaetzl
Department of Geography, Michigan State University
128 Geography Building
East Lansing, MI 48824-1117, USA
email: soils@msu.edu

G. O. Schwab
(deceased)

Udo Schwertmann
Institut für Bodenkunde, TU München
Am Hochanger 2
85354 Freising-Weihenstephan, Germany
email: uschwert@wzw.tum.de

H. Magdi Selim
Department of Agronomy and Environmental Management
Louisiana State University
Sturgis Hall
Baton Rouge, LA 70803, USA
email: mselim@agcenter.lsu.edu

Johnson Semoka
Sokoine University of Agriculture, Department of Soil Science
P.O. Box 3008
Morogoro, Tanzania
email: jsemoka@suanet.ac.tz

C. Shang
Department of Crop and Soil Environmental Sciences
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061-0404, USA
email: chshang@vt.edu

Arieh Singer
Seagram Centre for Soil and Water Sciences
Hebrew University of Jerusalem
P.O. Box 12
Rehovot 76100, Israel
email: singer@agri.huji.ac.il

Peter Smart
Department of Civil Engineering, University of Glasgow
Glascow, G12 8LT, UK
email: geofun@gla.ac.uk

Yoong K. Soon
Beaverlodge Research Farm
P.O. Box 29
Beaverlodge, AB T0H 0C0, Canada
email: Soony@agr.gc.ca

Otto Spaargaren
World Data Centre for Soils
P.O. Box 353
6700 AJ Wageningen, The Netherlands
email: otto.spaargaren@wur.nl

Donald L. Sparks
Plant and Soil Sciences, University of Delaware
152 Townsend Hall
Newark, DE 19716, USA
email: dlsparks@udel.edu

Garrison Sposito
Department of Environmental Science, Policy and Management
College of Natural Resources, University of California
Berkeley, CA 94720-3114, USA
email: gsposito@nature.berkeley.edu

F. Stagnitti
School of Life and Environmental Sciences and Centre for Applied
Dynamical Systems & Environmental Modelling
Deakin University
P.O. Box 423
Warrnambool 3280, Australia
email: frank.stagnitti@deakin.edu.au

Siobhán Staunton
UMR Rhizosphère & Symbiose
INRA, place Viala
34060 Montpellier Cedex, France
email: staunton@ensam.inra.fr

T. S. Steenhuis
Department of Biological and Environmental Engineering
Cornell University
Ithaca, NY 14853-5701, USA
email: tss1@cornell.edu

Gary G. Steinhardt
Department of Agronomy
Lilly Hall of Life Sciences
Purdue University
915 W. State Street
West Lafayette, IN 47907-2054, USA
email: gsteinhardt@purdue.edu

Witold Stępniewski
Wydział Inżynierii Środowiska Politechniki Lubelskiej
ul. Nadbystrzycka 40B
20-618 Lublin, Poland
email: W.Stepniewski@fenix.pol.lublin.pl

Georges Stoops
Laboratorium voor Mineralogie, Petrologie en Micropedologie
Universiteit Gent
Krijgslaan 281, S8
Gent 9000, Belgium
email: Georges.stoops@UGent.be

Peter van Straaten
Department of Land Resource Science
University of Guelph
Guelph, ON N1G 2W1, Canada
email: pvanstra@uoguelph.ca

Teresa Taboada Rodríguez
Departamento Edafologia y Quimica Agricola
Facultad de Biologia
Universidade de Santiago de Compostela
Campus Universitario Sur s/n
15782 Santiago de Compostela, Spain
email: edteresa@usc.es

B. K. G. Theng
Landcare Research
Private Bag 11052
Manawatu Mail Centre
Palmerston North 4442, New Zealand
email: thengb@landcareresearch.co.nz

Paul W. Unger
3603 Thurman St.
Amarillo, TX 79109, USA
email: pwunger@suddenlink.net

Pablo Vidal-Torrado
Depto de Ciencia do Solo, ESALQ/USP
University of São Paulo
Avenida Pádua Dias, 11
13418-900 Piracicaba, Brazil
email: pablo@esalq.usp.br

Jon S. Warland
Department of Land Resource Science
University of Guelph
Guelph, ON N1G 2W1, Canada
email: jwarland@uoguelph.ca

Charles E. Weaver
Earth and Atmospheric Sciences
Georgia Institute of Technology
311 Ferst Drive
Atlanta, GA 30332-0340, USA
email: cw5@mail.gatech.edu

W. O. Williamson
College of Earth and Mineral Sciences
University of Pennsylvania
0216 Steidle Building
University Park, PA 16802, USA

Hans F. Winterkorn
(no address)

C. Wesley Wood
Department of Agronomy and Soils
234 Funchess Hall, Auburn University
Auburn, AL 36849-5412, USA
email: woodcha@auburn.edu

Eiju Yatsu
91 Iwase
Matsudo-shi 271-0076, Japan

Iain M. Young
Scottish Informatics, Mathematics, Biology, and Statistics
(SIMBIOS) Centre, University of Abertay
Bell Street
Dundee, DD1 1HG, UK
email: I.Young@abertay.ac.uk

R. J. Zasoski
Soils and Biochemistry Program
University of California
One Shields Avenue
Davis, CA 95616-8627, USA
email: rjzasoski@ucdavis.edu

Lucian W. Zelazny
Department of Crop and Soil Environmental Sciences
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061-0404, USA
email: zelazny@vt.edu

Preface

> "It is interesting to contemplate a tangled bank, clothed with many plants of many kinds, with birds singing on the bushes, with various insects flitting about, and with worms crawling through the damp earth, and to reflect that these elaborately constructed forms, so different from each other, and dependent upon each other in so complex a manner, have all been produced by laws acting around us."
>
> Charles Darwin[1]

Darwin's tangled bank is the biosphere in poetic microcosm, and the "damp earth" he refers to is soil. Soil is arguably the most complex of all geological materials, a combination of mineral and organic constituents in solid, aqueous and gaseous forms, organized into a loose, porous, horizonated, plant-bearing material, that is constantly changing. It forms as a result of a complex series of interactions and feedbacks between lithosphere, hydrosphere, atmosphere and, biosphere. As the natural geological cover of most of the land surface of the earth, it is the focus of this encyclopedia.

Alfred North Whitehead[2] once wrote that the European philosophical tradition "consists of a series of footnotes to Plato". It might similarly be said that human history is little more than a footnote to the exploitation of soil that started with the Agricultural, or Neolithic, Revolution, 10 000 years ago. All the magnificent cultural artifacts of civilization, from cathedrals to efficient plumbing systems, are the direct heritage of this exploitation, and the big question today concerns what humanity must do to sustain the heritage. At the most fundamental level this is equivalent to asking what we must do to sustain our food-production system.

By way of answer, consider Felipe Fernández-Armesto's[3] definition of civilization: "a relationship to the natural environment, recrafted by the civilizing impulse, to meet human demands". To sustain the food-production system, we need to avoid making our demands so great, and our recrafting so extreme, that the biosphere in which we are embedded breaks down as a life-support system. Unfortunately, agriculture, the very technology we depend upon to maintain our complex societies, is strategically situated to threaten the biosphere at a vulnerable bottleneck, the soil. Soil occupies a kind of choke point through which virtually all of the fluxes of energy and matter that keep the terrestrial biosphere functioning, are squeezed between different compartments of the landscape, and for about ten millennia we have been commandeering an ever growing area of the soil for human use.

Our ecological footprint has expanded to modify, more or less completely, about a third of the earth's soils, while threatening a second third. Most of the expansion has happened since the steam locomotive opened up the grassland biomes of the western hemisphere to the markets and bellies of the Old World. Cheap energy from fossil fuel made the expansion possible, driving the human population, the ultimate crop of the soil from the point of view of *Homo sapiens*, to an exuberant burst of exponential growth. The pressure of our numbers requires that the soil provide us with ever more food, fibre and energy, as well as living space. As a consequence we have become a potent geological force, unique to the Holocene, and our activities in manipulating the soil, constitute a massive intervention into the external geological cycle. All the natural tendencies for soil to erode, to acidify, to salinize, or to become hydromorphic, depending on factors such as climate, texture and drainage, have been magnified and exaggerated at certain times and in certain places, into pathological states. Now we are a threat not only to terrestrial biomes, but also to the ecology of freshwater biomes, and even the sea as sediment loaded with agrichemicals contributes to hypoxia along coastal regions.

The fact that we have not yet invented an agricultural system that is truly sustainable means that we cannot say with any certainty that our civilization is sustainable. Disasters such as the dustbowl in the Midwestern USA, and extensive salinization in the region of the Aral Sea, have seen systems fail within two or three generations, and even where agriculture has persisted for five thousand years or more, Egypt and Northern China being the prime examples, it has been because of fortunate geological circumstances rather than human ingenuity. Hence the

---

[1] Darwin, Charles. 1859. On the Origin of Species by means of Natural Selection, or the Preservation of favoured races in the struggle for life. London: John Murray. 502 p.

[2] Whitehead, A. N. 1929. Process and reality, an essay in cosmology. Gifford lectures delivered in the University of Edinburgh during the session 1927–1928. Cambridge University Press, 1929. 509 p.

[3] Fernández-Armesto, Felipe. 2001. Civilizations: culture, ambition, and the transformation of nature. New York: Free Press. 545 p.

pessimism of Angus Martin[4], who, writing as an ecologist, asks: "How many millennia of deforestation, dust storms and soil erosion has it taken for us to realize that our agricultural methodology has had serious flaws in it from the start?"

Yet, history shows that we have the intelligence, imagination and courage to tackle large issues such as the problem of sustainability, and compilations such as this encyclopedia are proof that our knowledge of soils, incomplete and provisional as all science is, has grown comprehensive enough to solve the technical problems involved. If we could figure out how to solve the socio-political ones, humanity might yet achieve a sustainable civilization. Without doubt it will demand a monumental effort of cooperation on a global scale. Bill Rees[5], inventor of the concept of the ecological footprint, puts it this way: "Sustainability is the greatest collective exercise the human race will ever have to undertake".

The objective of this second edition of the Encyclopedia of Soil Science is, in a single volume, to provide an entry point into the study of that part of the solid earth that is absolutely necessary, not only to the sustainability of civilization, but more fundamentally to the sustainability of a flourishing biosphere. The basic facts, concepts and uses of the soil are presented alphabetically in the volume, which combines features of both encyclopedia and glossary. The longer articles characteristic of the former are combined with shorter, dictionary-style definitions of frequently used terms, commonly found in the latter. The intended readership is the scientist, engineer, technologist, environmentalist and planner, with an interest in soils and a concern for planet Earth. The Soil Science volume, In combination with other volumes in Springer's Encyclopedia of Earth Sciences[6], this volume on Soil Science, contributes to a comprehensive and rigorous view of the environment in which we live.

The original Encyclopedia of Soil Science was compiled by Rhodes W. Fairbridge and Charles W. Finkl, Jnr., and first published as long ago as 1979. This second edition builds on their work, and I was fortunate enough to be able to call upon those two very experienced editors for advice.

I am sorry that Rhodes did not live to see this volume in print.

Ward Chesworth

---

[4] Martin, Angus. 1975. The Last Generation: the End of Survival. Glasgow: Fontana. 188 p.

[5] Rees, William E. 2007. Human eco-footprints: straying off the sustainability trail. The Kenneth R. Farrell Distinguished Public Policy Lectureship, delivered at the University of Guelph, May 16, 2007.

[6] In particular the volumes covering Environmental Science, Geomorphology, Geochemistry, Sedimentology, Field Geology, Applied Geology, Hydrology and Water Resources, Remote Sensing, World Climatology, and Coastal Science.

A

A HORIZON

See *Horizon, Profile, Horizon Designations*.

ABIOTIC

Describes soil constituents (for example quartz, kaolinite), processes (hydrolysis, redox reactions), or factors (temperature, relative humidity, salinity for example), that are inorganic in nature, and that are capable of forming or acting in the absence of life. However, since even the most rudimentary of soils contains organisms, organic constituents and processes inevitably interact with and impact upon the inorganic ones. In 1840, Justus von Leibig suggested that a biological population is limited by whichever extensive factor (particularly abiotic ones such as inorganic nutrient concentrations) is in shortest supply (Lomolino et al., 2006, p.79).

Bibliography

Lomolino, M.V., Riddle, B.R., and Brown, T.H., 2006. *Biogeography*, 3rd edn. Sunderland, MA: Sinauer Associates, 845 pp.

Cross-reference

Law of the Minimum

ABRASION

The wearing away by surface friction of solid bodies (minerals and rocks for example) when brought into contact with each other by such agents of erosion as wind, water, ice or animals (including *Homo sapiens*). The reaction of a mineral with water at an abraded surface yields a characteristic pH. A typical range of abrasion pH is 6–7 for clay minerals and quartz, 7–8 for micas, 8 for calcite, 8–11 for silicates other than micas (Porta et al., p 442).

Bibliography

Porta, J., Lopez, M., and Roquero, C., 1994. *Edafologia para la agricultura y el medio ambiente.* Madrid: Editions Mundi-Prensa, 807 pp.

ABRUPT TEXTURAL CHANGE

A phrase used in the WRB Classification to mean either a doubling of the clay content within a vertical distance of 7.5 cm if the overlying horizon has less than 20% clay, or an absolute increase in clay of 20% within 7.5 cm if the overlying horizon has 20% or more clay. In this case some part of the lower horizon should have at least twice the clay content of the upper horizon (FAO, 2001, Annex 2).

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

ABSORPTION

The assimilation of one substance by another, or by an organism (water or aqueous solution by plants for example). Absorption of chemical elements by roots may modify the chemistry (pH and redox potential for example) in the immediate soil environment. This has been called the “rhizosphere effect” (McBride, 1994, P. 310).

Bibliography

McBride, M.B., 1994. *Environmental Chemistry of Soils*. New York: Oxford University Press, 406 pp.

Cross-reference

Sorption Phenomena

ACID DEPOSITION EFFECTS ON SOILS

Acid deposition has been implicated as a factor contributing to forest decline and surface water acidification in eastern North America and Europe. Acid deposition increased continuously in North America and Europe during the 1900s reaching peak levels in the 1970–1980s. In contrast, acid deposition in northeast Asia has increased rapidly in the past decade due to industrial development and will probably exceed levels observed previously in the most polluted areas of central and eastern Europe (Grübler, 1998). Increased emissions will severely threaten the sustainable basis of many natural and agricultural ecosystems in the region. Although unequivocal evidence directly linking acidic deposition to ecosystem damage may often be lacking, there is considerable data implicating acid deposition with recent deterioration in the health of terrestrial and aquatic ecosystems.

The mean annual pH of precipitation in eastern North America and Europe is in the range of 3.0 to 4.7; however, individual storm events have been recorded with pH values as low as 2. The deposition of anthropogenic sources of H^+ in the most polluted regions of Europe exceeds 7 $kmol_c\ ha^{-1}\ yr^{-1}$ compared to about 1 $kmol_c\ ha^{-1}\ yr^{-1}$ in eastern North America (Pearson and Stewart, 1993; NADP/NTN, 2004). The impact of acid deposition on terrestrial and aquatic ecosystems is mediated primarily through interactions with soil biogeochemical processes. Ecosystems in humid environments experience an internal production of acidity associated with biogeochemical processes that may overshadow the effects of acid deposition. However, for a number of ecosystems, primarily in Europe, the external sources of acidity greatly exceed the contribution from internal sources (van Breemen et al., 1984). Some terrestrial ecosystems are relatively resilient to strong acid loadings due to acid buffering reactions by soils that neutralize the acid (H^+) inputs. While a number of intermediate buffering reactions occur, the ultimate acid sink is chemical weathering. If acidic inputs exceed the soil buffering capacity, the soil becomes acidified which can lead to the export of ecologically significant quantities of H^+ and aluminum to surface waters. In addition, soil acidification may increase leaching of plant nutrients (e.g., NO_3^-, SO_4^{2-}), decrease levels of nutrient cations (e.g., Ca^{2+}, Mg^{2+}, K^+), increase concentrations of potentially toxic metals (e.g., Al^{3+}, Cu^{2+}, Zn^{2+}), alter the solubility of organic compounds, and impose changes in populations of soil organisms.

Forms and quantities of acidic deposition

The principal anthropogenic sources of acid deposition are sulfuric acid (H_2SO_4), nitric acid (HNO_3) and ammonium (NH_4^+) derived from sulfur dioxide (SO_2), nitrogen oxides (NO_x), and ammonia (NH_3), respectively. These compounds are emitted primarily by the burning of fossil fuels, industrial activities and agricultural and livestock production. Ammonia interacts in the atmosphere and on the surface of vegetation to form NH_4^+, which may subsequently undergo nitrification in the soil to produce nitric acid:

$$NH_4^+ + 2O_2 = 2H^+ + NO_3^- + H_2O$$

Bulk precipitation includes both wet (soluble components) and dry (particulate material and washout of adsorbed/reacted gases captured by vegetation) deposition. Dry deposition appears to be roughly equivalent to wet deposition for sulfate and nitrate (Binkley et al., 1989), while dry deposition appears to be the dominant source of NH_4^+ (van Breemen et al., 1982). Cloud water (fog) deposits are especially concentrated having 5 to 30 times more acidic components than the bulk precipitation originating from the same air mass. Thus, those ecosystems receiving frequent inputs of fog may receive significantly greater inputs of acidic components. Total deposition rates for all acidic components are considerably higher in Europe than for eastern North America (Table A1). Emission of SO_2 and sulfate deposition have declined 38–82% in Europe and 52% in the United States over the past decade, while emissions of NO_x and nitrogen deposition showed a smaller declined of 17–20% (Prechtel et al., 2001; Wright et al., 2001; U.S.-EPA, 2003).

Soil processes neutralizing acidic inputs

In many ecosystems, acid consumption may be attributed to the replacement of the normal weak acids, generally carbonic and organic acids, by strong acids (e.g., H_2SO_4 and HNO_3). In this case, acid deposition does not add to the background acidity of the system, but instead replaces it altogether by suppressing the dissociation of these weak acids. Therefore, there may be no net increase in the rate of soil acidification due to acidic deposition of strong acids.

Both internal and external sources of acidity are largely neutralized within the soil profile by a number of coupled reactions between the soil solution, solid-phase, and biological components (van Breemen et al., 1983). If these reactions fail to completely neutralize the acidity, the excess H^+ is exported from the ecosystem in the drainage waters. The dominant proton consuming processes responsible for neutralizing the acidity are shown in Table A2.

Weathering of primary minerals

The ultimate acid sink in soils is the weathering of primary minerals. The process of hydrolysis results in the transfer of

Table A1 Total deposition (wet + dry deposition) rates $kmol_c\ ha^{-1}\ yr^{-1}$ of acid and acid forming components in atmospheric deposition

Acid component	Eastern North America	Highest deposition regions of Europe
Sulfate	0.2 – 1.3[†][§]	5.2[‡]
Nitrate	0.13 – 0.43[†][§]	1.1 – 1.2[‡][¶]
Ammonium	0.06 – 0.55[†][§]	3.4 – 7.2[¥]

[†] Binkley et al., 1989; [§] NADP/NTN, 2004; [‡] Ulrich, 1984; [¶] van Breemen and van Dijk, 1988; [¥] Pearson and Stewart, 1993.

Table A2 Examples of important reactions active in the consumption and production of H^+ in soils

H^+-consuming reaction		H^+-producing reaction
Weathering	$M^+(AlSi_3O_8) + 7H_2O + H^+ = M^+ + Al(OH)_3 + 3H_4SiO_4$	Reverse weathering
H^+/M^{n+} exchange	$M^{n+}\text{-exch} + nH^+ = nH^+\text{-exch} + M^{n+}$	M^{n+}/H^+ exchange
Anion Adsorption	$\text{Ads-(OH)}_2 + A^{n-} + nH^+ = \text{Ads-A} + nH_2O$	Anion desorption
Assimilation of anions	$n\text{R-OH} + A^{n-}(aq) + nH^+(aq) = nH_2O + n\text{R-A}$	Mineralization of anions
Al dissolution	$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	Al precipitation

M = cation; *A* = anion; *exch* = cation exchange site; *Ads* = adsorption site; *R* = organic molecule.

acid (H^+) to CO_3^{2-} and HCO_3^- to form HCO_3^- and H_2CO_3, respectively, in the weathering of carbonate minerals and to $H_3SiO_4^-$ to form H_4SiO_4 in the weathering of silicate minerals. Associated with this H^+ transfer is the release of base cations (e.g., Ca^{2+}, Mg^{2+}, K^+ and Na^+) from the primary minerals. Weathering of carbonates and silicates proceeds simultaneously in the soil environment; however, carbonate weathering reactions are kinetically much more rapid. Carbonate minerals are present in some sedimentary rocks and their metamorphic equivalents, in the scarce igneous rock carbonatite, and in soils found in arid and semi-arid environments. When carbonate minerals are present, the soil is capable of neutralizing acidic deposition rapidly and totally, maintaining the solution pH near a value of 8. As the carbonates become depleted, the pH of the soil will drop and dissolution of silicates becomes the dominant weathering reaction.

Silicate minerals comprise greater than 90% of the minerals present in the Earth's crust and represent an almost unlimited sink for neutralization of acidic deposition. Hydrolysis of silicate minerals results in the release of base cations from the silicate lattice with the consumption of protons equal to the equivalents of base cations released. The amount and rate of acid neutralization depend on the base cation concentration of the mineral, the structure (stability) of the mineral, amount of surface area exposed to weathering, temperature, and the H^+ concentration of the soil solution. When comparing basalt versus granite, basalt will have a greater acid neutralization capacity due to higher concentrations of base cations and a mineralogical assemblage that is less stable with respect to chemical weathering (e.g., olivine and pyroxene in basalt versus quartz and K-feldspar in granite). Deeper soils with finer particle-sized parent material (e.g., glacial till versus bedrock) provide a greater surface area for chemical weathering to act upon. Weathering rates show an exponential increase with increasing temperature resulting in greater acid neutralizing capacity in warmer regions (White and Blum, 1995). Weathering rates increase with increasing H^+ concentrations below a pH value of 5; the H^+ dependence of weathering rates is equal to about $[H^+]^{0.5}$.

While weathering of silicate minerals theoretically has a high capacity to neutralize acid, silicate weathering is a non-equilibrium process limited by reaction kinetics. In reviews of weathering rates based on watershed mass balance studies, Sverdrup and Warfvinge (1988) and Sverdrup (1990) found that most watersheds have a proton consumption rate between 0.1 and 1.5 kmol H^+ ha^{-1} yr^{-1}. These rates compare with acid deposition rates of up to 7 kmol H^+ ha^{-1} yr^{-1}. Therefore, silicate-weathering reactions do not keep pace with the higher loadings of acid deposition, especially when considering that internal proton sources add to the total amount of proton loading in an ecosystem.

Cation exchange reactions

Cation exchange reactions are similar to weathering reactions in their effect on acid/base chemistry. The negatively charged exchange sites are electrically balanced by base cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) and acidic cations (Al^{3+} and H^+). Exchange reactions neutralize acidity by exchanging base cations for H^+ leading to a decrease in the base saturation. In contrast to weathering reactions, exchange reactions are reversible and very rapid. Thus, the soil solution rapidly equilibrates with exchangeable cations, and the equilibrium between the soil solution and exchangeable cations controls the soil solution composition in the short-term. Base cations liberated by mineral weathering are redistributed between the soil solution and exchange sites to attain a new equilibrium. The pool of exchangeable base cations available for pH buffering is the product of the base saturation times the cation exchange capacity (CEC). As long as the base saturation remains above about 10–20%, the acid load in the soil solution will be effectively buffered by exchange reactions. When the base saturation is depleted below levels of 10–20%, those remaining base cations are more tightly held and are less available for pH buffering (Reuss and Johnson, 1986). The base cations released from the exchange sites can be leached from the soil profile with mobile anions (e.g., SO_4^{2-} and NO_3^-) originating from strong acid inputs. Some acid neutralization also occurs as pH dependent exchange sites become protonated leading to a loss of CEC as the pH is lowered.

Anion retention

The retention of anions by sorption or biological uptake consumes protons by removing mobile anions that would otherwise induce the leaching of base cations from the soil profile (Figure A1). Sulfate has a moderate capacity for sorption while NO_3^- has essentially no affinity for sorption to the solid-phase. Sulfate sorption is a concentration dependent process, which means that the capacity to sorb SO_4^{2-} increases as the soil solution SO_4^{2-} concentrations increase. As the SO_4^{2-} retention capacity of soils is exceeded, SO_4^{2-} is leached to deeper soil layers and ultimately to surface waters. Because SO_4^{2-} leaching is always accompanied by cation leaching, leaching of SO_4^{2-} will cause soil acidification (depletion of base cation pools). Sulfate sorption occurs primarily on the surfaces of Al/Fe oxides and hydroxides through a combination of specific and non-specific sorption mechanisms. Thus, soils containing high concentrations of these minerals will have a greater affinity for anion sorption. Anion sorption capacity also increases as the solution pH drops reaching a maximum at approximately pH 4. The SO_4^{2-} sorption reaction is rapid and it appears that the process is not completely reversible leading to an irreversibly adsorbed SO_4^{2-} fraction.

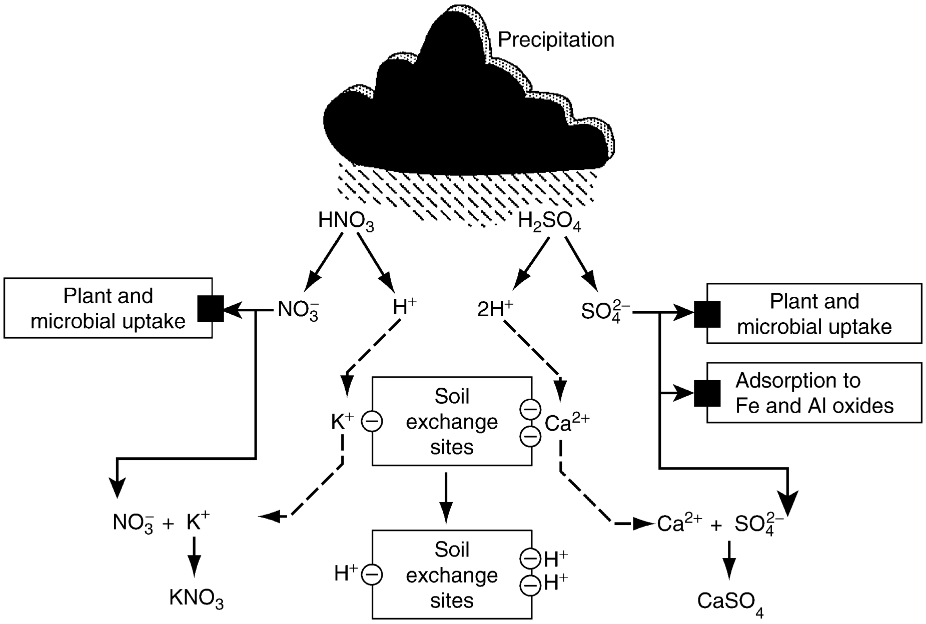


Figure A1 Atmospheric deposition of nitric and sulfuric acids acidify the soil through replacement of exchangeable base cations with H^+ and the subsequent leaching of base cations from the soil with the strong acid anions.

Biological uptake of SO_4^{2-} and NO_3^-, originating as strong acid inputs, ameliorates soil acidification by removing mobile anions that could otherwise induce the leaching of base cations. The assimilation of anions is a H^+ consuming reaction while the uptake of cations is a H^+ liberating reaction (Table A2). When plants assimilate more anions than cations, there is a net consumption of protons and vice versa. With regard to S, the nutritional requirement for most forests is low (<5 kg ha^{-1} yr^{-1}) and is greatly exceeded by the sulfur deposition rate of many acid impacted ecosystems. There appears to be some increase in the sulfur content of forests in response to increased S deposition, but the increased S accumulation in biomass represents only a small part of the total ecosystem capacity to accumulate sulfur; the majority being adsorbed to soil surfaces.

Nitrogen may be taken up either as a cation (NH_4^+) or anion (NO_3^-). Uptake of one mole of NH_4^+ results in the transfer of one mole of H^+ to the soil solution and thus soil acidification. The same magnitude of acidification occurs if NH_4^+ is first oxidized to NO_3^- producing $2H^+$, followed by the uptake of NO_3^- which consumes one H^+; the net effect being the production of one H^+. If however, nitrogen deposition occurs as HNO_3 and the NO_3^- is biologically assimilated, there is no acidification because the accompanying H^+ is neutralized by the uptake process. The net nitrogen retention capacity of aggrading coniferous forest is generally in the range 5–30 kg N ha^{-1} yr^{-1} (Johnson, 1992). In addition to plant uptake, there is appreciable N immobilization by microbial and abiotic soil processes resulting in increased N storage in soil organic matter pools (Johnson et al., 2000). Therefore, in nitrogen-limited ecosystems, NO_3^- uptake may substantially neutralize the acidity added from atmospheric sources. However, there is evidence that N deposition rates may exceed the forest requirement in some parts of Europe and North America leading to a state of "nitrogen saturation" (Aber et al., 1989; Fenn et al., 1998). Any nitrogen in excess of the nutritional requirement is subject to leaching as NO_3^- from the soil profile resulting in acidification through retention of H^+ by the soil and the release and leaching of base cations in the drainage waters. In Europe, sites with deposition less than 10 kg N ha^{-1} yr^{-1} have low NO_3^- concentrations in stream water, whereas all sites receiving >25 kg N ha^{-1} yr^{-1} have elevated concentrations (Wright et al., 2001).

Aluminum dissolution

If all of the above mentioned acid neutralizing processes fail to maintain the soil pH above 5, Al dissolution becomes an important acid neutralizing reaction. The dissolution reaction consumes three moles of H^+ for each mole of Al^{3+} released: $Al(OH)_3 + 3\ H^+ = Al^{3+} + 3\ H_2O$. Neutralization of H^+ by dissolution of Al results in potentially high concentrations of soluble Al^{3+} (up to 370 μmol l^{-1} at Solling, FRG, Cronan et al., 1989). The dissolved Al originates from a number of solid-phase pools including exchangeable, organically complexed, hydroxy-Al interlayer material, clay mineral lattices, and primary minerals (Dahlgren and Walker, 1993). The kinetics of Al dissolution are rapid for exchangeable and organically complexed forms, but are very slow for clay and primary mineral dissolution (Dahlgren et al., 1989; Dahlgren and Walker, 1993). Therefore, acid neutralization by Al dissolution depends on the kinetics and quantity of the Al-phase being dissolved. The solid-phase pools of Al represent a very large acid neutralizing capacity and prevent most mineral soils from becoming acidified below a pH range of approximately 4.2–4.5. The major problem with H^+ neutralization by Al dissolution is that Al^{3+} is toxic when present at elevated levels. Concentrations of aquo Al^{3+} in excess of 10 μmol l^{-1} have been shown to be toxic to aquatic organisms including fish (Baker and Schofield, 1982), while conifers grown in solution and soil cultures show significant detrimental effects at Al concentrations of approximately 200–250 μmol l^{-1} (Cronan et al., 1989). Some agricultural crops show Al toxicity symptoms at levels as low as 0.4 μmol l^{-1} (Adams and Moore, 1983).

Example of acidification and recovery of a soil horizon

Results from a laboratory study examining soil chemical processes active during acidification and recovery from sulfuric acid inputs are shown in Figure A2 (Dahlgren et al., 1990). With the onset of acidification, acid neutralization was dominated by sulfate sorption and base cation release. As the exchangeable cations were depleted and sulfate sorption reached equilibrium between the input concentration and the solid-phase, Al dissolution became the dominant proton neutralizing reaction. The recovery stage was characterized by the release of previously sorbed SO_4^{2-}. Thus, SO_4^{2-} desorption reactions were a source of acidity that continued to be neutralized by Al dissolution even during the recovery stage. The retention of base cations by the solid-phase during the recovery stage also contributed a small amount of acidity as the exchangeable cation composition equilibrated to a new equilibrium having a greater base saturation. There is a considerable lag in both the acidification and recovery stages due to proton buffering by sulfate sorption/desorption, base cation retention/release, and Al dissolution. The contribution of chemical weathering reactions was too slow to exhibit an influence in this study.

Similar processes have been demonstrated for acid neutralization in impacted ecosystems. Measurable changes in soil acidification in heavily impacted regions of Europe are only observed in the upper 30 cm of the soil profile. The observed changes include decreased pH, depletion of exchangeable base cations and solid-phase aluminum pools, decreased C/N ratios and increased concentrations of adsorbed SO_4^{2-}. Soil acidification proceeds progressively downward in the soil as the buffering capacity of the upper soil horizons is exhausted.

Decreases in sulfur (38–82%) and nitrogen (20%) deposition in Europe over the past decade have allowed a preliminary analysis of the recovery stage (Prechtel et al., 2001; Wright et al., 2001). Sulfate concentrations in stream waters have decreased significantly; however, acidification reversal was delayed (Prechtel et al., 2001). Release of adsorbed sulfate leads to the delay of acidification reversal (Figure A2). Sulfate fluxes in catchments with deeply weathered soils and high sulfate storage capacity responded more slowly to decreased deposition than catchments with thin soils and relatively small sulfate storage capacity. Compared to the sulfur response, there was an overall lack of significant trends in nitrate leaching in stream waters of Europe following a 20% reduction in nitrogen deposition over the past decade (Wright et al., 2001). This analysis suggests that recovery from nitrogen saturation is a slow process that requires many decades, at least at levels of N deposition typical for Europe. In contrast, field experiments with roofs to exclude acid deposition all show immediate and large decreases in NO_3^- leaching following large reductions in N deposition. These experiments showed that terrestrial ecosystems exhibit extreme hysteresis in NO_3^- leaching in response to N deposition; increased NO_3^- leaching occurs first after many decades of high N deposition, but decreased NO_3^- leaching occurs immediately following decreases in deposition. Reductions in particulate emission throughout Europe and North America have further delayed recovery from acidification due to the decrease in base cation deposition associated with particulate matter (Driscoll et al., 1989).

Acid deposition stresses on ecosystems

The direct impact of acid deposition on biological processes is often difficult to determine. High H^+ concentrations lead to elevated levels of soluble Al^{3+}, which have been shown to produce severe ramifications on terrestrial and aquatic species. High Al^{3+} concentrations can be directly toxic to plants resulting in a death of fine roots and mycorrhizae symbionts and can interfere with the acquisition of base cations and other nutrients from the soil solution inducing nutrient deficiencies and imbalances in plants. Not only the Al^{3+} concentrations,

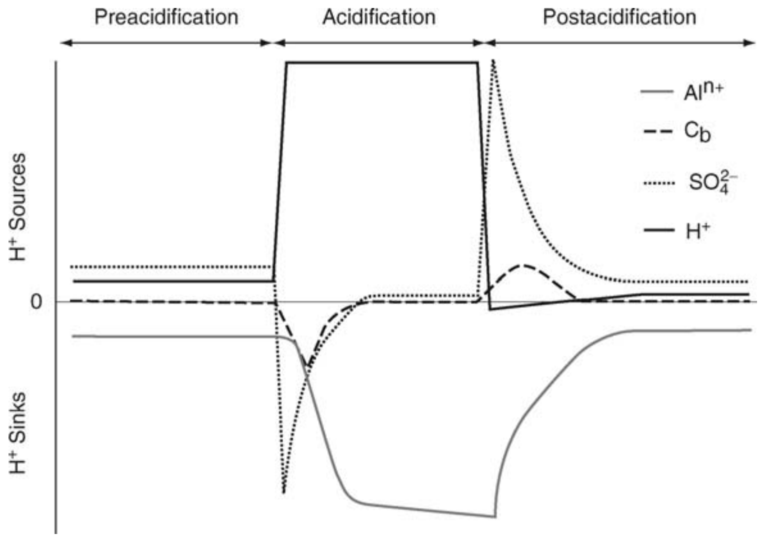


Figure A2 Proton-producing and -consuming reactions regulating acid/base chemistry during acidification and recovery of a soil horizon from sulfuric acid inputs (Al^{n+}: Al precipitation/dissolution; C_b: base cation retention/displacement from cation exchange sites; SO_4^{2-}: sulfate adsorption/desorption; H^+: strong acid input/release of protons).

but also the Al/Ca ratio of the soil solution appears to be an important factor regulating nutrient acquisition (Cronan and Grigal, 1995). Base cation (Ca^{2+}, Mg^{2+} and K^{+}) deficiencies develop as the base saturation is depleted due to displacement of base cations by acidic cations and the base cations are subsequently leached from the rooting zone with associated mobile anions (e.g., SO_4^{2-} and NO_3^{-}). A loss of membrane-bound calcium makes some tree species more susceptible to freezing damage, while calcium and magnesium deficiencies make some trees more susceptible to insect infestations and drought stress. Increased acidity also affects adsorption, mobility and chelation capacity of metal-complexing organics and mobility and bioavailability of heavy metals, such as Pb, Zn, Cu, Mn and Cd.

In nitrogen limited ecosystems, the deposition of additional N may initially increase plant growth inducing deficiencies of other nutrients, such as base cations or phosphorous. As ecosystems become nitrogen saturated, nitrate leaching can lead to elevated nitrate concentrations in surface and ground waters. Higher soil nitrate concentration leads to increased denitrification resulting in production of N_2O, a powerful greenhouse gas. Nitrogen deposition lowers the C/N ratio of organic matter potentially leading to an initial increase in the decomposition rate. However, as the soils become more strongly acidified, there appears to be a change in the composition of microbial populations, which may ultimately lead to decreased decomposition (Greszta et al., 1992). The effect of acidification on microbial processes appears to be highly variable depending on several characteristics of the ecosystem. Increased availability of nitrogen in terrestrial ecosystems also affects species diversity, often promoting an increase of invasive species (Tillman, 1987).

Deposition of nitrogen on lakes and their watersheds leads to increased algal biomass and a loss of water clarity (Tarnay et al., 2001). Severe lake acidification (low pH and elevated Al^{3+}) has been shown to adversely impact lower food-web transfers (i.e., phytoplankton-zooplankton) that ultimately impact the higher components of the food web (i.e., fish). Aquatic species diversity is progressively changed as aquatic ecosystems become acidified. Effects of acidification include long-term increases in mortality, emigration, and reproductive failure of fish, as well as short-term acute effects (Driscoll et al., 2003). Acidification of lakes and streams can increase the amount of methyl mercury available in aquatic systems (Driscoll et al., 1994). Coastal eutrophication is becoming common in regions with elevated nitrogen deposition leading to excessive production of algal biomass, blooms of toxic algal species, hypoxia, fish kills, and loss of important plant and animal diversity (Jaworski et al., 1997).

Table A3 Characteristics of soils and ecosystems most susceptible to acidification

Soil/ecosystem characteristic
Naturally acidic soil – reduced acid neutralizing capacity
Shallow soil – low soil water residence time
Coarse texture – low surface area and residence time
Few easily weatherable minerals – low acid neutralization by chemical weathering
Parent materials with low base cation content – few bases released upon weathering
High precipitation – low soil water residence time
Soils with restrictive layer that reduces water permeability – low soil water residence time
Low CEC and base saturation – low buffering capacity
Low content of Al and Fe oxides/hydroxides – low anion sorption
High fertility status – low capacity to retain additional nutrients
Low vegetation coverage – low uptake of strong acid anions

Characteristics of acid sensitive soils

Characteristics of soils most susceptible to the adverse effects from acid deposition are shown in Table A3. Shallow, coarse-textured soils with acid pH values, low base saturation and base-poor parent material are the most susceptible to severe acidification by acid deposition. The greater the pool of easily weathering minerals, exchangeable base cations, and Al// hydroxides, the greater the potential for neutralization by mineral weathering, exchange reactions, and anion sorption, respectively. Ecosystems with abundant vegetation have a greater potential for acid neutralization by uptake of strong acid anions (SO_4^{2-}, NO_3^{-}).

Randy A. Dahlgren

Bibliography

Aber, J.D., Nadelhoffer, K.J., Steudler, P., and Melillo, J.M., 1989. Nitrogen saturation in northern forest ecosystems. *BioScience*, **39**: 378–386.

Adams, F., and Moore, B.L., 1983. Chemical factors affecting root growth in subsoil horizons of coastal plain soils. *Soil Sci. Soc. Am. J.*, **47**: 99–102.

Baker, J.P., and Schofield, C.L., 1982. Aluminum toxicity to fish in acidic waters. *Water, Air, Soil Pollut.*, **18**: 289–309.

Binkley, D., Driscoll, C.T., Allen, H.L., Schoeneberger, P., and McAvoy, D., 1989. *Acidic Deposition and Forest Soils: Context and Case Studies in the Southeastern United States.* New York: Springer-Verlag.

van Breemen, N., and van Dijk, H.F.G., 1988. Ecosystem effects of atmospheric deposition of nitrogen in the Netherlands. *Environ. Pollut.*, **54**: 249–274.

van Breemen, N., Burrough, P.A., Velthorst, E.J., van Bobben, H.F., de Wit, T., Ridder, T.B., and Reijnders, H.F.R., 1982. Soil acidification from atmospheric ammonium sulphate in forest canopy throughfall. *Nature*, **299**: 548–550.

van Breemen, N., Mulder, J., and Driscoll, C.T., 1983. Acidification and alkalinization of soils. *Plant Soil*, **75**: 283–308.

van Breemen, N., Driscoll, C.T., and Mulder, J., 1984. Acidic deposition and internal proton sources in acidification of soils and waters. *Nature*, **307**: 599–604.

Cronan, C.S., and Grigal, D.F., 1995. Use of calcium/aluminum ratios as indicators of stress in forests. *J. Environ. Qual.*, **24**: 209–226.

Cronan, C.S., April, R., Bartlett, R.J., Bloom, P.R., Driscoll, C.T., Gherini, S.A., Henderson, G.S., Joslin, J.D., Kelly, J.M., Newton, R.M., Parnell, R.A., Patterson, H.H., Raynal, D.J., Schaedle, M., Schofield, C.L., Sucoff, E.I., Tepper, H.B., and Thornton, F.C., 1989. Aluminum toxicity in forests exposed to acidic deposition: the Albios results. *Water, Air, Soil Pollut.*, **48**: 181–192.

Dahlgren, R.A., and Walker, W.J., 1993. Aluminum release rates from selected spodosol Bs horizons: effect of pH and solid-phase aluminum pools. *Geochim. Cosmochim. Acta*, **57**: 67–66.

Dahlgren, R.A., Driscoll, C.T., and McAvoy, D.C., 1989. Aluminum precipitation and dissolution rates in spodosol Bs horizons in the northeastern USA. *Soil Sci. Soc. Am. J.*, **53**: 1045–1052.

Dahlgren, R.A., McAvoy, D.C., and Driscoll, C.T., 1990. Acidification and recovery of a spodosol Bs horizon from acidic deposition. *Environ. Sci. Technol.*, **24**: 531–537.

Driscoll, C.T., Likens, G.E., Hedin, L.O., Eaton, J.S., and Bormann, F.H., 1989. Changes in the chemistry of surface waters. *Environ. Sci. Technol.*, **23**: 137–143.

Driscoll, C.T., Yan, C., Schofield, C.L., Munson, R., and Holsapple, J., 1994. The mercury cycle and fish in the Adirondack Lakes. *Environ. Sci. Technol.*, **28**: 136A–143A.

Driscoll, C.T., Whitall, D., Aber, J., Boyer, E., Castro, M., Cronan, C., Goodale, C.L., Groffman, P., Hopkinson, C., Lambert, K., Lawrence, G., and Ollinger, S., 2003. Nitrogen pollution in the northeastern United States: sources, effects, and management options. *BioScience*, **53**: 357–374.

Fenn, M.E., Poth, M.A., Aber, J.D., Baron, J.S., Bormann, B.T., Johnson, D.W., Lemly, A.D., McNulty, S.G., Ryan, D.F., and Stottlemeyer, R., 1998. Nitrogen excess in North American Ecosystems: predisposing factors, ecosystem responses, and management strategies. *Ecol. Appl.*, **8**: 706–733.

Greszta, J., Gruszka, A., and Wachalewski, T., 1992. Humus degradation under the influence of simulated 'acid rain'. *Water, Air, Soil Pollut.*, **63**: 51–66.

Grübler, A., 1998. A review of global and regional sulfur emission scenarios. *Mitig. Adapt. Strat. Global Change*, **3**: 383–418.

Jaworski, N.A., Howarth, R.W., and Hetling, L.J., 1997. Atmospheric deposition of nitrogen oxides onto the landscape contributes to coastal eutrophication in the Northeast United States. *Environ. Sci. Technol.*, **31**: 1995–2005.

Johnson, D.W., 1992. Nitrogen retention in forest soils. *J. Environ. Qual.*, **21**: 1–12.

Johnson, D.W., Cheng, W., and Burke, I.C., 2000. Biotic and abiotic nitrogen retention in a variety of forest soils. *Soil Sci. Soc. Am. J.*, **64**: 1503–1514.

NADP/NTN, 2004. National Atmospheric Deposition Program (NRSP-3)/ National Trends Network. NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820.

Pearson, J., and Stewart, G.R., 1993. The deposition of atmospheric ammonia and its effects on plants. *New Phytol.*, **125**: 283–305.

Prechtel, A., Alewell, C., Armbruster, M., Bittersohl, J., Cullen, J.M., Evans, C.D., Helliwell, R., Kopácek, J., Marchetto, A., Matzner, E., Meesenburg, H., Moldan, F., Moritz, K., Veselý, J., and Wright, R.F., 2001. Response of sulphur dynamics in European catchments to decreasing sulphate deposition. *Hydrol. Earth System Sci.*, **5**: 311–325.

Reuss, J.O., and Johnson, D.W., 1986. Acid deposition and acidification of soils and waters. *Ecological Studies 59*. New York: Springer-Verlag

Sverdrup, H.U., 1990. The kinetics of base cation release due to chemical weathering. Lund, Sweden: Lund University Press.

Sverdrup, H., and Warfvinge, P., 1988. Weathering of primary silicate minerals in the natural soil environment in relation to a chemical weathering model. *Water, Air, Soil Pollut.*, **38**: 387–408.

Tarnay, L., Gertler, A.W., Blank, R.R., and Taylor, G.E., 2001. Preliminary measurements of summer nitric acid and ammonia concentrations in the Lake Tahoe Basin air-shed: implications for dry deposition of atmospheric nitrogen. *Environ. Pollut.*, **113**: 145–153.

Tilman, D., 1987. Secondary succession and the pattern of plant dominance along experimental nitrogen gradients. *Ecol. Monogr.*, **57**: 189–214.

U.S.-EPA, 2003. Latest findings on national air quality: 2002 status and trends. U.S. EPA Publication No. 454/K-03-001.

White, A.F., and Blum, A.E., 1995. Effects of climate on chemical weathering in watersheds. *Geochim. Cosmochim. Acta*, **59**: 1729–1747.

Wright, R.F., Alewell, C., Cullen, J.M., Evans, C.D., Marchetto, A., Moldan, F., Prechtel, A., and Rogora, M., 2001. Trends in nitrogen deposition and leaching in acid-sensitive streams in Europe. *Hydrol. Earth System Sci.*, **5**: 299–310.

Cross-references

Acid Soils
Acidity
Nitrogen Cycle
Podzols
Sorption Phenomena
Sulfur Transformations and Fluxes
Thionic Soils

ACID SOILS

Acid soils are defined in terms of redox-pH master variables in Figure A3. In the WRB system of classification, the relevant reference soil groups with widest distribution are Acrisols, Ferralsols and Podzols, which are the main focus of this article (Table A4). Acid soils also occur in Andosols, Arenosols, Alisols, Albeluvisols, Cambisols, Histosols, Leptosols, Plinthosols, Planosols, Fluvisols, Regosols and Umbrisols. In those Fluvisols and mine soils (Espoli-Anthropic Regosols) containing pyrite, extreme acidity develops on oxidation.

In the three groups of wide distribution, acidity ranges from a pH between 3.5 and 4 in the A horizons of Podzols to about 6 as an upper limit in Ferralsols. The values are set (see Figure A4) by the dissociation of H^+ from the carboxyl groups of humic materials (pK_a from 3.5 to 6), and by the system $H_2O–CO_2$, which enters the soil via atmospheric precipitation at a pH of 5.7. It may acquire a CO_2 concentration two orders of magnitude greater than the atmospheric value within the upper part of the solum, as a consequence of the metabolic activities of roots and of microorganisms (in breaking down organic matter). Gleyed varieties of all three soils are found in regions of high water-table lows such as river valleys for example.

The worldwide distribution of Acrisols, Ferralsols and Podzols is shown in Table A4. Acrisols and Ferralsols are predominantly soils of the humid tropics and subtropics, while Podzols, although common in areas with precipitation much greater than evapotranspiration, occur mainly in cold to temperate zones. An important consequence is that components from organic sources play a more important role in the genesis of Podzols, than in Acrisols and Ferralsols, simply because organic matter tends to have a much longer half-life in colder than in warmer climates. Another important consequence is the poor weathering displayed by the materials on which Podzols develop, which contrasts with Acrisols and Ferralsols. In this case, however, parent material and time also play a role.

Acrisols and Ferralsols

As well as tropical and subtropical occurrences, Acrisols and Ferralsols are also found to a lesser degree in the warmer parts of humid temperate regions. Their characteristic occurrence however is in cratonic regions (of S. America and Africa especially) on surfaces peneplained in Tertiary and Pleistocene times. Elsewhere, they are found on easily weathered basic igneous rocks, particularly pyroclastics, where leaching is facilitated by the porous, fragmental nature of the parent material.

Acrisols and Ferralsols are deep, highly weathered and leached soils that are stripped down to simple assemblages in the four-component system $SiO_2–Al_2O_3–Fe_2O_3–H_2O$. Except in gleyed varieties Fe is in the ferric state in the minerals goethite or hematite. As a result the solum is commonly yellow or red in color. Prolonged hydrolysis and leaching destroys all primary alumino-silicates, so that kaolinite (monosiallitization) and/or gibbsite (allitization) tend to dominate the clay fraction and account for the low CEC (Figure A5).

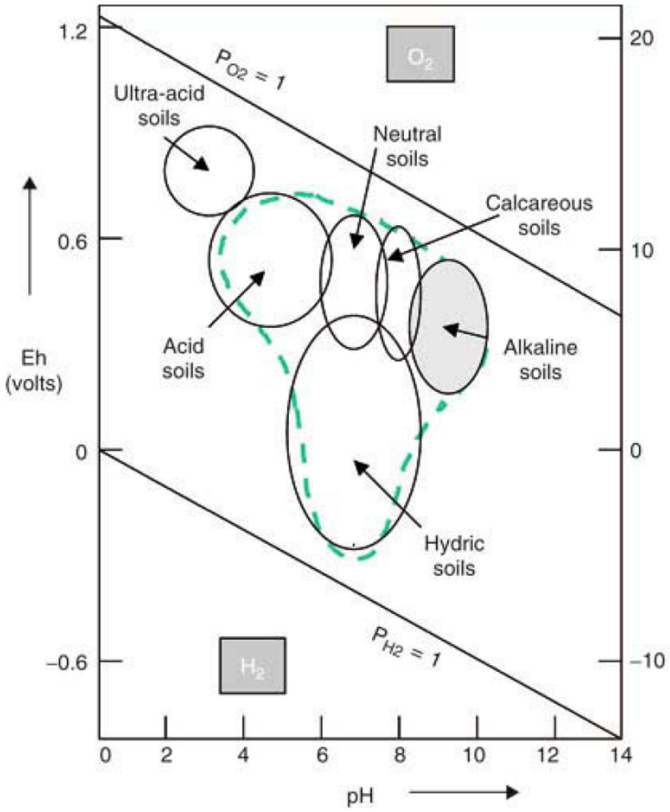
Podzols

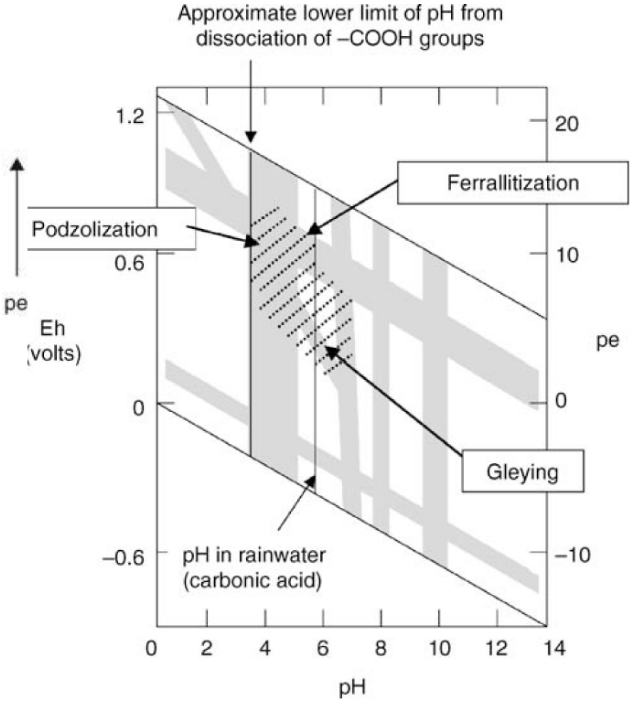
In essence, Podzols form by the titration of a material with a low capacity for buffering acid, against an excess of organic acids. The net release of acid breakdown products from organic debris is influenced by environmental conditions (favored when microbial activity is impaired) and type of vegetation. The acid buffering capacity of the parent material is determined by lithology and/or climate. As temperature decreases, lithology becomes less determinant in Podzol formation. Thus, whereas in tropical environments, Podzols form on sandy materials, which are almost exclusively quartzitic, in colder environments, parent material is more variable. The shifting point of this titration, which depends on both the total organic acid loading and the total base supplied, determines the depth at which the new phases form. That is, organic complexants percolating through the soil profile remove (a process called chelluviation) Fe and Al until the latter become saturated and precipitate, forming the B spodic horizon (a process called illuviation). The eluviated horizon takes on a bleached appearance, as only resistant minerals, such as quartz, remain, and is called the albic horizon. Root growth is promoted in the B spodic horizon – because of its greater water and nutrient availability and less acidity compared with the E eluviated horizon – further enhancing organic matter accumulation at depth.

The pedogenesis of other soils with incipient weathering and an acid trend, developed under similar environmental conditions to Podzols, (Haplic Umbrisols or any Umbric or Fulvic Andosols for example) could be described in a similar way. However, as in these soils the acid buffering capacity of the parent material is greater than in Podzols, the distance traveled by the organic ligands is less (in Umbrisols) or nil (in Andosols).

The clay fraction of a mature Podzol resembles that of an Acrisol or Ferralsol in tending to be enriched in the components $SiO_2–Al_2O_3–Fe_2O_3–H_2O$. However, the process is incipient, since unlike the tropical soils, Podzols, Umbrisols and Umbric or Fulvic Andosols tend to be on young (commonly postglacial) landscapes. Consequently amorphous or short-range order phases commonly occur. On older landscapes the amorphous and short-range order phases will age to progressively more stable minerals by the process known as (Ostwald) ripening. The specific ripening sequence will depend upon the activity of silica in the system (see Figure A6).

Podzols are found in Boreal regions of the cratons of the Northern hemisphere, as well as in temperate, wet zones such as the western Cordilleras of Canada, Chili and Alaska, and along sandy coasts of Western Europe (the Landes of Atlantic France for example). Out of nearly half a billion hectares worldwide, all except some 30 million are in temperate to cool regions. The balance is in the tropics, particularly on alluvial quartz sands. Found along the Rio Negro and in the Guyanas of South America, in SE Asia (Kalimantan, Sumatra, Papua) and in northern Australia.





ure A4 Soil forming processes found among acid soils, displayed on the pedogenic grid.

Table A4 Distribution of the three major groups of acid soils (in thousands of hectares)

	Africa	Australasia	Europe	North America	North and C. Asia	South and C. America	South and SE Asia	Total
Acrisols	92 728	32 482	4 170	114 813	148 241	341 161	263 005	996 600
Ferralsols	319 247	0	0	0	0	423 353	0	742 600
Podzols	11 331	8 459	213 624	220 770	21 825	5 522	5 982	487 513

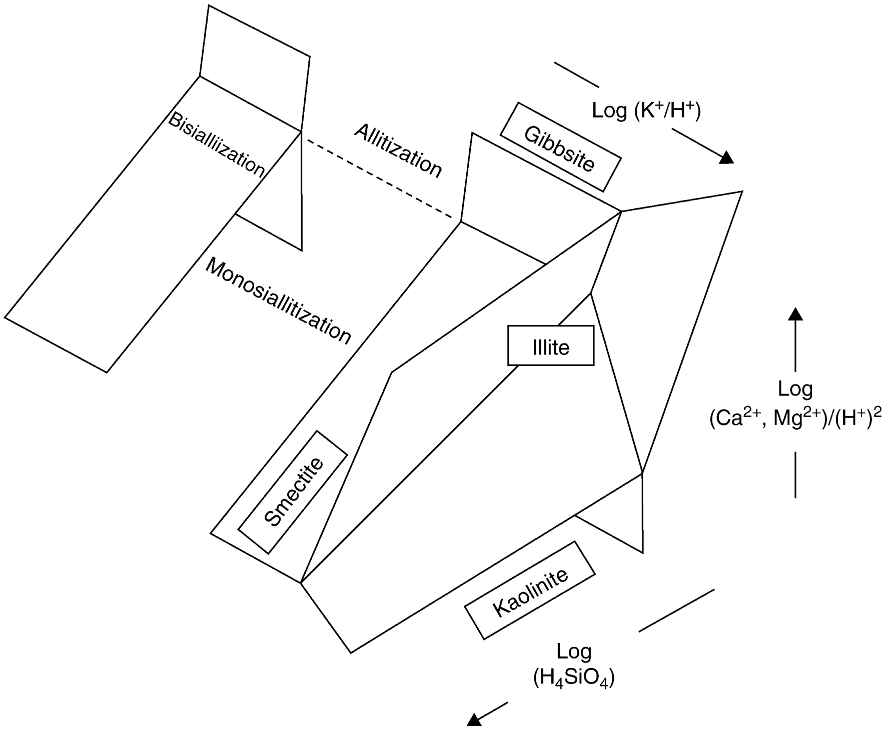


Figure A5 Mineral formation in acid pedogenesis tends to lead to kaolinitic or gibbsitic assemblages in Acrisols and Ferralsols. The chemical evolution of the soil is towards the bottom right hand corner of the schematic diagram (modified from Chesworth, 1980).

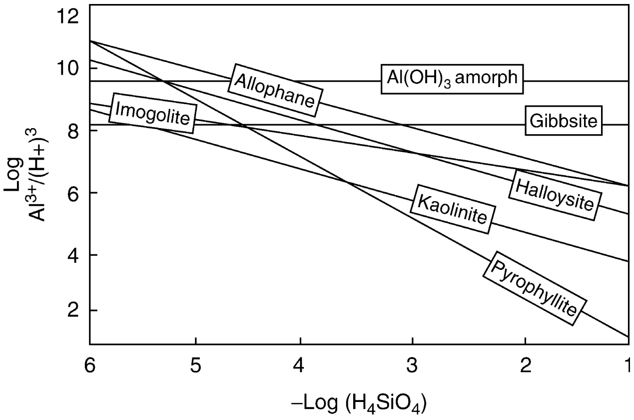


Figure A6 Diagram to illustrate Ostwald ripening. In the system SiO_2–Al_2O_3–H_2O the sequence of minerals that form at $-\log(H_4SiO_4) = 4$, for example, might be allophane, halloysite, kaolinite.

Agricultural problems of acid soils

High acidity is accompanied by a low cation-exchange capacity and a low base saturation, both of which lead to problems when these soils are utilized in agriculture. Nutrient deficiency and high levels of exchangeable aluminum are the main problems. Al toxicity is a particular management problem. Al toxicity occurs mainly when $pH(H_2O) < 5$, and CEC is >60% Al. The deleterious effect of this so-called alic character is greater in those acid soils poor in organic matter in which 2 : 1 clay minerals are abundant. High levels of exchangeable and soluble Al also promote P fixation and slow down nitrification and N_{20} fixation, leading to deficiency of these nutrients. All this impairs plant growth, leaf functionality (because of yellowing and defoliation), and root development, which, in turn, increases plant susceptibility to other stresses and plant diseases, thereby further decreasing crop yields.

Acid soils require liming and constant fertilization when used in agricultural production. Macronutrients and, in some cases, micronutrients (e.g., molybdenum) have to be added.

In Acrisols and Ferralsols, the exchange capacity of the organic matter is very important because the clay fraction is made up of minerals of low cation-exchange capacity. However the organic matter of these soils is rapidly mineralized under tropical climates, with labile organic C only present at the surface as a consequence of recent deposition of plant and animal residues. In some cases, there can be a fraction of recalcitrant organic C stabilized by sorption processes on to Al and Fe oxihydroxides (such as in some Umbric Acrisols and Ferralsols).

In addition to problems already noted, most Podzols have additional problems. They form generally on sandy materials and may therefore be droughty by reason of excessive drainage. Furthermore, the leaching out of iron and its subsequent accumulation in lower horizons may lead to a thin, impervious iron pan. Drainage may then be restricted so that the soil develops hydromorphic properties. Drainage may be improved by breaking up the iron pan.

Felipe Macías, Marta Camps Arbestain, and Ward Chesworth

Bibliography

Chesworth, W., 1980. The haplosoil system. *Am. J. Sci.*, **280**: 969–985.

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Acrisols
Andosols
Clay Mineral Alteration in Soils
Clay Mineral Formation
Ferralsols
Podzols
Weathering Systems in Soil Science

ACID SULFATE SOILS

See *Thionic or Sulfidic soils*.

ACIDITY

Soil acidity is a term used to describe acid soils; i.e., soils with a pH value <7.0 (Gregorich, 2001). When used as a quantitative term, soil acidity is considered a capacity factor and refers to the total acidity contained in a given soil or soil horizon. Soil pH, a measure of the negative logarithm of the hydrogen ion activity in the soil solution, is used as an indicator of the degree of acidity or alkalinity in soil (Table A5). Another term that is sometimes associated with the degree of acidity of a soil as a function of soil pH is soil reaction.

When used in a qualitative manner, the term soil acidity refers to a variety of possible chemical processes, which are known to occur in acid soils (Thomas and Hargrove, 1984; Sumner et al., 1991; Rengel, 2003). The combined interaction of these processes influences the amount and speciation of nutrient ions in the soil solution and thus their availability for plant growth. In general, an increase in soil acidity is associated with a decrease in the availability of nutrient ions (particularly calcium (Ca^{2+}), magnesium (Mg^{2+}), phosphorus, and molybdenum) and an increase in the presence of acidic cations (hydrogen (H^+), manganese (Mn^{2+}), aluminum (Al^{3+}), and iron (Fe^{3+})) which are known to be toxic to most plants and soil microorganisms (Ritchie, 1989; Robson and Abbott, 1989). The exact mechanisms that result in the deleterious effects observed with an increase in soil acidity have been reviewed elsewhere (Clark, 1984; Foy, 1984). However, toxicity due to the increased activity of Mn^{2+}, H^+, and especially Al^{3+} ions in the soil solution is recognized as the most common cause of reduced yields. For most agronomic crops, it is the dominance of Al^{3+} on the ion-exchange complex in acid soils that directly affects plant growth (Kamprath, 1970). Because of this, the term soil acidity is sometimes assumed to be synonymous to the presence and subsequent chemical reactions of Al^{3+} ions in acid soils. This is not always true, especially in organic soils, and the use of the term soil acidity in this context should be avoided.

Table A5 Descriptive terms commonly used to describe the degree of acidity or alkalinity of a soil[a]

Descriptive terms	pH range
Extremely acid	<4.5
Very strongly acid	4.5 – 5.0
Strongly acid	5.1 – 5.5
Moderately acid	5.6 – 6.0
Slightly acid	6.1 – 6.5
Neutral	6.6 – 7.3
Slightly alkaline	7.4 – 7.8
Moderately alkaline	7.9 – 8.4
Strongly alkaline	8.5 – 9.0
Very strongly alkaline	>9.1

[a] Source: Soil Science Society of America (1987).

The amelioration of an acid soil with lime to remove the deleterious effects of soil acidity on plant growth requires knowledge of the relationship between the acidity present and soil pH. This is necessary in order to avoid over-liming which also can have a negative impact on plant growth (Kamprath, 1971). Titration of an acid soil with a strong base is one way to obtain the desired relationship between acidity and soil pH. Sources of acidity that react with base include exchangeable acidity and residual acidity. Exchangeable acidity, or salt-replaceable acidity, refers to the acidic cations (primarily Al^{3+} and Fe^{3+}) that can be replaced from the ion-exchange complex by an unbuffered salt solution, such as potassium or sodium chloride (Gregorich, 2001). Measurable amounts of exchangeable H^+ may also be present due to the acid functional groups associated with soil organic matter (SOM) (Stevenson, 1982).

The remaining soil acidity that cannot be replaced by an unbuffered salt solution is called the residual acidity. Quantification of the residual acidity in an acid soil is difficult because the rate of reaction with base is generally slower than with exchangeable acidity. Sources of residual acidity include Al^{3+} and Fe^{3+} tightly bound by SOM and the acid-functional groups located on the edges of layer silicate minerals and the surfaces of Fe and Al oxides and oxyhydroxides (Thomas and Hargrove, 1984; Sumner et al., 1991). Liming criteria based on exchangeable acidity alone usually requires a multiplication factor to account for the presence of residual acidity. This factor ranges between 1.5 and 3.3 for most acid soils (van Lierop, 1990), demonstrating that residual acidity is not an insignificant fraction of the total acidity. Additional sources of acidity that release H^+ to the soil solution include oxidation-reduction or redox reactions, addition of soluble salts (fertilizers), and base cation (Ca, Mg, K) removal during plant uptake (acidification of the rhizosphere) (Thomas and Hargrove, 1984). These sources are more transient in nature and are not included in most quantitative laboratory procedures used to determine the amount of acidity in a soil. The acidity generated from these transient sources, however, must be accounted for in any successful management scheme to optimize crop yields.

Methodology

Methods to determine soil acidity can be divided into two groups: (1) methods that are designed to give quantitative estimates of the total or some fraction of soil acidity in a given soil, and (2) soil test (quick) methods designed to determine the lime requirement of a large number of different types of acid soils (see Sparks, 1996).

Exchangeable acidity

The most common quantitative procedure for determining exchangeable acidity (exchangeable H^+ and Al^{3+}) is extraction with a neutral solution of potassium chloride (1 kmol m^{-3} KCl; Thomas, 1996). The basic procedure employs the titration of an aliquot of the extracting solution to the phenolphthalein endpoint with standardized base. The equivalents of base added corrected to the volume of the extracting solution is the estimate of total exchangeable acidity. This is followed with addition of sodium fluoride (1 kmol m^{-3} NaF) to release the hydroxyl ions (OH^-) added with base that are bound to the Al^{3+} in the original extract. Back titration with standardized acid yields the quantitative estimate of exchangeable Al^{3+}. A positive difference between the estimates of total exchangeable acidity and exchangeable Al^{3+} is a measure of the exchangeable H^+ present in the soil. Modifications to the basic procedure generally consist of direct determination of the Al^{3+} in the extract either by atomic absorption spectroscopy or using one of several different colorimetric procedures (Barnhisel and Bertsch, 1982; Bloom and Erich, 1989). Direct determination of Al^{3+} avoids a positive bias in the procedure due to titration to the phenolphthalein endpoint.

Single extractions of exchangeable acidity (H^+ and Al^{3+}) using unbuffered salt solutions is quantitative for pure layer silicate minerals (Thomas, 1982), but not for most soils (Oates and Kamprath, 1983). Successive extractions of soils, especially soils containing measurable amounts of SOM, results in the continued release of Al to the extracting solution. The source of this residual extractable Al is assumed to be Al^{3+} tightly bound to SOM. Other extracting salt solutions that have been used in an attempt to include this residual extractable Al fraction in the estimate of exchangeable acidity include lanthanum chloride (1 kmol m^{-3} $LaCl_3$) and copper chloride (1 kmol m^{-3} $CuCl_2$) (Bloom et al., 1979; Juo and Kamprath, 1979). At pH values <7, lanthanum is a trivalent ion (La^{3+}) and its use is meant to promote ion exchange with Al^{3+} bound to SOM. The cupric ion (Cu^{2+}) is known to have a high affinity for the functional groups contained in SOM (Bloom, 1981), and it is reasoned that it should replace Al^{3+} ions not readily displayed by mono- or divalent base cations. Both extracting solutions are quantitative when dealing with SOM extracts or peat, but still continue to release Al with successive extractions of soil samples. One source of this additional release of Al may be dissolution of layer silicate minerals or hydroxy-Al-interlayered 2 : 1 layer silicate minerals (HIM) as a result of the acidity (pH < 4) of the equilibrated soil-extracting solution suspensions (Oates and Kamprath, 1983). The terms extractable acidity or extractable Al are often used instead of exchangeable acidity or exchangeable Al because of the inability of unbuffered salt solutions to distinguish between different sources of acidity in whole soils (Barnhisel and Bertsch, 1982).

Total potential acidity is determined in acid soils using the barium chloride (1 kmol m^{-3} $BaCl_2$) – triethanolamine (0.2 kmol m^{-3} TEA) procedure (Thomas, 1982). The term potential acidity refers to the exchangeable plus residual acidity contained in a soil as referenced to a given pH value. A $BaCl_2$ solution, containing TEA (pH 8.2) as a buffer, is allowed to equilibrate with a soil sample. After filtration, the filtrate is titrated with standardized acid to the methyl red – bromocresol green end point. The equivalents of acid required are taken as the measure of the total potential acidity present in the soil. The pH of 8.2 selected for the TEA buffer solution corresponds to the H^+ activity maintained in solution by calcium carbonate ($CaCO_3$) in equilibrium with the partial pressure of carbon dioxide (CO_2) in the atmosphere. The basic premise of the procedure is that a soil in equilibrium with free calcium carbonate (lime) will have a pH = 8.2, and by definition, contain no exchangeable or residual acidity. Variations to the original $BaCl_2$-TEA procedure include leaching with a neutral salt solution prior to addition of the $BaCl_2$-TEA solution. This modification provides an estimate of both the exchangeable and residual acidity in a soil.

Potentiometric titrations of acid soils with strong base (e.g., sodium, potassium, or calcium hydroxide) to a fixed endpoint provides not only a measure of the exchangeable and residual acidity present, but also an indication of how the amount of acidity varies with solution pH. The slope of the relationship between the equivalents of base added and suspension pH provides an estimate of the buffer capacity of a soil in a given pH range. Buffer capacity refers to the ability of the soil to resist changes in pH. The primary limitation of this procedure, however, is the slowness of the neutralization reaction near the end-point (Thomas and Hargrove, 1984). The shape of the relationship between equivalents of base added and suspension pH is also a function of the concentration and charge of the neutral salt cation used during the titration. The time required to complete the titration prohibits its use as a routine method for a large number of soil samples.

Lime requirement

Soil test methods designed to determine the lime requirement of a soil are generally based on the assumption that there is an optimum soil pH for the growth of a given crop on a given soil type. The amount of lime required is the amount needed to change the initial soil pH to the optimum soil pH. However, the methods selected for determining the lime requirement of a soil must also be applicable to a wide range of different soil types and be capable of processing relatively large numbers of soil samples in a short period of time. The most common approach used today that meets these criteria is to equilibrate the soil with a buffer solution (Table A6). The buffer solution itself is usually a mixture of two or more buffers such that there is a linear change in pH with incremental additions of acid (H^+) over a range of several pH units (e.g., pH 7 to pH 4). This linear change in pH with incremental addition of acid is in turn calibrated to the lime requirement for a particular soil group; the later being determined from lime incubation studies or titration with base. Allowances are also made for the crop to be grown, depth of rooting volume, composition and particle size of liming material and method of incorporation (van Lierop, 1990). Using this approach, the lime requirement for a soil is essentially equal to the change in the pH of the buffer solution after equilibration with the acidic soil.

The basic limitation of this approach is the accuracy and precision possible when the procedure is used on a routine basis with large numbers of soil samples. A change of +0.1 pH units can represent a difference in lime requirement of between 400 to 600 kg of lime ha^{-1}. Interlaboratory comparisons have suggested differences in pH measurements of as much as +0.4 pH units may occur for the same soil samples (van Lierop, 1990). Differences of this order of magnitude represent substantial errors in the estimation of the lime requirement for a soil. Buffer solutions also tend to be less sensitive in predicting lime requirement for soils with pH values >6. Offsetting these potential errors is the reality that most lime requirement recommendations are not strict quantitative

Table A6 Common names and composition of buffer solutions used to determine lime requirements[a]

Name	Buffer reagents	Comments single buffer procedures
Shoemaker, McLean, and Pratt (SMP)	*p*-nitrophenol, potassium chromate, triethanolamine	curvilinear calibration, best for high lime requirement soils, over-liming possible for low lime requirement soils
Mehlich	triethanolamine, acetic acid	designed to neutralize exchangeable acidity, no optimum pH assumed
Woodruff	*p*-nitrophenol, magnesium oxide, calcium acetate	curvilinear calibration, best for low lime requirement soils
Adams and Evans	*p*-nitroprenol, boric acid	designed for low lime requirement soils (ultisols)
Nômmik	imidazole, malic acid, sodium or potassium acetate	calibrated to pH 7.0, limited calibration data available
Yuan	imidazole, pyridine, tris[b], potassium chromate	requires two soil-buffer pH readings, May underestimate lime requirement
SMP-Double Buffer	*p*-nitrophenol potassium chromate, triethanolamine	requires two soil-buffer pH readings, improves prediction for low lime requirement soils

[a] Sources: Yuan, 1974; McLean, 1978; Adams, 1984; van Lierop, 1990.
[b] tris (hydroxymethyl)-aminomethane.

estimates and that the potential error associated with the pH measurement is not likely to cause major problems compared to the advantages of the buffer procedures.

Alternative methods for determining the lime requirement of a soil include estimating lime requirement from soil properties without directly measuring soil acidity, and calculating lime application rates necessary to only neutralize exchangeable Al^{3+} (van Lierop, 1990). Indirect lime requirement determinations are based on statistical correlations between the lime requirement and soil properties (usually exchangeable Al^{3+}, SOM, and clay content) and the desired change in soil pH. The approach is accurate but does require calibration with different soil types before use. Liming to neutralize exchangeable Al^{3+} is based on the fact that crop yield responses to liming are inversely correlated with exchangeable Al^{3+} (Kamprath, 1970). If the cost of liming is a factor for successful crop production, lime application rates based on exchangeable Al^{3+} provides a way to increase yields with limited economic resources. This may, however, require more frequent addition of lime in order to maintain the desired soil pH (van Lierop, 1990).

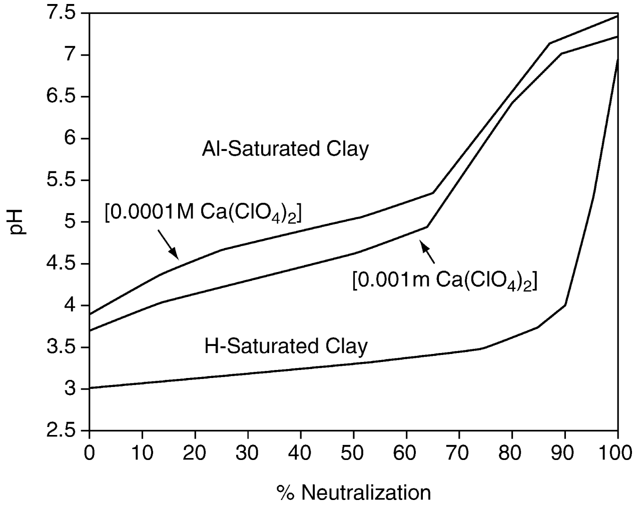


Figure A7 Theoretical titration curve for an Al-saturated and a H-saturated layer silicate mineral.

Applications

Exchangeable acidity

Acid attack of primary and secondary aluminosilicate minerals during chemical weathering is the primary source of exchangeable Al^{3+} in acid soils. Attempts to generate H^+-saturated layer silicate minerals have demonstrated that such preparations are unstable. The presence of H^+ ions to balance the net negative charge of the layer silicate minerals accelerates their dissolution with release of Al^{3+} and silicic acid (H_4SiO_4) to solution. The Al^{3+} ions, in turn, replace the neutralized H^+ ions in balancing the net negative charge of the layer silicate mineral. If allowed to go to completion, the dissolution reaction will continue until the clay is essentially 100% saturated with Al^{3+} ions (no exchangeable H^+ remains). Potentiometric titrations of montmorillonite suspensions, which are freshly prepared and truly H^+-saturated, yield titration curves, which resemble those of a strong mineral acid (Figure A7). Such behavior is consistent with the observation that little or no exchangeable H^+ remains associated with aged layer silicate mineral suspensions. These results also explain why appreciable amounts of exchangeable H^+ are not associated with clay minerals in acid mineral soils.

During the conversion to an Al^{3+}-saturated clay, there is essentially no net change in the equivalents of acidity originally added to form the H^+-saturated clay. This is because of the ability of Al^{3+} ions to undergo hydrolysis in aqueous systems. Hydrolysis can be described as a series of consecutive proton transfer reactions between hydrated metal ions and water molecules that result in the release of H^+ ions and the formation of monomeric hydrolytic Al species (Baes and Mesmer, 1976). The only difference between H^+ produced by Al hydrolysis as opposed to being present as exchangeable H^+ is that the extent of the hydrolysis reaction is a function of the activity of H^+ ions in solution; i.e., hydrolysis of an acidic cation resembles the behavior of a weak acid rather than a strong acid.

Once an Al^{3+} ion is displaced from a layer silicate mineral by ion exchange, it will begin the step-wise release of H^+ as represented by the following equations:

$$Al(H_2O)_6^{3+} + H_2O = Al(OH)(H_2O)_5^{2+} + H_3O^+ (K_1) \quad (1)$$

$$Al(H_2O)_6^{3+} + 2H_2O \rightleftharpoons Al(OH)_2(H_2O)_4^{+} + 2H_3O^+ \ (K_2) \quad (2)$$

$$Al(H_2O)_6^{3+} + 3H_2O \rightleftharpoons Al(OH)_3(H_2O)_3^{0} + 3H_2O^+ \ (K_3) \quad (3)$$

where K_1, K_2, and K_3 are the respective dissociation constants.

Because of its small ionic radius, the Al^{3+} ion assumes a six-fold coordination with the surrounding water molecules. The subsequent hydrolysis is similar in reaction to a polyprotic weak acid with the respective pK values (the negative logarithm of the dissociation constant) indicative of the pH of maximum buffer capacity. The monomeric hydrolytic Al species that is produced at each step can undergo further ion-exchange reactions, or in the presence of base, continue to undergo hydrolysis until the original Al^{3+} ion is completely neutralized.

Unlike a polyprotic weak acid, the titration of an Al^{3+}-saturated layer silicate mineral does not result in a plot of equivalents of base added versus equilibrium pH with three distinct buffer regions (Figure A7). This is because the chemistry of hydrolysis of Al^{3+} beyond the first hydrolysis reaction (p$K_1 = 5.0$) becomes confounded by secondary polymerization reactions that result in the formation of polynuclear hydroxy-Al species of differing basicity (OH : Al ratios; Bertsch, 1989). Because of their relatively high positive charge density, these polymeric Al species are attracted to and stabilized on the surfaces of the negatively charged layer silicate minerals (Adams, 1984). In soils, they also interact with the functional groups of SOM. These surface bound polymeric Al species continue to undergo hydrolysis and react with added base, but the exact pK values for these reactions are not known. The result of this combination of reactions is that the titration curve of an Al^{3+}-saturated layer silicate mineral is in general characterized by only one broad buffer region (Figure A7). Below the average pK for this buffer region, Al^{3+} is the dominant ion both in solution and on the ion-exchange surface of the clay mineral. The actual concentration of Al^{3+} in solution and the observed pH is a function of the concentration and charge of the neutral salt cation used during the titration. With addition of base, polymeric Al species are formed at the expense of exchangeable Al^{3+}, and the concentration of Al^{3+} in solution decreases until essentially no exchangeable Al^{3+} remains associated with the layer silicate mineral. This point does not represent 100% neutralization, however, since the charged polymeric species are still bound to the clay surface. The negative charge associated with the layer silicate mineral requires a higher concentration of hydroxyl ions (OH^-) in solution to complete the neutralization reaction (i.e., a higher pH). Complete neutralization of the original Al^{3+} results in 100% base saturation of the clay.

An analogous series of reaction occurs when base (e.g., in the form of lime) is added to an acid mineral soil. A pH 5.5 is typically cited as the reference point above which no exchangeable Al^{3+} remains associated with the soil layer silicate minerals. The actual pH at which this occurs will vary between soil types and also within the same soil. Additions of fertilizer increase the concentration of neutral salt cations in the soil solution. This increase in ionic strength will lower the apparent soil pH for the same increment of lime addition (Figure A7). In terms of crop production, this can have the effect of obtaining maximum yields at lower pH values for the same soil series (Adams, 1984), especially for ultisols and oxisols. This salt effect on soil pH measurements is well known and it is recommended that samples from intensively fertilized soils be leached with water before determining soil pH, or that all soil pH measurements be referenced to a relatively concentrated salt solution. The two neutral salts commonly used for this purpose are calcium chloride (0.01 kmol m^{-3} $CaCl_2$) and potassium chloride (1 kmol m^{-3} KCl) (Peech, 1965).

Other acidic cations that can undergo hydrolysis and release H^+ ions include Fe^{3+}. In the pH range of most mineral soils (pH > 4), the hydrolysis of Fe^{3+} displaced from the exchange surface of soil clay minerals is not considered an important source of exchangeable acidity. The equilibrium constants for the hydrolysis reactions of Fe^{3+} favor the formation of the hydrolyzed species at lower pH values than Al^{3+}. Hydrolysis of Fe^{3+} following the oxidation of ferrous iron species (Fe^{2+}), however, is an important source of acidity and will be discussed later.

The majority of extractable or exchangeable H^+ present in acid soils is associated with the acid functional groups of SOM. SOM is formed from microbial decomposition of plant and animal tissue added to soils. As a result, SOM is heterogeneous with respect to composition, chemical structure, and quantity and type of acid functional groups (Stevenson, 1982). These functional groups behave as weak acids and have been assigned pK values, but these are only approximate values and titration of SOM extracts seldom yields defined buffer regions. This is due in part to the distribution of the functional groups within SOM, and the change in stereochemistry that occurs as the net negative charge of SOM increases with addition of base (Stevenson, 1982). Titration curves of SOM tend to be linear over a defined pH range, beyond which the majority of H^+ bound to the functional groups, has been neutralized (Magdoff and Bartlett, 1985).

The quantity of extractable H^+ removed by a neutral salt solution from SOM is a function of the concentration and charge of the neutral salt cation and the final pH of the soil suspension. It can be argued, therefore, that the H^+ associated with SOM is both a source of exchangeable acidity and residual acidity, depending on the laboratory procedure selected and the chemical properties of a particular soil. The density of acid functional groups per unit mass for SOM (>600 $cmol_c$ kg^{-1}) is substantially greater than that for most clay minerals, such that relatively small amounts of SOM (<1.5 to 6.5%) can contain substantial amounts of H^+. However, it is generally believed that the potential negative charge represented by this bound H^+ is only available following a neutralization reaction. Lime requirement determinations for acid soils containing mostly organic matter (Histosols) now use buffer pH procedures rather than neutral salt solutions (van Lierop, 1990).

Residual acidity

The acid functional groups associated with SOM, especially the carboxyl groups (R–COOH), are also capable of forming complexes with metal ions (Stevenson and Vance, 1989). In many acid soils, complexation with Al^{3+}, Fe^{3+}, and Mn^{2+} may account for 60–80% of the potential negative charge of SOM. These ions (especially Fe^{3+} and Al^{3+}) are not considered exchangeable with mono- or divalent base cations at the concentrations of base cations typically found in soil solutions. They only react with added base when the ligand competition between OH^- ions and the SOM functional groups favor formation of the monomeric hydrolytic metal species. This typically occurs at pH values >4.5. Additions of organic matter to soils can reduce Al toxicity to crop growth without changing soil pH and can decrease KCl-exchangeable Al^{3+} (Hargrove and Thomas, 1981).

The acid functional groups of the mineral components of soils, which have the greatest abundance and reactivity, are the silanol and aluminol groups. These are present at the edges of layer silicate minerals and on the surface of the Fe and Al oxides and oxyhydroxides. The dissociation of H^+ can be represented as follows:

$$-MOH_2^{+N} = -MOH^{+N-1} + H^+ \tag{4}$$

where M represents a Fe, Al, or Si ion that is part of the mineral structure but that comes in direct contact with water molecules. This reaction is similar to that of a weak acid in that the degree of protonation or deprotonation is a function of pH; i.e., the net charge on these surfaces is a function of pH. The H^+ bound to these surface functional groups is not considered exchangeable with mono- or divalent base cations. Indeed, the chemistry of these functional groups is such that, at pH values that favor a net positive charge, an increase in ionic strength (addition of neutral salt) favors an increase in net positive charge (removal of H^+ from solution) (Parfitt, 1980). Removal of H^+ associated with these surface functional groups can only be achieved by neutralization with base.

In many acid mineral soils with variable charge, the hydroxyl silanol or aluminol group associated with the Fe and Al minerals is a significant portion of the total soil acidity. Often, the equivalence of $CaCO_3$ required to shift soil pH from 6.5 to 7.0 can be 2 to 4 times that required from pH 5.5 to 6.0 (Fox, 1980). Attempting to lime these soils to an optimum soil pH, as determined for soils that are dominated by constant-charge layer silicate minerals, can require an exorbitant amount of lime. In such instances, optimum yields are obtainable with neutralization of exchangeable Al^{3+}, provided sufficient exchangeable Ca^{2+} is present for root growth. These soils are also more susceptible to over-liming (Fox, 1980).

Other sources of acidity

The remaining sources of soil acidity are not quantifiable by the routine analytical methods used to estimate exchangeable acidity or lime requirement. These sources of acidity are more temporal in nature deriving from a number of factors including a unique soil characteristic or chemical composition, anthropogenic or natural inputs, and cultural management practices. One, or a combination of two or more of these factors can result in the generation of soil acidity that potentially can have the same deleterious effect on plant growth as the more traditional sources of acidity.

Oxidation–reduction

Oxidation reactions that follow the drainage of wetlands, or a falling water table, can generate substantial amounts of soil acidity (van Breemen, 1987). The chemical reactions that are the primary source of this acidity are based on the transformations of iron. Ferrous ion (Fe^{2+}) is generated from the reduction of ferric oxides and oxyhydroxides if a soil containing organic matter is submerged for more than a few days. Drainage of the soil results in the conversion of the Fe^{2+} ions to Fe^{3+} ions. The resulting Fe^{3+} ions undergo hydrolysis and releases H^+ ions to the soil solution. In acid-sulfate soils, soils containing strip mine spoils, or other soils containing significant quantities of pyrite (FeS_2), a source of Fe^{2+} ion is already present in the soil and exposure to oxygen can result in very low pH values ($p\tilde{H}$ 2) (McFee et al., 1981). The following overall reaction illustrates the quantity of moles of H^+ released as the result of the combined oxidation of the Fe^{2+} cation and sulfide anion, coupled with hydrolysis of the Fe^{3+} ion:

$$2FeS_2 + 7H_2O + 7.5O_2 = 4SO_4^{2-} + 8H^+ + 2Fe(OH)_3 \tag{5}$$

If allowed to go to completion, the above reaction can produce amounts of H^+ that make liming impractical as a management alternative. In such instances, the management scheme of choice is to keep the soils flooded as much as possible to prevent the oxidation of pyrite (Thomas and Hargrove, 1984).

Fertilizers

Commercial fertilizers (especially those containing ammonical-N, P and elemental S) are anthropogenic sources of soil acidity that are added to soils to increase crop yields. These soluble salts react to release H^+ and soluble anions, which can promote leaching of base cations from the soil. Microbiologically mediated nitrification is the dominant reaction involving NH_4^+-based fertilizers (e.g., NH_4NO_3) resulting in the formation of nitric acid (Adams, 1984):

$$NH_4NO_3 + 2O_2 = 2NO_3^- + 2H^+ + H_2O \tag{6}$$

Chemolithotrophic sulfur bacteria (typically *Thiobacilli*) are responsible for the oxidation of elemental S utilizing the energy released to fix carbon dioxide (CO_2) into organic matter (Tisdale et al., 1985):

$$CO_2 + S + 0.5O_2 + H_2O = [CH_2O] + SO_4^{2-} + 2H^+ \tag{7}$$

Elemental S has traditionally been used as a soil acidulant to promote soil acidity in the reclamation of alkaline soils. More recently it has been incorporated into commercial fertilizers to increase their S content. For concentrated P fertilizers (e.g., monocalcium phosphate) hydrolysis is the primary reaction that releases H^+ ions (Tisdale et al., 1985):

$$H_2O + Ca(H_2PO_4)_2 = CaHPO_4 + H_3PO_4 \tag{8}$$

The potential impact on the soil environment from these soluble salts depends in part on the method of application. Band application concentrates the fertilizer within the soil, favoring conditions that can result in extremely low pH values in the band ($pH < 1.5$ for triple superphosphate). Broadcast application followed by tillage disperses the fertilizer throughout the soil but extremely acid conditions can still form around the individual fertilizer granules. This results in partial dissolution of soil clay minerals and release of Al^{3+} and Fe^{3+} ions. In most soils, this fertilizer-produced acidity is rapidly neutralized, but the net reaction is still an increase in soil acidity.

Identification of the source of the N or P fertilizer allows the calculation of the potential acidity that can be released after addition to the soil (Table A7). For example, if ammonium sulfate is used, about 7.1 kg of pure calcium carbonate ($CaCO_3$) per kg of N added is necessary to neutralize the potential acidity added with the fertilizer. In practice, the amount of acidity generated is substantially less because of competing chemical and biological reactions. These include loss of N as NH_3 through volatilization, denitrification of NO_3-N, which

Table A7 Maximum amount of calcium carbonate ($CaCO_3$) required to balance the acidity produced by nitrogen (N) fertilizers[a]

Material	Nitrogen content ($g\ kg^{-1}$)	$CaCO_3$ equivalent ($kg\ CaCO_3\ kg^{-1}$ of N)
Ammo-phos A	110	6.8
Anhydrous ammonia	822	3.6
Calcium nitrate	150	0.0
Cottonseed meal	67	3.2
Dried blood	130	3.5
Potassium nitrate	130	0.0
Sulfate of ammonia	205	7.1
Tobacco stems	28	2.5
Urea	466	3.6

[a] Source: Tisdale et al., 1985.

Table A8 Amount of calcium carbonate ($CaCO_3$) required to balance the acidity produced by crop removal of exchangeable calcium (Ca) and magnesium (Mg)[a]

Crop	Yield ($kg\ ha^{-1}$)	Ca ($kg\ ha^{-1}$)	Average harvest Mg ($kg\ ha^{-1}$)	$CaCO_3$ equivalent ($kg\ ha^{-1}$)
Corn[b]				
whole plant	13000	52.0	32.5	264
grain	5400	0.8	6.5	29
Soybean[b]				
whole plant	6400	76.8	32.0	324
grain	1900	5.7	6.7	42
Small grains[c]	5300	18.6	13.3	101
Tobacco[b]	2240	62.0	25.0	258

[a] Sources: Walsh and Beaton, 1973; Westerman, 1990.
[b] Corn (*Zea mays* L.); soybean (*Glycine max* (L.) Merr.); tobacco (*Nicotiana* sp.).
[c] Small Grains: Barley (*Hordeum vulgare* L.); oats (*Avena* sp.)/wheat (*Triticum* sp.).

consumes H^+ ions, direct plant uptake of NH_4^+ ions, or plant uptake that removes unequal equivalents of anions and cations from the soil solution (Thomas and Hargrove, 1984; Tisdale et al., 1985). Uptake of NO_3^- in excess of cations will result in the release of OH^- and organic acid anions from the plant roots to maintain electrical neutrality. These anions either neutralize or bind with the H^+ ions in the soil solution such that the net acidity released from addition of a N-fertilizer could be zero. Such a result is highly unlikely under field conditions and is known not to occur for anions such as sulfate (SO_4^{2-}) and phosphate ($H_2PO_4^-$). For most sources of acid producing N, P, and S fertilizers, the actual soil acidity released is assumed to be half to two-thirds the maximum calculated value (Table A7).

Plant uptake

The extent of soil acidity generated by plant uptake of base cations (predominately calcium and magnesium) is a function of soil type (cation exchange capacity), cropping rotation, and management decisions concerning the crop residues. Plant species vary in their degree of cation uptake but in each case the basic reaction is the exchange of a base cation for a H^+ ion at the soil-root interface. Removal of Ca^{2+} and Mg^{2+} ions from the exchange complex of the soil (the primary source of these ions in soil) requires the release of the H^+ ions to maintain overall charge balance in the soil solution. Intensive cropping of a soil can remove significant amounts of these base ions, especially if all of the above ground portion of the crop is removed (for example, as with for corn (*Zea mais* L.) silage or tobacco (*Nicotiana* sp.)) (Table A8). Base cation removal with forage crops can be even higher because of the potential for several harvests per growing season. It has been shown that yields of alfalfa (*Medicago sativa* L.) approaching 10 metric tons result in the production of soil acidity requiring 600 kg $CaCO_3\ ha^{-1}$ for neutralization (Nyatsanga and Pierre, 1973). Management schemes that incorporate the crop residue back into the soil minimize the overall change in base cation content of the soil associated with crop production (Power and Legg, 1978). However, the base cations returned in this manner are not immediately available for plant uptake, nor are they capable of neutralizing the acidity released during their incorporation into the growing plant. Furthermore, the uptake of base cations by most crops occurs over a relatively short period of time (10–14 weeks) during a growing season. It is not uncommon to see a decrease in soil pH by 1 pH unit during this period of intense demand for nutrient ions, especially in soils with relatively low cation exchange capacities (e.g., $<5\ cmolc\ kg^{-1}$). Limited availability of base cations during this time will have the same deleterious effects on crop growth as an increase in soil acidity.

Acidic deposition

Another potential source of soil acidity that arises from anthropogenic inputs is acidic deposition. Acidic deposition is composed primarily of N and S acid-forming compounds that undergo gas-phase oxidation and aqueous-phase reactions in the atmosphere to form nitric and sulfuric acids (Tanner, 1989). Partial neutralization of these acids by ammonia (NH_3) in the atmosphere results in H^+, NH_4^+, NO_3^-, and SO_4^{2-} being the dominant ions in acidic rainwater (Berdèn et al., 1987) and in dry deposition (Murphy and Sigmon, 1989). Acidic deposition, therefore, represents both an episodic and continuous input of ions into the soil ecosystem. These ions can have both a beneficial and a harmful effect. The inputs of S and N can have a positive impact on plant growth, while the inputs of H^+ coupled with the strong acid anions can promote leaching of base cations and mobilization of toxic ions such as Al^{3+}.

Current loading rates from acidic deposition are <2 kmoles $H^+\ ha^{-1}\ yr^{-1}$ except for areas located near point sources of N and S acid-forming substances, or in high-elevation ecosystems that are also impacted by acidic cloud-water (Berdèn et al., 1987; Aneja et al., 1992; Mohnen, 1992). In many rural areas the loading rate is <1 kmoles $H^+\ ha^{-1}\ yr^{-1}$ (Ulrich, 1991), which is equivalent to that neutralized by 50 kg of pure calcium carbonate $ha^{-1}\ yr^{-1}$. Compared to the acidity generated by fertilizer additions and through plant uptake (Tables A7 and A8), the amount of acidity being deposited from atmospheric deposition is small; and it is generally accepted that continued inputs of acidic deposition on intensively managed soil systems will have no effect on soil acidity (McFee, 1983; Tabatabai, 1985). Forages and native pastures, however, represent agronomic ecosystems that can be considered sensitive to acidic deposition (Irving, 1983). The rhizosphere in such ecosystems is concentrated in the top few cm of soil, which remains relatively undisturbed for long periods of time. Due to grazing and mechanical harvesting, there is a regular export of base cations. Replacement of these base cations is generally left to natural weathering processes for pastures that are not highly managed. Forages and pastures located on soils with inherently low buffer capacity, low organic matter content, and receiving low management input will be susceptible to increases in soil acidity due to acidic deposition. Such soils (ultisols and alfisols) are predominant throughout the southeastern United States (Buol, 1983) where substantial acreages (14–16 million ha) are devoted to forages and pastures. The average lime application rate per hectare throughout this region in 1980 was <220 kg yr^{-1}. Assuming a realistic economic application rate of 4500 kg ha^{-1}, only 1 out of every 20 ha received lime. Expressed another way, this means that it will take 20 years before each hectare will receive just one lime application. Acidic deposition during this period will be equivalent to $\sim$1000 kg of $CaCO_3$ ha^{-1}. These figures demonstrate what is meant by low management input and suggest that a negative impact of acidic deposition through an increase in soil acidity is a distinct possibility.

Soils associated with forested ecosystems are considered to be the most susceptible to change induced by acidic deposition. For example, at the Walker Branch Watershed, which is located on the U.S. Department of Energy's Oak Ridge Reservation in Anderson County, Tennessee in the USA, the total estimated input of H^+ from atmospheric deposition is 1.5 kmoles H^+ ha^{-1} yr^{-1} (75 kg $CaCO_3$ equivalent ha^{-1} yr^{-1}) (Johnson and Lindberg, 1989).

Internal generation of H^+, due to formation of carbonic acid and net accumulation of base cations in the vegetation, is 1.6 kmoles H^+ ha^{-1} yr^{-1}. The current rates of acidic deposition have essentially doubled the total H^+ loading at this location. This in turn has accelerated the leaching of base cations (K^+, Ca^{2+}, and Mg^{2+}) from the forest canopy by 50%. This accelerated loss of cations from the canopy foliage can increase soil acidity if it is not balanced by internal H^+ sinks such as weathering, or reaction with the weak acid functional groups associated with SOM or Fe and Al oxides and oxyhydroxides. It has been argued that most forested ecosystems developed on non-calcareous parent material in humid environments cannot compensate for the continued inputs of H^+ from acidic deposition (Ulrich et al., 1980). The soils associated with these ecosystems will continue to acidify leading to the loss of soil nutrients due to leaching, and mobilization of toxic metals (primarily Al^{3+} and Mn^{2+}) in the soil solution and in the stream waters draining these ecosystems.

Objections to this line of reasoning are based on the argument that the effects of acidic deposition on soils in forested ecosystems can only be evaluated from the standpoint of how these acidic inputs interact with the natural processes of soil acidification (Rosenqvist, 1978; Krug and Frink, 1983; Tabatabai, 1985). Soil formation in humid temperate climates is an acidifying process, and the simple correlation between areas of high acidic deposition (>1 kmole ha^{-1} yr^{-1}) and the presence of acidic soils and stream waters is not sufficient cause to conclude that acidic inputs will increase soil acidity in these ecosystems. Many of the forests of northern Europe and eastern North America have undergone substantial changes in land use policy in the past 200 years. As many of these forests are now aggrading, the natural soil acidification that accompanies such regrowth cannot be attributed to acidic deposition (Krug and Frink, 1983). Even at the Walker Branch Watershed, intensive studies have indicated that, despite accelerated leaching due to H^+ inputs from acidic deposition, a significant change in soil acidity in the next few decades is very unlikely (Johnson and Lindberg, 1989). Lack of an appreciation of natural soil acidification processes, combined with results from intensive studies dealing with whole watersheds receiving acidic deposition, have forced a reevaluation of how these acidic inputs could enhance soil acidity in forested ecosystems (Johnson et al., 1991; Robarge and Johnson, 1992). It is now accepted that it is very unlikely that changes in soil acidity induced by acidic deposition can be quantitatively described by a single index parameter (Matzner, 1989), and that there has probably been too much emphasis on changes in soil pH and cation depletion as a necessary and expected effect of acidic deposition on soil systems (Johnson et al., 1991). Of more importance is how the natural acidification processes within a given ecosystem predispose that system to the way it will respond to acidic inputs, particularly to the inputs of the mineral acid anions NO_3^- and SO_4^{2-}. These mechanisms are briefly discussed in the next section and in more detail elsewhere (Matzner, 1989; Ulrich, 1991; Robarge and Johnson, 1992).

Discussion

The majority of the concepts discussed in the previous sections were reported on and subsequently validated during the 1950s and 1960s (Thomas and Hargrove, 1984). The successful lime requirement programs that have been developed as a result of this work have formed the foundation for modern agriculture for the past 30 years in regions dominated by acid soils. More recent research efforts have focused on the problems associated with soil acidity and changes in modern agriculture management techniques, the challenge of developing low input systems to replace shifting (slash and burn) agriculture, and environmental concerns about the effects of acidic deposition on soil systems. Examples from each of these subject areas are discussed to illustrate that our knowledge concerning the components, mechanisms and interactions that comprise soil acidity is still incomplete.

Subsoil acidity

In many acid soils, acidity is not confined to the surface of the soil profile but extends down into the subsoil (e.g., ultisols). Root growth is often confined to the surface horizons in these soils because of this subsoil acidity (primarily exchangeable Al^{3+} and H^+). The lack of root penetration into the subsoil means that the soil water stored there is unavailable to support plant growth. The inability of plants to gain access to this water is especially important in regions receiving adequate annual rainfall, but that are characterized by growing seasons during which drought conditions frequently occur at critical physiological stages of crop growth (Reicosky et al., 1977). Lack of adequate available soil water during these periods significantly decreases yields. Application of lime to neutralize surface soil acidity in these soils has little immediate effect on subsoil acidity because the overall neutralization reaction requires that the Ca^{2+} ions remain in the surface horizon (Thomas and Hargrove, 1984):

$$\begin{aligned}&2Al^{3+}\text{-soil} + 3CaCO_3 + 3H_2O = \\ &\qquad 3Ca^{2+}\text{-soil} + 2Al(OH)_3 + 3CO_2\end{aligned} \tag{9}$$

Deep placement of lime has not proven to be an economic amelioration procedure because of the expense involved in the technique. It is possible to introduce lime slurries into the subsoil but the volume of soil affected is relatively small and the increase in yields obtained, if any, do not justify the costs associated with this procedure.

Amelioration of subsoil acidity is currently accomplished with surface applications of calcium salts; primarily gypsum $Ca(SO)_4 \cdot 2H_2O$ (McCray and Summer, 1990). Limited retention of the SO_4^{2-} anion in the surface horizon provides the necessary mobile anion for movement of the Ca^{2+} ion into the subsoil. The net result is an increase in exchangeable Ca^{2+} at the expense of exchangeable Al^{3+}. The exact mechanism for the decrease in exchangeable Al^{3+} is still subject to debate, but may be due to the formation of soluble $AlSO_4^+$ complexes which are leached from the soil, or to the formation of aluminum sulfate precipitates (e.g., jurbanite). The SO_4^{2-} ions would also particiate in ligand exchange reactions at the surface of the Fe and Al oxides and oxyhydroxides:

$$\mathrm{M-(OH)_2 + SO_4^{2-} = M-(OH)SO_4^- + OH^-} \qquad (10)$$

where M represents either Fe or Al. The OH^- ions released by this ligand exchange reaction would in turn neutralize exchangeable Al^{3+}. The adsorbed SO_4^{2-} can either remain on the oxide surface, or form a separate solid phase due to the relatively high concentrations of SO_4^{2-} in the soil solution. This proposed reaction would favor an increase in subsoil pH, but a positive change in pH is not always associated with the application of gypsum. Subsoil pH is not considered a reliable indication of an improvement in conditions that favor root growth.

The amounts of gypsum necessary to ameliorate subsoil acidity depend on soil type, but surface applications may approach 10 Mg ha^{-1}. Leaching of exchangeable K^+ and Mg^{2+} from the surface horizons is a potential problem at these high loading rates, especially in soils with relatively low cation exchange capacities (<5 cmolc kg^{-1}). Supplemental additions of K and Mg fertilizers are necessary under these conditions to maintain crop growth (McCray and Summer, 1990).

Addition of gypsum allows the amelioration of subsoil acidity within one or two growing seasons, but it is becoming clear that long term application of fertilizer and lime to surface horizons alone can facilitate the accumulation of sufficient base cations in the subsoil to promote root growth. This is particularly true for the subsoils of ultisols in the southeastern USA (Hardy et al., 1990). Continuous cultivation for over 30 years has resulted in reduction of 23 to 100% of the exchangeable Al^{3+} in subsoils under managed versus unmanaged sites. The primary restriction to plant growth in the argillic horizons of these ultisols is now related to physical properties, and, with the proper subsoiling techniques, soil water stored in these horizons is available for plant growth. Similar changes are occurring in the subsoils of cultivated soils within the middle and upper parts of the Atlantic Coastal Plain and the Piedmont regions of the southeastern United States (Buol, 1985).

No-till planting

Another tillage practice that can influence soil acidity is no-till planting. No-till crop production systems involve little or no mixing of the soil and leaves crop residues on the soil surface as a protective mulch to minimize soil erosion (Larson et al., 1978). Additional benefits associated with no-till planting include increased water infiltration (minimal surface crusting), decreased soil evaporation, and an increase in SOM content and soil microbial population (Blevins et al., 1983). The disadvantage in regards to soil acidity is that no-till planting precludes mixing of crop residues, lime, and fertilizers with the surface soil. In continuous no-tillage crops such as corn (*Zea mays* L.), N applications are restricted to the soil surface or the top 5 to 8 cm of the soil if incorporated during planting. Release of H^+ ions due to nitrification (enhanced by the increase in soil microbial populations), coupled with greater Ca^{2+} loss through leaching due to the presence of NO_3^- anions and increased infiltration of water, combine with crop uptake of base cations to decrease soil pH more rapidly with depth than with conventional tillage treatments (Table A9). This decrease in soil pH and loss of exchangeable Ca^{2+} is matched with an increase in exchangeable Al^{3+}, which in turn reduces yields. This increase in soil acidity can also result in the inactivation of herbicides often used to kill the sod before planting. Lower crop yields and poor control of weeds are visual indicators of low surface soil pH in no-till plantings (Thomas, 1986).

Because the acid-producing effect of application of N fertilizers is concentrated in the soil surface, neutralization is accomplished with surface application of lime in no-till plantings. The management questions that need to be addressed, however, are the frequency and amount of lime required to maintain optimum yields. For example, over-liming can result in possible enhancement of N volatilization (as NH_3) from urea-based fertilizers. Failure to add enough lime may limit the replacement of base cations removed by crop uptake from deeper in the surface soil. Proper sampling design for determining lime requirement is also a problem. Stratification caused by the acidification reactions limits the usefulness of traditional soil sampling procedures. No-till plantings may require sampling as a function of depth for proper lime recommendations. These management problems illustrate why soil acidity is considered one of the most serious problems encountered in no-till plantings, and why no-till soils require different management techniques than those used with conventionally tilled soils (Thomas, 1986).

Acid tolerant genotypes

Management schemes that include neutralization of soil acidity by lime assume that an adequate source of liming material is available that can be economically applied and mechanically incorporated into the soil. For low-input agriculture systems this option is often not available. In these systems, successful management techniques must include crops with a genetic tolerance to soil acidity (Foy, 1984). Screening for plant tolerance to acidity must take into account all of the possible toxic conditions that may exist in acid soils (Scott and Fisher, 1989). Acid soil toxicity affects the growth of different plants through different physiological and biochemical pathways, depending

Table A9 Effect of lime on continuous corn (*Zea mais*) grain yield using no-till planting[a]

Year	Yield (q ha^{-1})		Yield increase (%)	Surface pH	
	No lime	Lime		No lime	Lime
1965	50.2	60.9	21.3	4.8	5.1
1966	73.2	75.4	3.0	4.8	5.1
1967	65.5	79.3	21.1	4.5	5.2
1968	57.5	84.1	46.3	4.5	5.7
1969	69.4	97.6	39.3		
1970	74.7	90.6	21.3	4.5	5.7
1971	73.0	98.4	34.8	–	–
1972	45.6	82.3	80.5	4.9	6.4

[a] Source: Tables 1 and 2, Moschler et al., 1973.

Table A10 Major constraints and responses of plant growth under acid soil conditions[a]

Constraint	Response	Affected part
$>$ H^+ concentration	H^+ toxicity	Root
$>$ Al^{3+} concentration	Al toxicity	Root
$>$ Mn^{2+} concentration	Mn toxicity	Shoot
$<$ base cation concentration	Ca, K, Mg deficiency	Whole plant
$<$ P and Mo solubility	P, Mo deficiency	Whole plant
Inhibition of root growth	Nutrient and water deficiency	Whole plant
Increase in leaching	Nutrient deficiency	Whole plant

[a]Source: Clark, 1984; Foy, 1984; Marschner, 1991.

on the genetic inheritance of an individual plant species (Table A10).

Because Al^{3+} ions dominate the exchange complex in acid mineral soils, the presence of monomeric Al^{3+} ions in soil solution is considered to be the most common acidity impediment for plant growth (Foy, 1984). Plant response to high Al concentrations includes reduction of cell division in root apices, DNA replication, P availability at root membranes, and interference with sugar phosphorylation enzymes. More recent work has demonstrated that polynuclear hydroxy Al species (especially triskaidekaaluminum; $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ or Al_{13}) are also toxic to plant growth (Kinraide, 1991). The fact that these polycationic Al species may be present in aqueous Al solutions used to screen for Al tolerance questions earlier conclusions concerning the role of monomeric Al species in the response of plants to Al toxicity; but it is not yet clear to what extent these polycationic Al species may actually occur in soil solutions. Evidence also continues to accumulate that Al constraints to root growth can be partially alleviated by Ca additions (Alva et al., 1986; Noble et al., 1988). Calcium is important to maintain cell wall structure, membrane stability, and regulation of enzymes in plants (Clark, 1984). Several nutrient culture studies have shown that it is the ratio of Ca to Al that is important in alleviating Al constraints to growth (Cameron et al., 1986; Noble et al., 1988). This suggests that the presence of Ca from the application of gypsum is as important in reducing subsoil acidity as the potential formation of relatively insoluble aluminum-sulfate compounds. Hydrogen-induced root injury occurs at $pH < 4$ (Islam et al., 1980) and involves changes in root membrane permeability, interference in nutrient transport, and loss of organic substrates and absorbed cations (Foy, 1984). Toxicity due to H^+ ions is of concern in acid organic soils and possibly from nitrification and hydrolysis reactions of fertilizers. Toxicity from Mn in acid soils is not related to a decrease in root growth, but from the excessive accumulation of Mn in the shoots of plants grown on soils with high exchangeable Mn levels (Kamprath, 1984).

A number of screening methodologies have been developed for identification of acid tolerant genotypes (Howeler, 1991). These methodologies have advantages and disadvantages, and more attention needs to be given to activities of individual species in solution, especially for Al (Kinraide, 1991). These techniques, combined with a growing understanding of the physiological basis of tolerance (Bennet and Breen, 1991; Taylor, 1991), has lead to the identification of acid tolerant germ plasm for a number of crop species, both in the temperate regions and the tropics. However, these screening procedures assume that plants are passive role players in regards to soil acidity. This is not the case, and as living systems, plants can choose between two strategies (tolerance or avoidance) for adapting to acidity constraints (Marschner, 1991). The strategy of choice appears to be avoidance as reflected in the ability of plants to *(a)* increase the pH of the rhizosphere, *(b)* release organics to chelate toxic cations, and *(c)* employ mycorrhizae to increase root surface area. The single factor approach of most acid-tolerant screening procedures do not account for the active response of plants to acid conditions. This may account for the limited success achieved with laboratory selected acid-tolerant species when grown under field conditions. Although evidence continues to accumulate that selection based on laboratory screening techniques can be used to develop genotypes adapted to the toxic conditions of acid soils (Furlani et al., 1991; Ritchey, 1991), and that breeding programs will lead to the development of tolerant cultivars for major crop and pasture species (Howeler, 1991).

Acidic deposition

Concern about the potential negative impacts of acidic deposition on forested soils is an example of a problem dealing with soil acidity on the scale of whole watersheds, geographical regions, or even whole countries. Liming or selection of acid tolerant species is not a management alternative in these situations. The only effective approach to reduce the potential impacts of acidic deposition is through control of emissions of the acid-forming precursor compounds. Setting goals for emission controls is complicated by the fact that the major constituents of acidic deposition are also components of the natural processes of soil acidification, which occur in all forested ecosystems, especially those found in humid environments. Valid questions that must be addressed are whether current rates of deposition are sufficient to induce change, and whether this change can be detected. The later question is especially important because historical data characterizing forested ecosystems is generally not available, or is subject to different interpretations due to changes in land use patterns with time. In most cases this negates any determination of change induced by acidic deposition by simply comparing bulk soil characterization measurements (e.g., soil pH, cation exchange capacity, or exchangeable Al^{3+} or Ca^{2+}). Emphasis instead must be placed on the natural soil acidification processes and how acidic inputs can act to destabilize a forested ecosystem.

Processes within forested soils can be considered as a cycling of ions within an ecosystem (Ulrich, 1983). The major components of this cycle are: inputs (atmospheric deposition, weathering of soil minerals), outputs (leaching), plant uptake, and mineralization (decomposition of organic matter). If an ecosystem is in steady state, the fluxes from inputs and outputs will be equal and net H^+ production or consumption will be minimized. Temporal discouplings do occur in these stable ecosystems, for example during N transformations, since many forested soils have a potential for high mineralization and nitrification rates (Swank, 1986; Gundersen and Rasmussen, 1990); but internal buffering reactions (e.g., exchangeable Ca^{2+} and Mg^{2+}) act to limit the intensity of these reactions. The H^+ generated by nitrification is eventually balanced by H^+ consuming reactions (mineral weathering). Inputs of N from acidic deposition, however, can increase the total N pool within a soil and eventually overwhelm the resistance of the ecosystem to H^+ production during N transformations (Ulrich, 1983; Gundersen and Rasmussen, 1990). When this occurs, nitrification following mineralization will force a decrease in soil solution pH and the generation of an excess of NO_3^- anions. In these naturally acid soils, the decrease in pH will in turn favor an increase in soil solution Al and an increase in the leaching of base cations. This change in soil acidity is not due to the concentration of NO_3^- in individual acidic deposition events, nor is it due to changes in static soil parameters. The change is due to the dynamics of N cycling within the ecosystem; i.e., the internal cycling of N has become saturated (Ågren and Bosatta, 1988).

Another example of how acidic deposition can destabilize a soil process involves the normal transport of Al within the soil profile (Driscoll and Schecher, 1990). Mobilization and subsequent deposition of Al is an integral part of soil genesis in well-drained acid soils. This is because the bicarbonate anion (HCO_3^-) and dissolved organic acids are normally the dominant anions in the soil solution. Bicarbonate concentrations are elevated in the soil solution of the surface soil horizons because of an excess of carbon dioxide (CO_2) released from mineralization and root respiration into the soil atmosphere (i.e., there is an increase in the partial pressure of CO_2):

$$CO_{2aq} + H_2O = H_2CO_3 = H^+ + HCO_3^- \tag{11}$$

As the soil solution drains from the surface horizons, there is a drop in the partial pressure of CO_2 in the soil atmosphere, which causes the dissolved CO_2 to degas, resulting in the removal of the HCO_3^- ion from solution (Reuss, 1991). Since this reaction is a H^+ consuming process, it promotes the hydrolysis of Al^{3+} and deposition of an Al oxide or hydroxide, for example:

$$Al^{3+} + 3HCO_3^- = \underset{\text{gibbsite}}{Al(OH)_3} + 3CO_2 \tag{12}$$

A similar result will occur for dissolved organic acids following mineralization. In either case, the removal of the transient anion must result in the deposition of Al, either within the soil profile or in the sediment of surface waters draining the watershed (Driscoll and Schecher, 1990).

Continued loading of N and S from acidic deposition on these soils results in a gradual change of the dominant anions in the soil solution from HCO_3^- and dissolved organic acids to NO_3^- and SO_4^{2-}. Dissolved NO_3^- and SO_4^{2-} are not transient anions and remain in the soil solution as it moves through the soil profile. This in turn results in the apparent mobilization of dissolved Al^{3+}, causing elevated concentrations of Al in the soil solution and surrounding surface waters (Driscoll and Schecher, 1990). This change in soil solution Al^{3+} concentrations does not require a change in soil acidity (decrease in soil pH, change in cation exchange capacity, or an increase in exchangeable Al^{3+}).

Summary

Soil acidity is one of the most important factors regulating the species distribution and composition within an ecosystem, and in limiting crop yields. The acidification of soils is the consequence of a combination of natural and anthropogenic processes. Aluminum is generally accepted as the toxic agent in most acid mineral soils, but uncertainty still exists about the toxicity of different species of aluminum in the soil solution and the effect other ions have on mediating this toxicity. In organic soils, aluminum toxicity is probably not the dominant constraint to plant growth. Industrialization has resulted in the release of acids to the atmosphere, much of which has been deposited in terrestrial ecosystems. Our knowledge of soil acidity in regards to liming and crop production has proven inadequate in understanding how these inputs of anthropogenic acids will degrade naturally acid soils and the streams that drain them. Closer examination of natural soil acidification processes is required to understand how anthropogenic acid inputs can cause changes in soil acidity. Continued study of these natural soil acidification processes will in turn answer many questions concerning the ecophysiological mechanisms by which soil acidity limits plant growth. Such information will aid in the development of acid tolerant genotypes for use in low-input agricultural systems as alternatives to shifting (slash and burn) agriculture.

Wayne P. Robarge

Bibliography

Adams, F., 1984. Crop response to lime in the southern United States. In Adams, F., ed., *Soil Acidity and Liming.* Madison: American Society of Agronomy, pp. 211–265.

Ågren, G.I., and Bosatta, E., 1988. Nitrogen saturation of terrestrial ecosystems. *Environ. Pollut.*, **54**: 87–113.

Alva, A.K., Edwards, D.G., Asher, C.J., and Blamey, F.P.C., 1986. Relationships between root length of soybean and calculated activities of aluminum monomers in nutrient solution. *Soil Sci. Soc. Am. J.*, **50**: 959–962.

Aneja, V.P., Robarge, W.P., Claiborn, C.S., Murthy, A., Soo-Kim, D., Li, Z., and Cowling, E.B., 1992. Chemical climatology of high elevation spruce-fir forests in the southern Appalachian mountains. *Environ. Pollut.*, **75**: 89–96.

Baes, C.F., Jr. and Mesmer, R.E., 1976. *The Hydrolysis of Cations.* New York: John Wiley, p. 489.

Barnhisel, R., and Bertsch, P.M., 1982. Aluminum. In Page, A.L., Chair, ed. comm., *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties*, 2nd edn. Madison, WI: Soil Science Society of America, pp. 275–300.

Bennet, R.J., and Breen, C.M., 1991. The aluminum signal: new dimensions to mechanisms of aluminum tolerance. *Dev. Plant and Soil Sci.*, **45**: 703–715.

Berdèn, M., Nilsson, S.I., Rosèn, K., and Tyler, G., 1987. Soil acidification extent, causes and consequences. Rep. No. 3292. Solna, Sweden: National Swedish Environmental Protection Board.

Bertsch, P.M., 1989. Aqueous polynuclear aluminum species. In Sposito, G., ed., *The Environmental Chemistry of Aluminum.* Boca Raton, FL: CRC Press, pp. 87–115.

Blevins, R.L., Smith, M.S., Thomas, G.W., and Frye, W.W., 1983. Influence of conservation tillage on soil properties. *J. Soil and Water Conserv.*, **38**: 301–305.

Bloom, P.R., 1981. Metal-organic matter interactions in soil. In Dowdy, R.H., Chair, ed. comm., 1981. *Chemistry in the Soil Environment.* Madsion, WI: Soil Science Society of America, pp. 129–150.

Bloom, P.R., and Erich, M.S., 1989. The quantitation of aqueous aluminum. In Sposito, G., ed., *The Environmental Chemistry of Aluminum.* Boca Raton, FL: CRC Press, pp. 1–27.

Bloom, P.R., McBride, M.B., and Weaver, R.M., 1979. Aluminum organic matter in acid soils: buffering and solution aluminum activity. *Soil Sci. Soc. Am. J.*, **43**: 448–493.

van Breemen, N., 1987. Effects of redox processes on soil acidity. *Netherlands J. Agric. Sci.*, **35**: 271–279.

Buol, S.W., ed., 1983. Soils of the Southern States and Puerto Rico. *Southern Cooperative Series Bulletin 174.* Raleigh, NC: North Carolina State University, p. 105.

Buol, S.W., 1985. Mineralogy classes in soil families with low activity clays. In Kittrick, J.A., ed., *Mineral Classification of Soils.* Madison, WI: American Society of Agronomy, pp. 169–178.

Cameron, R.W., Ritchie, G.S.P., and Robson, A.D., 1986. Relative toxicities of inorganic aluminum complexes to barley. *Soil Sci. Soc. Am. J.*, **50**: 1231–1236.

Clark, R.B., 1984. Physiological aspects of calcium, magnesium and molybdenum deficiencies in plants. In Adams, F., ed., *Soil Acidity and Liming.* Madison, WI: American Society of Agronomy, pp. 99–170.

Driscoll, C.T., and Schecher, W.D., 1990. The chemistry of aluminum in the environment. *Environ. Geochem. Health*, **12**: 28–49.

Fox, R.L., 1980. Soils with variable charge: agronomic and fertility aspects. In Theng, B.K.G., ed., *Soils with Variable Charge.* Lower Hutt, New Zealand: New Zealand Society of Soil Science, pp. 195–224.

Foy, C.D., 1984. Physiological effects of hydrogen, aluminum and manganese toxicities in acid soil. In Adams, F., ed., *Soil Acidity and Liming.* Madison, WI: American Society of Agronomy, pp. 57–97.

Furlani, P.R., Quaggio, J.A., and Gallo, P.B., 1991. Differential responses of sorghum to aluminum in nutrient solution and acid soil. *Dev. Plant and Soil Sci.*, **45**: 953–958.

Gregorich, E.G., 2001. *Soil and Environmental Science Dictionary.* Boca Raton, FL: CRC Press, 577 pp.

Gundersen, P., and Rasmussen, L., 1990. Nitrification in forest soils: effects from nitrogen deposition on soil acidification and aluminum release. *Rev. Environ. Contam. Toxicol.*, **113**: 1–50.

Hardy, D.H., Raper, C.D., Jr., and Miner, G.S., 1990. Chemical restrictions of roots in ultisol subsoils lessened by long-term management. *Soil Sci. Soc. Am. J.*, **54**: 1657–1660.

Hargrove, W.L., and Thomas, G.W., 1981. Effect of organic matter on exchangeable aluminum and plant growth in acid soils. In Dowdy, R.H., Chair, ed. comm., *Chemistry in the Soil Environment.* Madison, WI: Soil Science Society of America, pp. 151–166.

Howeler, R.H., 1991. Identifying plants adaptable to low pH conditions. *Dev. Plant and Soil Sci.*, **45**: 885–904.

Irving, P.M., 1983. Acidic precipitation effects on crops: a review and analysis of research. *J. Environ. Qual.*, **12**: 442–453.

Islam, A.K., Edwards, D.G., and Asher, C.J., 1980. pH optima for crop growth: results of a flowing solution culture experiment with six species. *Plant Soil*, **54**: 339–357.

Johnson, D.W., and Lindberg, S.E., 1989. Acidic deposition on Wallker Branch watershed, In Adriano, D.C., and Havas, M., eds., *Acidic Precipitation,* Vol. 1. Berlin: Springer-Verlag, pp. 1–38.

Johnson, D.W., Cresser, M.S., Nilsson, S.I., Turner, J., Ulrich, B., Binkley, D., and Cole, D.W., 1991. Soil changes in forest ecosystems: evidence for and probable causes. *Proc. R. Soc. Edinburgh Sec. B. Biol. Sci.*, **97**: 81–116.

Juo, A.S.R., and Kamprath, E.J., 1979. Cooper chloride as an extractant for estimating the potentially reactive aluminum pool in acid soils. *Soil Sci. Soc. Am. J.*, **43**: 35–38.

Kamprath, E.J., 1970. Exchangeable aluminum as a criterion for liming leached mineral soils. *Soil Sci. Soc. Am. Proc.*, **24**: 252–254.

Kamprath, E.J., 1971. Potential detrimental effects from liming highly weathered soils to neutrality. *Florida Soil and Crop Sci. Soc. Proc.*, **31**: 200–203.

Kamprath, E.J., 1984. Crop response to lime on soils in the tropics. In Adams, F., ed., *Soil Acidity and Liming.* Madison, WI: American Society of Agronomy, pp. 349–368.

Kinraide, T.B., 1991. Identity of the rhizotoxic aluminum species. *Dev. Plant and Soil Sci.*, **45**: 717–728.

Krug, E.C., and Frink, C.R., 1983. Acid rain on acid soil: a new perspective. *Science*, **221**: 520–525.

Larson, W.E., Holt, R.F., and Carlson, C.W., 1978. Residues for soil conservation. In Lewis, W.M., Chair, ed. comm., *Crop Residue Management Systems.* Madison, WI: American Society of Agronomy, pp. 1–15.

van Lierop, W., 1990. Soil pH and lime requirement determination. In Westerman, R.L., ed., *Soil Testing and Plant Analysis.* Madison, WI: Soil Science Society of America, pp. 73–126.

Magdoff, F.R., and Bartlett, R.J., 1985. Soil pH buffering revisted. *Soil Sci. Soc. Am. J.*, **49**: 145–148.

Marschner, H., 1991. Mechanisms of adaptation of plants to acid soils. *Plant Soil*, **134**: 1–20.

Matzner, E., 1989. Acidic precipitation: case study Solling. In Adriano, D.C., and Havas, M., eds., *Acidic Precipitation,* Vol. 1. Berlin: Springer-Verlag, pp. 39–83.

McCray, J.M., and Summer, M.E., 1990. Assessing and modifying Ca and Al levels in acid subsoils. *Adv. Soil Sci.*, **14**: 45–75.

McFee, W.W., Byrnes, W.R., and Stockton, J.G., 1981. Characteristics of coal mine overburden important to plant growth. *J. Environ. Qual.*, **10**: 300–308.

McFee, W.W., 1983. Sensitivity ratings of soils to acidic deposition: a review. *Environ. Exp. Bot.*, **23**: 203–210.

McLean, E.O., 1978. Principles underlying the practice of determining lime requirements of acid soils by use of buffer methods. *Commun. Soil Sci. Plant Anal.*, **9**: 699–715.

Mohnen, V.A., 1992. Atmospheric deposition and pollutant exposure of eastern United States forests. In Eagar, C., and Adams, M.B., eds., *Ecology and Decline of Red Spruce in the Eastern United States.* New York: Springer-Verlag, pp. 64–124.

Moschler, W.W., Martens, D.C., Rich, C.I., and Shear, G.M., 1973. Comparative lime effects on continuous no-tillage and conventionally tilled corn. *Agron. J.*, **65**: 781–783.

Murphy, C.E., Jr., and Sigmon, J.T., 1989. Dry deposition of sulfur and nitrogen oxide gases to forest vegetation. In Lindberg, S.E., Page, A.L., and Norton, S.A., eds., *Acidic Precipitation,* Vol. 3. Berlin: Springer-Verlag, pp. 217–240.

Noble, A.D., Foy, M.V., and Summer, M.E., 1988. Calcium-aluminum balance and the growth of soybean roots in nutrient solution. *Soil Sci. Soc. Am. J.*, **52**: 1651–1656.

Nyatsanga, T., and Pierre, W.H., 1973. Effect of nitrogen fixation by legumes on soil acidity. *Agron. J.*, **65**: 936–940.

Oates, J.M., and Kamprath, E.J., 1983. Soil acidity and liming: I. Effect of the extracting solution cation and pH on the removal of aluminum from acid soils. *Soil Sci. Soc. Am. J.*, **47**: 687–689.

Parfitt, R.L., 1980. Chemical properties of variable charge soils. In Theng, B.K.G., ed., *Soils With Variable Charge.* Lower Hutt, New Zealand: New Zealand Society of Soil Science, pp. 167–194.

Peech, M., 1965. Hydrogen-ion acitivity. In Black, C.A., ed., *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties.* Madison, WI: American Society of Agronomy, pp. 914–926.

Power, J.F., and Legg, J.O., 1978. Effect of crop residues on the soil chemical environment and nutrient availability. In Lewis, W.M., Chair, ed. comm., *Crop Residue Management systems.* Madison, WI: American Society of Agronomy, pp. 85–100.

Reicosky, D.C., Cassel, D.K., Blevins, R.L., Gill, W.R., and Naderman, G.C., 1977. Conservation tillage in the Southeast. *J. Soil and Water Conserv.*, **32**: 13–19.

Rengel, Z., 2003. *Handbook of Soil Acidity.* New York: Marcel Dekker, 496 pp.

Reuss, J.O., 1991. The transfer of acidity from soils to surface waters. In Ulrich, B., and Summer, M.E., eds., *Soil Acidity.* Berlin: Springer-Verlag, pp. 203–217.

Ritchey, K.D., 1991. Evaluating sweet potato tolerance to aluminum toxicity: comparison of rapid test method and field results. *Dev. Plant and Soil Sci.*, **45**: 939–945.

Ritchie, G.S.P., 1989. The chemical behavior of aluminum, hydrogen and manganese in acid soils. In Robson, A.D., ed., *Soil Acidity and Plant Growth.* Sydney: Academic Press, pp. 1–60.

Robarge, W.P., and Johnson, D.W., 1992. The effects of acidic deposition on forested soils. *Adv. Agron.*, **47**: 1–83.

Robson, A.D., and Abbott, L.K., 1989. The effect of soil acidity on microbial activity in soils. In Robson, A.D., ed., *Soil Acidity and Plant Growth.* Sydney: Academic Press, pp. 139–165.

Rosenqvist, I.Th., 1978. Alternative sources for acidification of river water in Norway. *Sci. Total Environ.*, **10**: 39–49.

Scott, B.J., and Fisher, J.A., 1989. Selection of genotypes tolerant of aluminum and manganese. In Robson, A.D., ed., *Soil Acidity and Plant Growth.* Sydney: Academic Press, pp. 167–203.

Sparks, D.L., 1996. *Methods of Soil Analysis. Part 3. Chemical Methods.* Madison, WI: Soil Science Society of America, American Society of Agronomy, 1390 pp.

Stevenson, F.J., 1982. *Humus Chemistry. Genesis, Composition, Reactions.* New York: John Wiley, p. 443.

Stevenson, F.J., and Vance, G.F., 1989. Naturally occurring aluminum-organic complexes. In Sposito, G., ed., *The Environmental Chemistry of Aluminum.* Boca Raton, FL: CRC Press, pp. 117–145.

Sumner, M.E., Fey, M.V., and Noble, A.D., 1991. Nutrient status and toxicity problems in acid soils. In Ulrich, B., and Sumner, M.E., eds., *Soil Acidity.* Berlin: Springer-Verlag, pp. 149–182.

Swank, W.T., 1986. Biological control of solute losses from forest ecosystems. In Trudgill, S.T., ed., *Solute Processes.* New York: John Wiley, pp. 87–139.

Tabatabai, M.A., 1985. Effect of acid rain on soils. *CRC Crit. Rev. Environ. Control.*, **15**: 65–110.

Tanner, R.L., 1989. Sources of acid, bases, and their precursors in the atmosphere. In Lindberg, S.E., Page, A.L., and Norton, S.A., eds., *Acidic Precipitation,* Vol. 3, Berlin: Springer-Verlag, 1–19.

Taylor, G.J., 1991. Current views of the aluminum stress response; the physiological basis of tolerance. *Curr. Top. Plant Dev. Biochem. Phys.*, **10**: 57–93.

Thomas, G.W., 1982. Exchangeable cations. In Page, A.L., Chair, ed. comm., *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties*, 2nd edn. Madison, WI: Soil Science Society of America, pp. 159–165.

Thomas, G.W., 1986. Mineral nutrition and fertilizer placement. In Sprague, M.A., and Triplett, G.B., eds., *No-Tillage and Surface-Tillage Agriculture – The Tillage Revolution.* New York: John Wiley, pp. 93–116.

Thomas, G.W., 1996. Soil pH and soil acidity. In Sparks D.L., ed., *Methods of Soil Analysis. Part 3. Chemical Methods.* Madison WI: Soil Science Society of America, American Society of Agronomy, pp. 475–490.

Thomas, G.W., and Hargrove, W.L., 1984. The chemistry of soil acidity. In Adams, F., ed., *Soil Acidity and Liming.* Madison, WI: American Society of Agronomy, pp. 3–56.

Tisdale, S.L., Nelson, W.L., and Beaton, J.D., 1985. *Soil Fertility and Fertilizers.* New York: MacMillan, p. 492.

Ulrich, B., 1983. A concept of forest ecosystem stability and of acid deposition as driving force for destabilization. In Ulrich, B., and Pankrath, J., eds., *Effects of Accumulation of Air Pollutants in Forest Ecosystems.* Dordrecht: D. Reidel, pp. 1–28.

Ulrich, B., 1991. An ecosystem approach to soil acidification. In Ulrich, B., and Summer, M.E., eds., *Soil Acidity.* Berlin: Springer-Verlag, pp. 28–79.

Ulrich, B., Mayer, R., and Khanna, P.K., 1980. Chemical changes due to acid precipitation in a loess-derived soil in Central Europe. *Soil Sci.*, **130**: 193–199.

Walsh, L.M., and Beaton, J.D., 1973. *Soil Testing and Plant Analysis.* Madison, WI: Soil Science Society of America, p. 784.

Westerman, R.L., ed., 1990. *Soil Testing and Plant Analysis.* Madison, WI: Soil Science Society of America.

Yuan, T.B., 1974. A double buffer method for the determination of lime requirement of acid soils. *Soil Sci. Soc. Am. J.*, **38**: 437–440.

Cross-references

Acid Deposition Effects on Soils
Acid Soils
Acidity
Acids, Alkalis, Bases and pH
Buffers, Buffering
Chemical Analyses
Nitrogen Cycle
Podzols
Sorption Phenomena
Sulfur Transformations and Fluxes
Weathering Systems in Soil Science

ACIDS, ALKALIS, BASES AND pH

These four basic concepts are all related to the concentration of hydrogen ions (protons) in a system. In the case of soil chemistry, the systems considered are always aqueous, and the proton is never present as such, but is hydrated as the H_3O^+ ion. Here, the common convention of discussing the four concepts in terms of $[H^+]$ will be followed, the square brackets indicating concentration.

The earliest relevant idea of importance in modern chemistry is the distinction between acidity and alkalinity due to Arrhenius. It is based on the dissociation of water into H^+ and OH^- ions. An acid aqueous solution has $[H^+] > [OH^-]$, an alkaline solution has $[H^+] < [OH^-]$, and a solution in which $[H^+] = [OH^-]$ is said to be neutral.

The most general idea of acids and bases is due to G. N. Lewis. A Lewis acid is a chemical species that can accept an electron pair, whereas a Lewis base is capable of donating an electron pair. The most commonly used (and useful) concept in soil and environmental science is the simpler one of Brønsted and Lowry. It defines acid as a proton donor and base as a proton acceptor. In the reaction:

$$\mathrm{HCN} = \mathrm{H}^+ + \mathrm{CN}^-$$

HCN (hydrocyanic acid) is the proton donor and therefore the acid, and CN^- is called the conjugate base. In terms of H_3O^+, the reaction is written:

$$\mathrm{HCN} + \mathrm{H_2O} = \mathrm{H_3O}^+ + \mathrm{CN}^-$$

By comparison, in the Lewis concept, H^+ (as an electron acceptor) is itself considered to be an acid.

The dimensionless parameter pH is defined as the negative logarithm of the thermodynamic activity of the hydrogen ion in an aqueous solution. The pH scale derives from the dissociation constant of water, K_w:

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-] = 10^{-14}$$

or

$$-(\log[\mathrm{H}^+]) + \log[\mathrm{OH}^-] = 14$$

$$\mathrm{pH} = -\log[\mathrm{H}^+]$$

so that

$$\mathrm{pH} = 14 + \log[\mathrm{OH}^-]$$

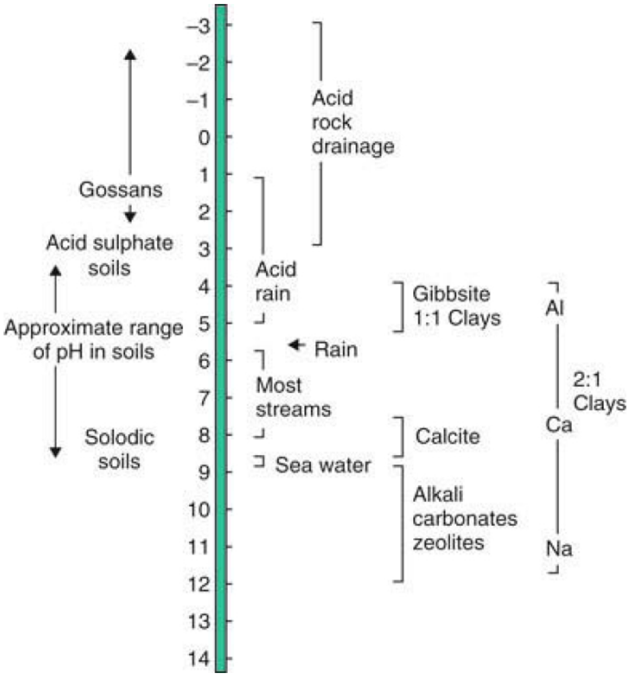


Figure A8 Approximate ranges of pH values for soils and other materials of the Earth's surface.

Conventionally, pH is shown on a scale of 0 to 14, and a common misconception is that these two values define maximum acidity and maximum alkalinity respectively. In fact values that fall outside of this range are possible, though rare, in weathering systems. Some typical pH values are shown in Figure A8.

Bibliography

Fraissard, J., and Petrakis, L., 1994. *Acidity and Basicity of Solids: Theory, Assessment and Utility.* Dordrecht: Kluwer Academic, 513 pp.

ACRISOLS

From Latin *acris* meaning *sour*, *very* acid, indicative of a low base saturation of the cation exchange capacity at pH 7.0.

Definition

Soils having

1. an *argic* horizon, which has a cation exchange capacity (in 1 M NH_4OAc at pH 7.0) of less than 24 $cmol_c\ kg^{-1}$ clay in some part, either starting within 100 cm from the soil surface, or within 200 cm from the soil surface if the *argic* horizon is overlain by loamy sand or coarser textures throughout, *and*
2. a base saturation of less than 50% (in 1 M NH_4OAc at pH 7.0) in the major part between 25 and 100 cm.

General characteristics

Soils characterized by the presence of a well-defined B horizon, with a blocky, prismatic, granular or massive structure (depending on water content, amount of Fe sesquioxides, and mineralogy of the fine fraction), which has a markedly increase in clay content (*argic* horizon) relative to the overlying horizons, and a cation exchange complex in which acidic cations (ionic Al species and, to a lesser extent, H^+, Fe^{+2}, Mn^{+2} among others) predominate over basic cations.

Mineralogical characteristics of the B horizon are variable, including *(i)* soils with 1 : 1 kaolinitic clay type (well-crystallized kaolinites, metahalloysites, or tubular halloysites) with or without the presence of gibbsite, and *(ii)* soils in which small amounts of more or less degraded mica are present. In both cases, the clay fraction is commonly associated with variable amounts of Fe sesquioxides (mainly goethite and/or hematite); the ratio of free Fe over total Fe of these soils is high (generally greater than 40%), which indicates an important degree of weathering and pedogenic evolution. These are, therefore, highly developed soils, formed under a tropical, subtropical, or even wet temperate (warm temperate in FAO usage) climate on old land surfaces, which have remained relatively stable during the recent Quaternary, and have been scarcely affected by recent glacial, fluvial, or colluvial processes.

The dominant pedogenic processes occurring in these soils are:

- *Weathering and argilization* of the most labile minerals present in the parent material, with clay formation under acidic or weakly acidic conditions, which favor the synthesis of 1 : 1 phyllosilicates and gibbsite, as well as the release of Fe with formation of crystalline free Fe forms. It is, therefore, a more or less intense *fermonosiallitization* (Pédro, 1983). The contents of Fe-, Al-, and Ti-oxides are comparable to those of Ferralsols or somewhat lower. The degree of weathering can be very intense, being mainly influenced by *(i)* the type of parent material (greater on igneous and metamorphic rocks of basic character), and *(ii)* both the intensity and duration of cation leaching and acidification processes.
- *Degradation and, ultimately, destruction of micas* present in the parent material with the release of K and transformation of micas to different intergrades mica-vermiculite, or even to Al-hydroxy-interlayered vermiculite, especially frequent in the A horizons. In the more advanced stages, these minerals become destroyed by acid hydrolysis.
- *Desaturation and aluminization* of the cation exchange complex by intense leaching processes, so that the amount of basic cations released by weathering is either similar to or smaller than the amount leached. This leads to a saturation of the CEC by Al and acidic cations, although a relative enrichment of basic cations may occur at surface, due to biotic pumping.
- *Clay translocation* from overlying horizons and the accumulation of clay in the *argic* horizon is not always easy to identify. Only when the amount of 2 : 1 clays is greater than that of 1 : 1 clays, or when kaolinitic clays are very crystalline and the amount of free Fe is low, illuvial features covering pore walls and aggregates are clearly identified. In other soils, illuvial features are very scarce and reduced to the presence of small birefringent bodies (*papules*) integrated into the matrix, which are attributed to either *(i)* features of a previous illuviation process, or *(ii) cutans* produced at the initial weathering stages of the parent material, more frequent at the base of the B2 horizon and in the saprolite. Moreover, in soils with abundance of either *(i)* halloysites, *(ii)* short-range order kaolinites, or *(iii)* kaolinites with significant isomorphic substitution of Al by Fe, illuvial features are hardly identified (even with detailed examination of thin sections). For this reason many researchers have proposed, on one hand, the exclusion of the illuvial genesis as a criterion for the definition of this reference soil group and, on the other, the inclusion of other processes that could explain the textural change. In this sense, it has been proposed as such processes *(i)* the occurrence of clay impoverishment caused by differential erosion in the surface horizons, *(ii)* preferential neoformation of clay in the B horizon (less acidic than the A horizon), or even *(iii)* the existence of textural discontinuities produced by polycyclism, after erosion and surface coverage with new material. Some researchers, and also some soil classifications, are considering the need to introduce a new group that would bring together all those soils of advanced weathering and desaturation, and with abundance of low activity clays (LAC), but that do not meet the requirements for a *ferralic* B horizon, and do not show a clear illuvial genesis. The following terms have been proposed: "Ferrosols" (Chinese classification), "Kurosols" (Australian classification), "red yellow podzolic soils" (Indonesian and Brazilian classification), "LAC-soils", "Kandisols", and "Kaolisols" (among others).

Morphology

Acrisols are characterized by the presence of an *ochric* or an *umbric* A horizon (10 to 30 cm depth), overlying an *argic* Bt horizon, which is deep, generally intensively colored (either yellow or brown to red), and whose structure ranges between prismatic, blocky, or granular, although in some cases, and under certain conditions, it can have a massive appearance. Often, there is either a thin grayish horizon or an *albic* E horizon between these two horizons, which is weakly structured and with an evident impoverishment of colloids, and which generally has an abrupt transition to the underlying Bt horizon. Redoximorphic features (known as gleyic soil properties in FAO usage) may appear at the base of the Bt horizon and, seasonally in the surface horizons in contact with the argic horizon in depressions especially.

Parent material

Acrisols are found on igneous, metamorphic, or sedimentary materials. Under wet tropical conditions, these soils are more frequently found on igneous and metamorphic rocks of acidic to intermediate character, although they may also be found on already weathered colluvial materials that accumulate in slopes of low hills. At intermediate latitudes, under subtropical to wet temperate climates (warm temperate – FAO) Acrisols tend to form readily on more easily weatherable rocks, such as schists and basic gneisses, granulites, amphibolites, gabbros, and, especially, on old, sedimentary materials with notable permeability, such as *(i)* deposits of major flood events (formations that in the Iberian Peninsula are known as “rañas”, and which are probably of Plio-Pleistocene age), and *(ii)* in the upper levels of Quaternary terraces (soils which tend to be absent in flooding valleys and on Holocene formations, and *(iii)* on fluvio-marine deposits present in old emerged platforms.

Climate

Formation of Acrisols occurs under climatic conditions that favor both leaching and intense weathering. These conditions are common in regions with a wet tropical/monsoonal, subtropical or warm temperate climate.

Topography

Formation of Acrisols requires long periods of geomorphologic stability. Therefore, these soils are more common in flat, undulating, or hilly landscapes, with gentle slopes, and with a predominance of conditions of biostasis produced by the presence of permanent vegetation cover. Under these conditions, Acrisols are found on old erosional surfaces and on depositional (piedmont) surfaces receiving already weathered materials from adjacent uplands.

Time

Even under the bio-physico-chemical conditions, Acrisols require a long formation period, being generally considered as fini-Tertiary to Pleistocene soils. When found under temperate climatic conditions, these soils are often relict soils formed under conditions of greater temperature and/or rainfall than those presently occurring; however, the effect of an acidification process caused by leaching during a long time period may lead to a convergence towards the same stage of evolution.

Lower level units of Acrisols

The following lower levels units are recognized: leptic, plinthic, gleyic, andic, vitric, umbric, stagnic, cutanic, lamellic and nitic, vetic (ECEC <6 mol$_c$ kg^{-1} clay). Moreover, other suffix qualifiers are proposed: abruptic, ferric, alumic, hyperdystric, (V $> 20\%$ in some part starting within 100 cm from soil surface), skeletic, rhodic (redder than 5YR), chromic, etc. (IUSS Working Group WRB, 2006). The criteria used for separation of lower level units are based on aspects such as: presence of hydromorphy, andic materials, Al activity, low activity clay, amount and distribution of organic matter and other characteristics.

Concordance with Soil Taxonomy

The different types of Acrisol correspond essentially with suborders of the Ultisols (aquult, humults, udults and ustults). Some Acrisols correspond to Oxisols with a kandic horizon. Some Acrisols (and Alisols) classify as alfisols in Soil Taxonomy.

Distribution

The geographical distribution of Acrisols is shown in the accompanying map (Figure A9). They are found associated and alternating with Nitisols, Ferralsols and Lixisols on old

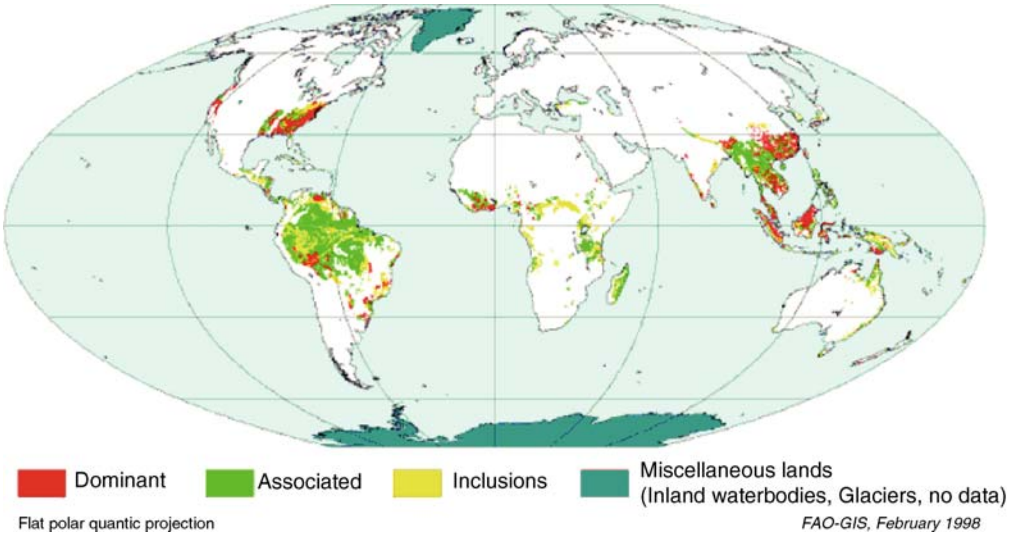


Figure A9 Acrisols of the world.

erosional surfaces and piedmont locations. On cratonic regions of the humid tropics, they commonly developed as the erosional products of Ferralsols, with the latter occur at a topographically higher level, on stable pediments or uplands. In mountain areas, Acrisols can be found on stable landscape positions of interfleuves, adjacent to Regosols and Cambisols on steeper and less stable slopes. On valley terraces Acrisols may occur on older examples with Luvisols or Cambisols on lower ones. Acrisols may occupy the better-drained areas of alluvial fans in the humid tropics, with Plinthosols and Gleysols in depressions.

Physical and chemical properties

The chief physico-chemical characteristic of Acrisols is the contrast in properties between the superficial horizons and the underlying argic horizon. The superficial horizons, with their lower clay content are less stable structurally and less capable of retaining water. Where a well-established cover of vegetation has developed, erosion is well controlled. If the cover is removed, erosion becomes a problem, with or without the complimentary problem of compaction. Compaction commonly leads to the retention of drainage waters and the development of darker chromas in the soil. In the B horizon, structural stability is good when Fe is high, though the union between Fe hydroxy phases and negatively charged colloids is less well developed than in Ferralsols, so that aggregates within Acrisols are less stable than in Ferralsols. Consequently clay in the Bt is more easily dispersed.

The acidity of Acrisols is greater in the surface horizons, where it is normally less than 4.5, than in the B, where the range 4.5 to 5.5 is common. At these pH levels soil chemistry tends to be determined by the behavior of Al, which dominates the exchange complex. In addition, the lower the pH the greater the amount of Al in solution in ionic form, either as simple ions, hydroxylated species or complexed to F^-. Al toxicity is the common result in Acrisols, and shows up as poor root growth, diminished rate of nitrification, and a high level of phosphate fixation. The domination of Al over exchangeable nutrient elements accounts for the low fertility of these soils.

Cation exchange capacity (CEC) at pH 7 is typical of a low activity clay soil – normally less than 16 $\text{cmol}(+)\text{kg}^{-1}$ of clay. It may be higher if residual mica or halloysite is present. The effective cation exchange capacity (ECEC) is much lower, and in some cases may be as low as 4 $\text{cmol}(+)\text{kg}^{-1}$ of clay). Presence of active Fe and Al surfaces in the solid phases may cause a moderate to high ability to adsorb anions such as phosphate, arsenate, sulfate, and fluoride, as well as organic anions.

Biophile elements (C and N for example) tend to be low in Acrisols as would be expected with low soil fertility. The vegetative cover may be forest, bush or herbaceous, with the species present being those, which tolerate low inherent fertility and high acidity.

Use

Agricultural use of Acrisols is limited chemically by low fertility, and the toxicity of Al. Physically, cultivation exposes these soils to significant erosion, and truncated profiles are common. The well-drained surficial part of the soil tends to be droughty in drier climates and shallow-rooting crops are at risk.

Liming and fertilization are the management practices necessary for the production of reasonable agricultural yields. Crops include tea, rubber, oil palm, coffee and sugar.

Environmental significance

In terms of the negative environmental significance of Acrisols, the obvious point is that that once the vegetation cover is removed, the A horizon is easily eroded. The acid nature of the acrisolic environment accounts for a second point. Metal structures, and metal-containing additives may release toxic amounts of metallic ions into the aqueous environment, where Acrisols are the dominant soils. Both of these negative features may be minimized however – the first by geotechnical treatment, contour ploughing, terracing and so on; the second by liming and by the addition of organic wastes and manures, which will tend to immobilize Al and other metals.

The argic horizon of Acrisols has a well-developed capability of filtering and retaining possible contaminants that enter soil water from atmospheric and anthropic sources. In addition the large area of Al and Fe dominant surface afforded by hydroxide and kanditic minerals, provides these soils with a considerable ability to fix anions, thereby protecting groundwater resources from anionic contamination. This latter characteristic is of course a negative feature when judged in terms of phosphate retention in an agricultural soil, but in the case, but in terms of the environmental value of this property, it has the positive effect of affording protection of groundwater from phosphate contamination, as well as providing protection against eutrophication to associated groundwaters.

Felipe Macías

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

IUSS Working Group WRB, 2006. World reference base for soil resources 2006. World Soil Resources Reports No. 103. Rome: FAO.

Pédro, G., 1983. Structuring of some basic pedological processes. *Geoderma*, **31**: 289–299.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Acid Soils
Acidity
Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Ferralsols
Tropical Soils
Weathering Systems in Soil Science

ACTIVITY RATIOS*

Introduction

Most studies of the composition of solutions in equilibrium with soils measure the concentrations of a single ionic component of interest, such as a plant nutrient element. If, however, incidental experimental variables such as electrolyte concentration or soil/solution ratio are altered, the concentration of that component also alters. This occurs because the surfaces of the clay and humus colloids of the soil contain negative electric

---

*This text originally appeared in Soil Science – ISBN 0879331763.

charges, and the incidental experimental variables alter the distribution of cations and anions between the charged surfaces and the solution. Thus it is impossible to characterize a soil with a unique value of the solution of any one ionic component.

This impasse can be overcome by relating the concentration (or better, the activity) of one ion to that of another, in the form of activity ratios (for two ions of similar charge) and activity products (for two ions of opposite charge). This article first explains the theoretical principles and goes on to practical applications and case studies.

Theory and definitions

Chemical potential, activity, and concentration

When considering chemical reactions, the term of the Gibbs free-energy *function* that relates to the chemical composition of the system is the *chemical potential*, μ. For a given component, μ is defined in terms of the *activity*, a, by the relationship:

$$\mu = \mu^\circ + RT \ln a \tag{1}$$

where R is the gas constant, T is the temperature in K, and μ° is the *standard chemical potential*, an arbitrary reference point given by the value of μ at unit activity.

The activity can be qualitatively described as "effective concentration," and it is related to the actual concentration, m mol dm^{-3}, by the activity coefficient, γ, that is, $a = m\gamma$. The activity coefficient has a value close to unity for very dilute solutions ($<10^{-4}$ mol dm^{-3}); but it decreases as the electrolyte concentration increases. In pure solutions it can be evaluated theoretically or determined experimentally by a variety of techniques (Robinson and Stokes, 1965).

The electrical double layer

When an electrically charged surface is in equilibrium with a solution, electrical neutrality is maintained by absorbed counter-ions, which produces an *electrical double layer*. The structure of such a double layer around a negatively charged surface is shown diagrammatically in Figure A10. The distribution of cations adjacent to the surface (Figure A10a) shows the *Stern layer*, a localized layer of cations near the surface, and the *Gouy*, or *diffuse layer*, occurring further from the surface. An exponential drop in electrical potential to zero in the external solution (Figure A10b) is associated with the electrical double layer. The excess of cations over anions in the solution balances the negative charge of the surface, their relative concentrations at a distance from the surface being as shown in Figure A10c.

The "thickness" of the double layer is thought of as the distance from the surface of a plane of charge with electrical capacity equal to that of the double layer. This thickness decreases as the valency and concentration of the electrolyte increase. For typical soil systems the double-layer thickness measures between 1 and 10 nm, but the distance from the surface at which the charge is totally neutralized will be several times greater than this (van Olphen, 1977).

The electrochemical potential

In the electrically charged system described previously, the electrochemical potential of an ion replaces the chemical potential as the appropriate term of the Gibbs free-energy function (Guggenheim, 1929). For a given ion species, this function is defined by:

$$\bar{\mu} = \bar{\mu}^\circ + zF\Psi + RT \ln a \tag{2}$$

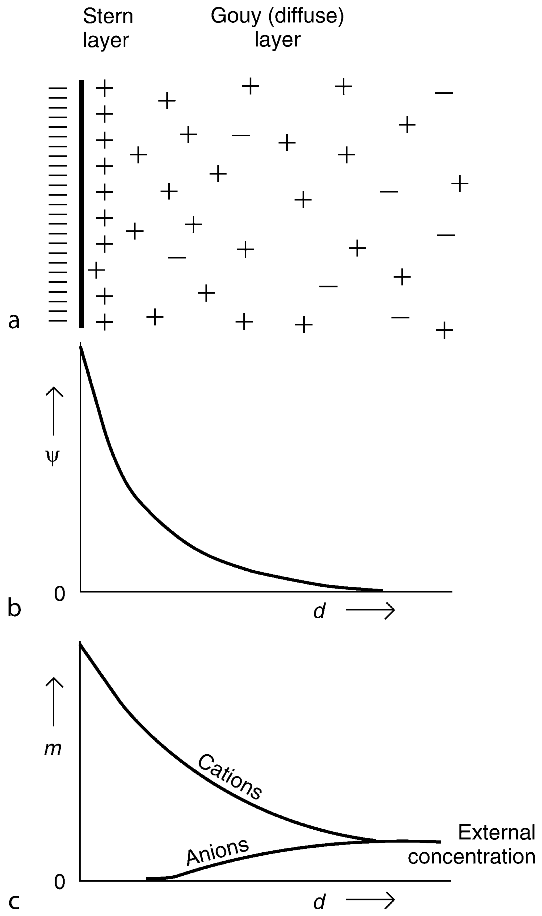


Figure A10 The electrical double layer. (**a**) Diagrammatic representation of the distribution of counterions adjacent to a negatively charged surface. (**b**) Electrical potential Ψ at a point in the solution as a function of distance d from the charged surface. (**c**) Concentration m of cations and anions in solution as a function of distance from the surface.

where z is the valency of the ion, F is Faraday's constant, and Ψ is the electrical potential in solution. At equilibrium, $\bar{\mu}$ must remain constant throughout the system, which requires the activity a to vary with distance from the surface because of the variation of Ψ. This variation depends on both the concentration of external electrolyte and the charge of the ions in the system.

Consider the electrochemical potential of two ions of differing charge, say, K^+ and Ca^{2+}, in a plane of constant potential Ψ. The electrochemical potentials are given by:

$$\bar{\mu}_K = \bar{\mu}^o_K + F\Psi + RT \ln a_K \tag{3}$$

and

$$\bar{\mu}_{Ca} = \bar{\mu}^o_{Ca} + 2F\Psi + RT \ln a_{Ca} \tag{4}$$

Subtracting Equation (4) from (2) × (3), we get:

$$2\bar{\mu}_K - \bar{\mu}_{Ca} = 2\bar{\mu}^o_K - \bar{\mu}^o_{Ca} + RT \ln \frac{(a_K)^2}{(a_{Ca})} \tag{5}$$

which may be simplified to:

$$f(\Delta\bar{\mu}) = \log\frac{(a_{\rm K})^2}{(a_{\rm Ca})} \tag{6}$$

Activity ratios

Equation (6) shows that a function of the difference in electrochemical potential is directly related to the logarithm of a ratio of the two ionic activities. Since $f(\Delta\bar{\mu})$ is a constant throughout the system, by definition the activity ratio must also be constant, and it defines the chemical potential of one ion with reference to that of another ion, even though the actual concentration of each individual ion may vary.

Similar reasoning may be applied to any ion pair, taking account of the sign and charge of the ions. In many natural soils, Ca^{2+} is the dominant cation, and it is therefore frequently used as the ion to which activities of other ions are related, producing activity ratios and products such as $a_{\rm Mg}/a_{\rm Ca}$; $(a_{\rm H})^2/a_{\rm Ca}$; $(a_{\rm Al})^2/(a_{\rm Ca})^3$; and activity products such as $a_{\rm Ca} \times (a_{\rm H2PO4})^2$; $a_{\rm Ca} \times a_{\rm HPO4}$. The activity ratios for cation pairs are often expressed in such forms as $\text{AR}_{\text{K–Ca}}$ or $\text{AR}_{\text{Mg–Ca}}$, and it is sometimes convenient to express the "reduced" activity ratio, (such as $a_{\rm K}/(a_{\rm Ca})^{1/2}$) on a negative logarithmic scale, which yields functions such as pK–1/2pCa, pH–1/2pCa, and pH_2PO_4 + 1/2pCa, which are frequently, but inaccurately, referred to as "potassium potentials," "phosphate potentials," etc.

The ratio law

Schofield (1947) proposed a "ratio law" governing the distribution of soil cations. He expressed it as follows: "When cations in a solution are in equilibrium with a larger number of exchangeable ions, a change in the concentration of the solution will not disturb the equilibrium if the concentrations of all the monovalent ions are changed in one ratio, those of all the divalent ions in the square of that ratio and those of all the trivalent ions in the cube of that ratio." It appears from this that the ratio Schofield referred to in this statement was that in which the concentration of ions was changed. However, it is clear from his paper that his emphasis was on the index of this ratio to be used for cations of different valency. His statement introduces another factor, namely, a change in the concentration of the solution. This change may be caused either by diluting the whole system (altering the soil/solution ratio) or by adding electrolyte. The ratio law defines the condition under which these changes will not disturb the equilibrium. In these situations the Ψ terms will cancel out in equations similar to Equations (2)–(5), provided the ion distribution at the surface is not altered. Thus the activity ratio should remain constant in spite of these changes.

The ratio law has subsequently been interpreted rather differently since it has been found experimentally that for a number of ion pairs and a variety of soils activity ratios and products remain approximately constant while solution concentrations vary up to 0.02 mol dm^{-3} (Beckett, 1971). The activity ratio has therefore become accepted as a relatively stable characteristic to describe the cation status of a soil because it changes little with the incidental experimental variables mentioned above.

There are, however, many soils for which the ratio law does not hold or holds only at lower electrolyte concentrations. A fundamental condition for conformity to the ratio law is the effective exclusion of anions from the cation adsorption sites in the inner parts of the electrical double layer (Figure A10). This occurs only if there is a high potential drop between the charged surfaces and the solution, which requires that the external electrolyte concentration is low and that the soils have a high surface negative charge. For soils of low surface negative charge, and particularly for variable charge soils which contain measurable amounts of surface positive charge, small changes in solution composition alter the relative proportions of cations on the soil surfaces, and activity ratios do not remain constant.

Activity ratios and cation-exchange equilibria

A cation-exchange model, in addition to the electrochemical model outlined previously, may also describe the distribution of cations between a soil surface and the solution. Consider, for example, the cation exchange reaction:

$$\text{soil Ca} + 2\text{KCL soil K}_2 + \text{CaCl}_2$$

There are a number of ways of formulating the equilibrium quotient for this reaction (Bolt, 1967), but the most satisfactory for practical purposes is probably the "corrected rational selectivity coefficient" (Helfferich, 1962), which defines the equilibrium coefficient $K^{\rm K}_{\rm Ca}$ in terms of the *equivalent fraction* of cations in the exchanger phase and the *activity* of cations in the solution phase. This treatment reduces to the following equation:

$$K^{\rm K}_{\rm Ca} = \frac{(q_{\rm K})^2}{q_{\rm Ca}q_0} \times \frac{a_{\rm Ca}}{(a_{\rm K})^2} \tag{7}$$

where $q_{\rm K}$ and $q_{\rm Ca}$ are the amounts of K^+ and Ca^{2+} adsorbed at the surface, and q_0 is the total charge (cation exchange capacity) of the exchanger, measured in mmol of charge per dm^3, $q_0 = q_{\rm K} + q_{\rm Ca}$. This selectivity coefficient is not usually constant for all conditions, but it can be related to the thermodynamic equilibrium constant K by introducing terms for the activity coefficients of ions in the adsorbed phase (Bolt, 1967).

According to Equation (7), the *activity ratio in solution* relates to two important properties of the soil: (1) the composition of the exchange phase, i.e., the relative proportions of K^+ and Ca^{2+} adsorbed at the negatively charged surface, and (2) the relative affinity of these cations for the soil surface as reflected by the selectivity coefficient $K^{\rm K}_{\rm Ca}$. Reasoning similar to that used here for potassium and calcium can be used for any cation pair.

Measurement and use of activity ratio

The equilibrium activity ratio $\text{AR}^{\rm e}$ of an ion pair for a soil sample serves to characterize the sample with respect to the free-energy difference of the two ions whether the ratio law holds or not. There are two rigorous ways of measuring this and one approximate way:

- Conventional chemical analysis of the soil solution allows ion concentrations to be determined and activities (hence activity ratios) to be calculated taking account of ion-pair formation. More directly, ion-selective electrodes allow direct determination of the activities of ions of interest, and hence the activity ratio (Yu, 1992).
- An *adsorption-desorption isotherm* is constructed by shaking a number of samples of the soil at a wider soil/solution ratio, say, 1:10, with incremental additions of the ion under investigation such as K^+ but at a constant concentration of the reference cation such as 5 or 10 mM $CaCl_2$. Chemical determination of the concentrations of K^+ allows the calculation of the amount desorbed or adsorbed (ΔK, mmol per kg

soil) at each point. A typical plot resulting from such an experiment is shown in Figure A11, and the equilibrium activity ratio, AR^{e}_{K-Ca} for the soil is obtained from the *null* point, $\Delta K = 0$, where potassium is neither lost to nor gained from the solution.

- An approximate value can be obtained by equilibrating a soil sample with a dilute electrolyte, say 5 mM $CaCl_2$ solution if Ca is the dominant cation in the soil at a low soil solution ratio such as 1 : 1. This ratio provides sufficient solution for analysis with a minimum desorption of exchangeable cations.

In addition to demonstrating the equilibrium activity ratio, the sorption isotherm shown in Figure A11 also shows how the activity can be expected to change when the ion is removed from a field soil by leaching or crop uptake or when it is added in fertilizers. The gradient of the isotherm ($\delta\Delta K/\delta AR$) defines the *buffer capacity* of the soil for the ion, but because the isotherms are rarely linear, a comparison of buffer capacities of different soils must be made at some standard AR value. The two linear regions of the curve illustrated in Figure A11 reflect potassium-calcium exchange on two different types of surface sites, and the two intercepts K_1 and K_2 give the capacity of these sites for retaining potassium.

Plant growth is complex and is controlled by a network of interactions so that the application of cation-activity ratios to growth studies is by no means straightforward (Beckett, 1972). Indeed there has been much controversy over whether plants respond to chemical potentials or to individual ion concentrations (Soon, 1985). This is difficult to resolve experimentally, because to do so requires systems in which both concentration and activity ratio vary independently. This would be very difficult to achieve without involving other nutrient interactions, and to the author's knowledge has not yet been done convincingly. However, the use of activity ratios and products is the only method of defining unambiguously the chemical potential of ions in a charges colloidal system such as soil. The use of individual ion concentrations may be satisfactory when comparing similar soils under similar incidental experimental conditions, but only when this restriction maintains both the reference ion concentration and the activity-coefficients constant.

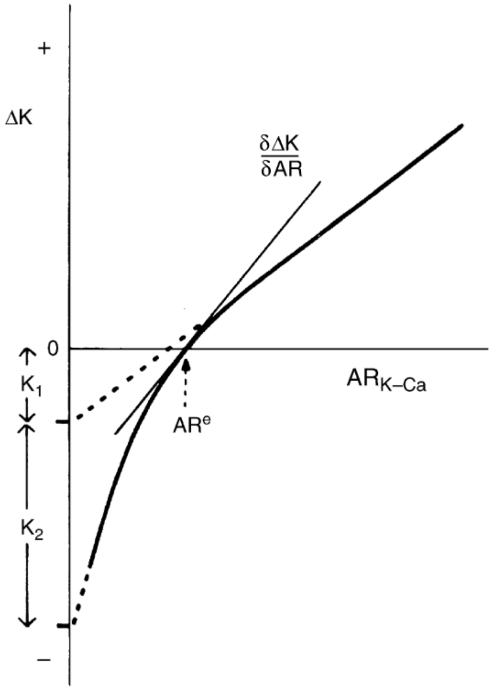


Figure A11 Sorption isotherm for potassium, with calcium as the reference cation. The diagram illustrates the estimation of the equilibrium activity ratio (AR^e), the buffer capacity ($\delta\Delta K/\delta AR$), and adsorption capacities (K_1 and K_2) of two different types of potassium-adsorbing sites.

Bryon W. Bache

Bibliography

Beckett, P.H.T., 1971. Potassium potentials – a review, *Potash Review*, Subject 5, 30th Suite, 1–41.
Beckett, P.H.T., 1972. Critical cation activity ratios. *Adv. Agron.*, **24**: 379–412.
Bolt, G.H., 1967. Cation exchange equations used in soil science. *Netherlands J. Agric. Sci.*, **15**: 81–103.
Guggenheim, E.A., 1929. The conceptions of electrical potential difference between two phases and the individual activities of ions. *J. Phys. Chem.*, **33**: 842–849.
Helfferich, F., 1962. *Ion Exchange.* New York: McGraw-Hill, 624 pp.
van Olphen, H., 1977. *An Introduction to Clay Colloid Chemistry.* 2nd edn. New York and London: Wiley, 318 pp.
Robinson, R.A., and Stokes, R.S., 1965. *Electrolyte Solutions.* London: Butterworth, 571 pp.
Schofield, R.K., 1947. A ratio law governing the equilibrium of cations in solution. *Proc. 11th Int. Cong. Pure Appl. Chemistry*, **3**: 257–261.
Soon, Y.K., ed., 1985. *Introduction in Soil Nutrient Availability.* New York: Van Nostrand Reinhold Company.
Yu, T.R., 1992. Electrochemical techniques for characterizing soil chemical properties. *Adv. Agron.*, **48**: 206–250.

ADOBE

Unburnt brick made of clay or clay-rich soil, and dried in the sun. Characteristic of building construction in Mexico and adjacent parts of the USA.

Bibliography

McHenry, P.G., 1996. *The Adobe Story: A Global Treasure.* Washington, DC/Albuquerque, NM: The American Association for International Aging/Center for Aging, University of New Mexico, 124 pp.

ADSORPTION

The concentration and bonding of a substance to the surface of a second substance. The bonding is relatively weak and temporary, as for example the adsorption of nutrient ions to clay particles in a soil. The materials in the soil that are capable of adsorbing are known collectively as the adsorption complex. The amount of a chemical species taken up by the adsorption complex at a given temperature may be plotted against the concentration of that species in the co-existing aqueous solution. The resulting graph is called an adsorption isotherm (McBride, 1994, p. 344–345).

Bibliography

McBride, M.B., 1994. *Environmental Chemistry of Soils.* New York: Oxford University Press, 406 pp.

Cross-reference

Sorption Phenomena

AGGREGATE

A composite body or granule within a soil, made up of mineral particles loosely held together. Characteristically the binding of the particles is a relatively minor amount of organic matter.

AGGREGATE STABILITY TO DRYING AND WETTING

Aggregate stability may be defined as the extent to which portions of soil remain intact when stressed by environmental factors. Here, the emphasis is on wetting and drying. For dry soil, the maximum possible stress is imposed by immersing portions in water. In the case of wet aggregates, possible weakening due to recent cultivation has to be taken into account. This effect is maximized by remoulding a soil at field capacity and then immersing wet portions in water. In the case of surface soil aggregates, mechanical stress and stress due to wetting are applied simultaneously by raindrops. Only an indirect simulation of the effect of rain is discussed here using end- over-end shaking. An indication of the likely effect of severe rain is also obtaining by finding out how wet a soil can be remoulding before the stability of a wet portion is reduced.

Breakup of aggregates on wetting

Slaking. The initial breakup of aggregates when immersed in water (Figure A12a,b) is caused by differential swelling and entrapped air (Renin, 1938). The relative importance of the two factors depends on the surface area of the clay present and the amount of clay. The magnitude of the stresses induced decreases with increasing water content of the aggregates prior to immersion.

The faster an aggregate is wetted, the greater its tendency to slake. Its rate of wetting depends on both the precise method of wetting used and permeability of the aggregate itself. Organic matter reduces slaking by enclosing the packets of clay particles present in an aggregate rather like a string bag, the packets of clay being free to swell up inside. Another effect of organic matter, if sufficient quantity is present, is to increase the soil-water contact angle so that the rate of wetting is reduced. Slaking of aggregates can also be prevented by engulfing the clay particles in a solid matrix either naturally, by the deposition of silica, for example, or artificially by adding cement.

Dispersion. After immersion in water and any slaking, soluble salts present in an aggregate begin to diffuse out into the surrounding water. If the electrolyte content of the water is sufficiently low, then clay particles may gradually separate from the aggregate due to the osmotic pressure difference induced between them (Figure A12c,d). Exchangeable sodium is normally the main cause of dispersion. Its effect is enhanced by the presence of magnesium rather than calcium ions on the other exchange sites, but reduced if sites are occupied by hydroxy aluminum ions. On a larger scale very fine aluminum and iron oxides can prevent dispersion by acting as cationic bridges between clay particles (El-Swaify and Emerson, 1975). By linking particles together, as already indicated, organic matter can also prevent dispersion despite the presence of appreciable exchangeable sodium. The presence of a source of divalent cations such as carbonate reduces dispersion by increasing the electrolyte content of the water.

Dispersion of wet, sheared aggregates. An aggregate in which there is no exchangeable sodium present does not normally disperse in water unless it has been sheared first when wet. During shearing water between some of the larger pores is forced in between the clay particles, thereby increasing their average distance apart. Then when the wet soil is immersed in water, the osmotic stress induced between the particles may be sufficient to cause dispersion. The same factors that control the ease of dispersion of unsheared aggregates affect in a similar way the value of the minimum average distance between clay

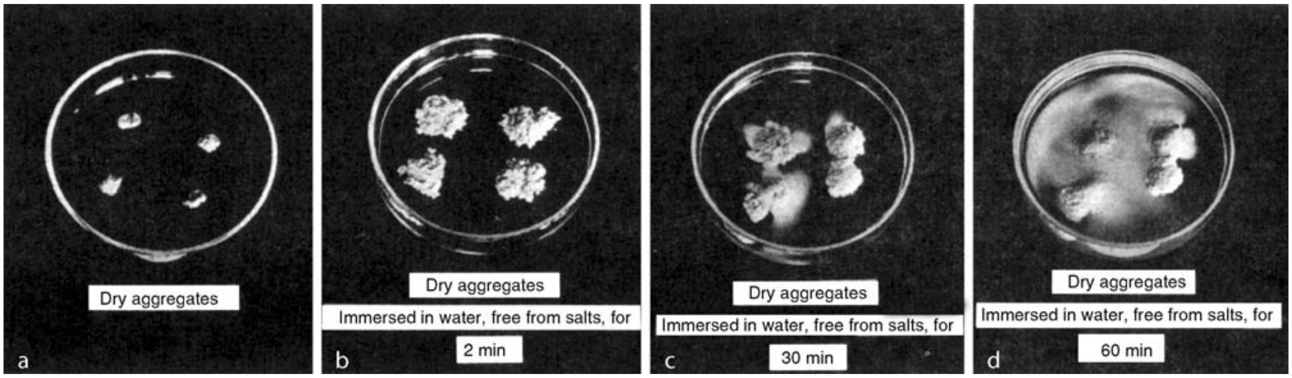


Figure A12 The breakup of aggregates on wetting where dry aggregates (**a**) at first rapidly slake in water (**b**) and then subsequently release clay at a slow rate by dispersion (**c, d**) (after Emerson, 1967).

particles, minimum water content of the aggregate, before dispersion occurs, with one exception. Organic matter, can act in two ways. First, if there are sufficient organic links between the clay packets, shearing is unable to break the links, and there is reduced dispersion (as for unsheared aggregates). Second, if there are only a few links and when these are broken by shearing, the individual polymer chains act as peptizing agents. Thus for some soils the surface aggregates may be more easily dispersed by shearing than the subsoil aggregates with similar clay content.

Measurement of aggregate stability

Water-stable aggregation. This is usually measured on a macroscale following Tiulin (1928) or a microscale after Middleton (1930). In the first, dry aggregates are wetted, then immersed in tap water and the size distribution of the slaked fragments determined by sieving. Methods of wetting and sieving have been standardized (Kemper, 1965; Kemper and Chepil, 1965). In the second, wetted aggregates are immersed in water contained in a cylinder, which is then shaken end over end. Aggregation is measured by the proportion of particles smaller than 50 µm in suspension compared with the proportion of particles smaller than 50 µm present in the aggregates. This method has been partially standardized (Quirk, 1950). Microaggregation combines breakup of aggregates due to slaking and aggregates due to subsequent attrition.

Aggregate coherence in water. In 1967, Emerson suggested classifying the stability of the structure of soil aggregates according to their reactions with water. The first reaction used was the slaking/dispersion of air-dry aggregates when immersed in water. Slaking by itself is an insufficient criterion, although its speed and severity are always assessed (Emerson, 1991). The difficulty is that aggregates may contain sufficient organic matter or inorganic cement to prevent slaking and spontaneous dispersion, but not so much as to prevent dispersion of the aggregates after working wet. In the current scheme (Figure A13), these aggregates are in classes 3–7 depending on the strength of the interparticle bonding. Strongly cemented aggregates are in class 7. No clay is released from such aggregates when shaken vigorously as a 1 : 5 suspension in water. When testing the dispersion of remoulded soil, 5 mm cubes are used instead of just portions of remoulded soil. The water content at which soil is remoulded is still either field capacity or that of aggregates smaller than 2 mm wet up with water at 10 kPa suction. However, class 3 has now been divided into 3a and 3b according to the severity of dispersion of the aggregates. Loveday and Pyle (1973) assessed the dispersion of aggregates in classes 1–3 after 2 h as well as 16 h. This enabled them to develop a *dispersion index, which* allows 16 levels of stability to be distinguished.

Application in the field

Conventionally the effect of organic content on the stability of soil aggregates to water has been assessed by measuring water-stable aggregation (Clarke and Marshall, 1947). However, these methods are not useful for elucidating the general causes of aggregate instability. For this determining the class number of a soil is a simple but powerful tool (Greenland, Rimmer and Payne, 1975). An advantage of using dispersion as the main diagnostic criterion is that it is easily seen in laboratory tests. When actual dispersion occurs in the field, the results are spectacular. Examples are piping failures through dam walls containing soil in class 1 when rapidly wet with water of low salt content; severe crusting on drying of surface soils in class 3a, if the soils are cultivated wet and rain follows soon after. However, even if actual dispersion does not occur, then the class number helps to show how structural damage can be avoided. For example, where soils are irrigated with water of low salt content, aggregates of clay subsoils in classes 1 or 2 may swell sufficiently to impair drainage. This can be overcome by adding gypsum. If a cultivated soil contains class 3a aggregates, then tillage and traffic under wet conditions should be minimized. Otherwise the structural porosity of the aggregates will be lost. Such damage can be mitigated by increasing the Ca-ion concentration in the soil solution, so moving the aggregates into class 4.

If a duplicate cube of soil is weighed and dried, values for the dry *bulk density* of the soil are obtained. These are the

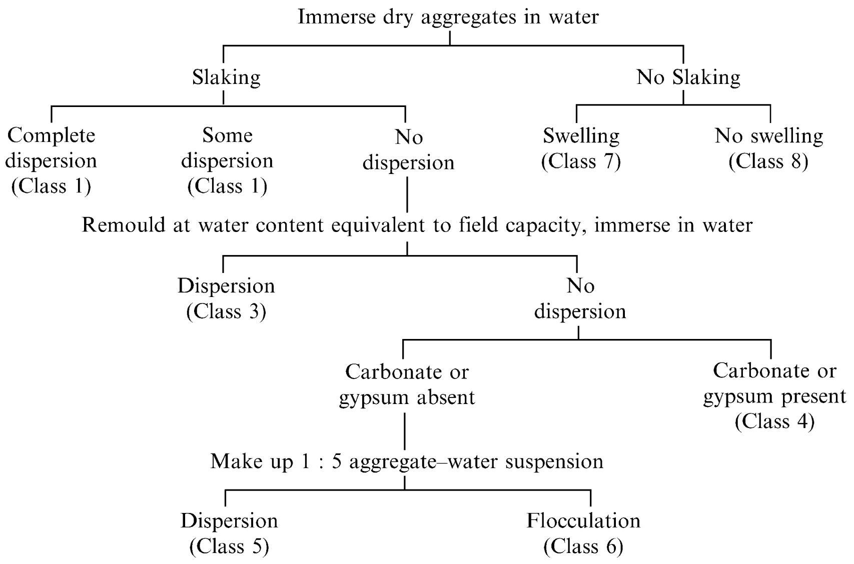


Figure A13 Scheme for determining class numbers of aggregates.

maximum possible dry bulk densities the soil or aggregates can attain in the field at field capacity or after drying. If the actual field values are measured, then the existing structural porosity can be determined. Values of minimum possible dry bulk density can be found from their values under permanent grass. The current structural status of the soil can then be assessed.

More detailed accounts of the mechanisms of aggregate breakup, inter-particle bonds, and field applications of the aggregate classification are given in Emerson (1991) and under the entry *Soil Structure.* Descriptions of the actual measurement of water-stable aggregation are given in Haver et al. (1972).

W. W. Emerson

Bibliography

Clarke, G.B., and Marshall, T.I., 1947. The influence of cultivation on soil structure and its assessment in soils of variable mechanical composition. *J. CSIR*, **20**: 162–175.

El-Swaify, S.A., and Emerson, W.W., 1975. Changes in the physical properties of soil clays due to precipitated aluminium and iron hydroxides. *Soil Sci. Soc. Am. Proc.*, **39**: 1056–1063.

Emerson, W.W., 1967. A classification of soil aggregates based on their coherence in water. *Aust. J. Soil Res.*, **5**: 47–57.

Emerson, W.W., 1991. Structural decline of soils, assessment and prevention. *Aust. J. Soil Res.*, **29**: 905–921.

Greenland, D.I., Rimmer, D., and Payne, D., 1975. Determination of the structural stability class of English and Welsh soils, using a water coherence test. *J. Soil Sci.*, **26**: 294–303.

Haver, L.D., Gardner, W.H., and Gardner, W.R., 1972. *Soil Physics.* New York: Wiley, 498 pp.

Kemper, W.D., 1965. Aggregate stability. In Black, C.A., ed., *Methods of Soil Analysis.* Madison, WI: American Society of Agronomy, pp. 499–510.

Kemper, W.D., and Chepil, W.S., 1965. Size distribution of aggregates. In Black, C.A., ed., *Methods of Soil Analysis.* Madison, WI: American Society of Agronomy, pp. 499–510.

Loveday, I., and Pyle, I., 1973. The Emerson dispersion test and its relationship to hydraulic conductivity. *Div. Soils Tech. Pap.* 15. Melbourne: CSIRO, 7 pp.

Middleton, H.E., 1930. Properties of soils which influence erosion. *U.S. Dept. Agric. Tech. Bull.,* 178.

Quirk, I.P., 1950. The measurement of stability of soil microaggregates in water. *Aust. J. Agric. Res.*, **1**: 276–284.

Tiulin, A.F., 1928. Aggregate analysis as a method for determining soil structure, *Per. Agric. Exp. Sta. Div. Chem. Rep.*, **2**: 77–122.

Cross-references

Aggregation
Bulk Density
Flocculation
Infiltration
Particle Density
Physical Chemistry
Soil Pores
Transport Processes
Water Budget in Soil
Water Movement

AGGREGATION

The soil is a complex multi-phase system made up of solid, liquid, and gaseous material. It contains solid particles of sand, silt and clay size. These are usually bound together as structural units called aggregates. An individual soil aggregate, also called a ped (Soil Survey Staff, 1993), can be defined as a naturally occurring cluster, or group, of soil particles in which the forces holding the particles together are much stronger than the forces between adjacent aggregates. The size distribution of the aggregates, their stability, and the amount and size distribution of the pore space between and within the aggregates characterize the soil structure. The terms "aggregation" and "soil structure" should not, however be used interchangeably: "aggregation" represents only one aspect of soil-structure formation while "soil structure" can result either from the building up of aggregates from dispersed materials or from the breaking down of larger coherent masses into favorably sized aggregates (Six et al., 2004).

From an agricultural point of view, the binding of soil particles into aggregates is essential for the production of optimum *soil tilth*. Soil tilth is a general term, which signifies the ability of the aggregates to withstand destruction by the impact of implements, raindrops, or running water so that the air-moisture regime is maintained at a favorable level for plant growth and microbiological activity (see *Tillage*).

A conceptual model

The five major factors involved in aggregate formation are soil fauna, microorganisms, roots, inorganic components and physical processes in the environment. References to the earlier work in this field will be found in the first edition of this Encyclopedia. Before the 1950s an overall conceptual model was lacking, and it was Emerson in 1959, who provided the breakthrough (Figure A14).

As quartz, clay, and organic matter are the main constituents of the soil aggregate or crumb, the various possibilities of bonding arrangements are summarized *grosso modo* in Figure A14. The clay particles are shown as *domains* consisting of several clay particles held together face to face. The domains may be held edge to face through aluminum bonds or edge to face, edge-to-edge, or face-to-face through organic colloids. These colloids can also bond clay particles to the surface of siliceous silt or sand particles. The critical advances since Emerson's work is summarized in Figure A15, from Six et al., 2004).

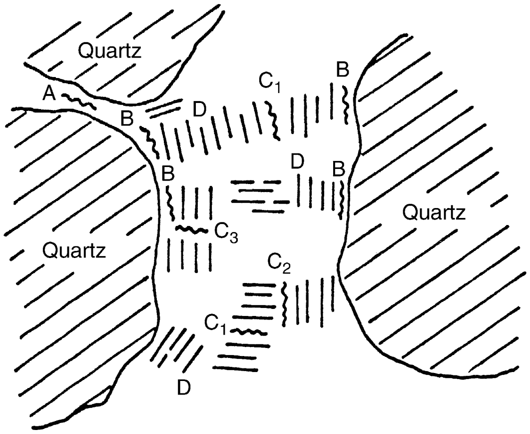
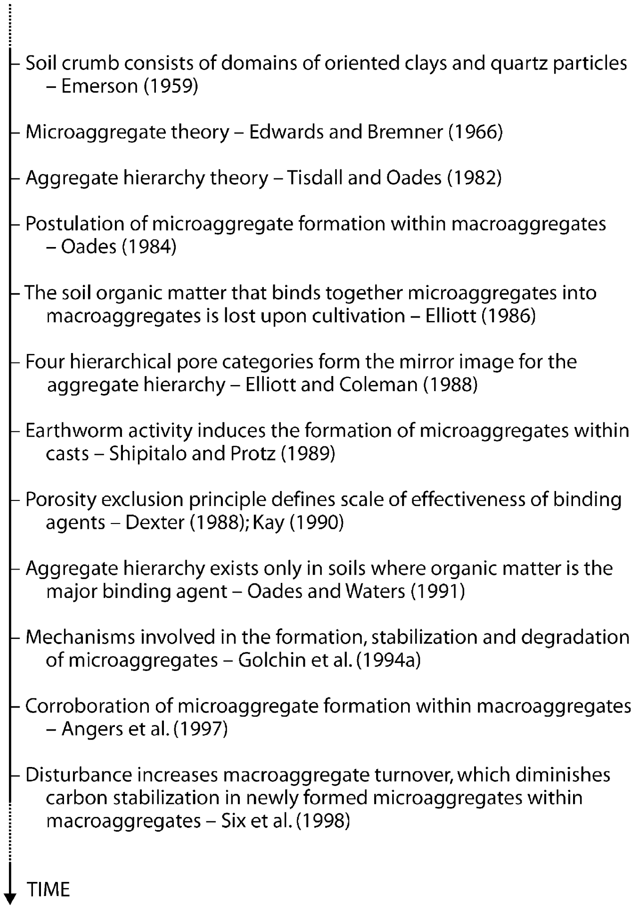


Figure A14 Suggested arrangements of quartz particles, clay domains, and organic matters in a soil *aggregate. A:* Quartz-organic colloid-quartz; *B:* quartz-organic colloid-clay domain; *C:* clay domain-organic colloid-clay domain; *C*$_1$: face-face; *C*$_2$: edge-face; *C*$_3$: edge-edge; *D*: clay domain edge-clay domain face (after Emerson, 1959).



- Soil crumb consists of domains of oriented clays and quartz particles – Emerson (1959)
- Microaggregate theory – Edwards and Bremner (1966)
- Aggregate hierarchy theory – Tisdall and Oades (1982)
- Postulation of microaggregate formation within macroaggregates – Oades (1984)
- The soil organic matter that binds together microaggregates into macroaggregates is lost upon cultivation – Elliott (1986)
- Four hierarchical pore categories form the mirror image for the aggregate hierarchy – Elliott and Coleman (1988)
- Earthworm activity induces the formation of microaggregates within casts – Shipitalo and Protz (1989)
- Porosity exclusion principle defines scale of effectiveness of binding agents – Dexter (1988); Kay (1990)
- Aggregate hierarchy exists only in soils where organic matter is the major binding agent – Oades and Waters (1991)
- Mechanisms involved in the formation, stabilization and degradation of microaggregates – Golchin et al. (1994a)
- Corroboration of microaggregate formation within macroaggregates – Angers et al. (1997)
- Disturbance increases macroaggregate turnover, which diminishes carbon stabilization in newly formed microaggregates within macroaggregates – Six et al. (1998)

Figure A15 Critical advances in the understanding of aggregation in soils, since Emerson's work.

The diversity of soil constituents implicated as aggregating agents has produced many theories explaining the processes involved in soil aggregation, with the role of the clay fraction or organic material being particularly stressed. Martin et al. (1955) for example, emphasized the importance of clay as the predominant binding agent in soil aggregation. They suggested that organic materials do not act primarily to hold clay, silt, and sand grains together, but rather their chief role may be to modify the forces by which clay particles *per se* are attracted to one another. According to this view, cohesiveness between clay particles is the binding force in aggregation rather than the cementing action of organic molecules. Other investigators have stressed the importance of organic substances, produced largely through microbial activity, to soil aggregation. From the point of view of soil structure, aggregation requires a binding together of flocculated particles. Nevertheless, flocculation and aggregation are not synonymous. The former is primarily electrokinetic, although *flocculation* (*q.v.*) can occur as a result of electrostatic attraction between the positive edges and negative forces of clay minerals. Thus flocculation may *aid* the aggregation process, but is not aggregation in itself.

As the formation of aggregates comprises a complex interrelationship of physical, biological, and chemical reactions, different kinds of mechanisms have been proposed to explain the formation of aggregation in the soil (see Six et al., 2004, for a thorough review).

Clay particles

The clay particles themselves cohere and thus entrap or bridge between larger sand and soil grains. The cohesive forces between the particles arise from physicochemical mechanisms such as:

- The van der Waals forces, which vary inversely as the cube of the distance between particles.
- The electrostatic attraction between negatively charged clay surfaces and positively charged clay edges.
- The linking of the particles together through cationic bridges. There is a linking system between particles consisting of the negatively charged surface of a particle and oriented water molecules.
- The cementation effects of organic matter, aluminum, and iron oxides. The iron oxides, in particular, may serve a dual purpose in aggregation. That part in solution may act as a flocculating agent, and the other part, which is more gelatinous in nature, may exert a cementation action.
- The surface tension of the curved menisci at the air-water interfaces that are mostly present in the soil. Cohesion in wet soils takes place between the molecules of the liquid phase as bridges or films between adjacent particles.

Organic matter

The organic colloidal material, produced largely through microbial activity, together with clay is responsible for the major portion of soil aggregation. Moreover, it is more effective than clay in causing the formation of stable aggregates with sand. The beneficial effects on soil aggregation originate from the integrated activity of microorganisms, fauna, and vegetation. Changes in aggregation following addition of organic material to soil indicate that aggregating effectiveness relates directly to microbial decomposition.

Organic residues and other products of microbial decomposition in the soil are thought to surround the soil particles and thus hold them together through cementing or encapsulating action. Organic material itself without biological transformation has little effect on soil structure. The conditions that favor high microbial activity result usually in early increased rates of aggregate formation due to fungal mycelia. However, high microbial activity also results in an increased rate of aggregate degradation due to an accelerated decomposition of the organic aggregating substances. Diverse bacteria, fungi, and actinomycetes are able to synthesize soil-binding substances. The major mechanism by which microorganisms effect soil aggregation involves the production of polysaccharides during microbial metabolism of organic matter in soil. The formation of aggregates by microorganisms may be explained by adsorption phenomena, physical entanglement, and cementation by microbial mucilages.

The action of organic compounds in effecting aggregation may be very complex and at best is little understood. Many have postulated that soil particles are held together in aggregates by the organic compounds. There is, however, considerable evidence that another important role of these compounds may be in modifying the expression of cohesive forces between clay particles through adsorption on the surfaces of the clay. Thus active organic materials may be thought of as acting both to hold soil particles together and in other cases to hold clay particles apart.

Aggregate formation

In light of the previous discussion, the following seems to best explain how aggregates are formed in agricultural soils. Aggregates result primarily from the action of natural agencies or any process by which parts of the soil are caused to clump together and separate from adjacent masses of soil. If soils are initially dispersed, flocculation is essential for aggregate formation; if they are partially puddle (see *Puddling*) or solid, fragmentation into smaller units is the first essential. Thus there are two kinds of processes involved. The first concerns the building up of aggregates from dispersed materials; the second involves the breaking down of large coherent masses into favorably sized aggregates. Since most soils become more dense and compact with continued farming, the second case is of greater interest.

Separation of parts of the soil mass may result from several factors such as the action of small animals, particularly earthworms as they ingest and intermix soil with partially decomposed organic matter and excrete the ingested material as surface casts or subsurface deposits, and the effect of *tillage* (*q.v.*), which is a function of the soil moisture content at the time of tillage.

Climate-dependent environmental variables include the effect of freezing and thawing where the aggregating action of frosts relates inversely to the rate of freezing and depends on the manner in which soil moisture crystallizes. Slow freezing results in the formation of few large ice crystals and large aggregates of soil particles. Since there is about a 9% increase in volume when water changes to ice, the pores are enlarged, which loosens the soil. Water is drawn from around the clay particles to the ice crystals during this process, creating a dehydration effect. The combination of ice-crystal pressure and dehydration causes aggregation. On the other hand, large numbers of small crystals are formed if the cooling is rapid and the integrated effect of many expansions is the breakdown of soil aggregates.

The effect of *wetting and drying* on aggregation is a function of the type of soil, the aggregate moisture at the time of wetting, and the intensity of the wetting treatment. The dehydration of a soil mass cannot be uniform, especially if the drying process is rapid. Consequently, unequal strains arise throughout the mass that tend to form *clods*. At least two processes operate to cause disruption of the clod into smaller units when the dried clod is wetted. The rapid intake of water causes unequal swelling throughout the clod, which produces fracturation and fragmentation along the cleavage planes. Moreover, the sorption of water into the capillaries results first in a compression of the occluded air and finally in a virtual explosion within the clod, as the pressure of the entrapped air exceeds the cohesion of the particles.

The *plant root system* is tremendously important, acting to separate and compress small clumps of soil, causing shrinkage and cracking due to desiccation, and making conditions favorable for the activity of microorganisms at the surface of these units. The exact mechanism of aggregate formation by plant root systems has not been established. The earliest explanation was based on pressures exerted by growing roots, which causes a separation to the soil particles adjacent to the root and a pressing together of these units into aggregates. In other words, each root hair that penetrates into large aggregates introduces a point of weakness. The penetration of sufficient root hairs produces granules. However, attempts to form aggregates by applying artificial pressure have failed to duplicate the water stability of natural field aggregates. This failure suggests that mechanical pressures of roots or soil fauna may not be basic aggregating mechanisms. Another possible aggregating factor is the dehydration of the soil in the vicinity of the root system as water is absorbed by the plant. This dehydration produces localized shrinkage and formation of fracture surfaces.

To conclude: aggregation is a complex process involving five major factors, with the current consensus, as reviewed by Six et al., 2004, emphasizing interactions between clay particles, polyvalent cations and soil organic matter. There is still a great need for the quantification of such interactions.

Roger Hartmann

Bibliography

Angers, D.A., Recous, S., Aita, C., 1997. Fate of carbon and nitrogen in water-stable aggregates during decomposition of $^{13}C^{15}N$-labelled wheat straw in situ. *Eur. J. Soil Sci.*, **48**: 295–300.

Dexter, A.R., 1988. Advances in characterization of soil structure. *Soil Till. Res.*, **11**: 199–238.

Edwards, A.P., and Bremner, J.M., 1967. Microaggregates in soils. *J. Soil Sci.*, **18**: 64–73.

Elliott, E.T., 1986. Aggregate structure and carbon, nitrogen, and phosphorus in native and cultivated soils. *Soil Sci. Soc. Am. J.*, **50**: 627–633.

Elliott, E.T., and Coleman, D.C., 1988. Let the soil work for us. *Ecol. Bull.*, **39**: 23–32.

Emerson, W.W., 1959. The structure of soil crumbs. *J. Soil Sci.*, **10**: 235–244.

Golchin, A., Oades, J.M., Skjemstad, J.O., and Clarke, P., 1994. Soil structure and carbon cycling. *Aust. J. Soil Res.*, **32**: 1043–1068.

Kay, B.D., 1990. Rates of change of soil structure under different cropping systems. *Adv. Soil Sci.*, **12**: 1–52.

Kay, B.D., 1998. Soil structure and organic carbon: a review. In Lal, R., Kimble, J.M., Follett, R.F., and Stewart, B.A. eds., *Soil Processes and the Carbon Cycle.* Boca Raton, FL: CRC Press, pp. 169–197.

Martin, J.P., Martin, W.P., Page, J.P., Raney, W.A., and Dement, J.D., 1955. Soil aggregation. *Adv. Agron.*, **7**: 1–37.

Oades, J.M., 1984. Soil organic matter and structural stability: mechanisms and implications for management. *Plant Soil*, **76**: 319–337.

Oades, J.M., and Waters, A.G., 1991. Aggregate hierarchy in soils. *Aust. J. Soil Res.*, **29**: 815–828.

Shipitalo, M.J., and Protz, R., 1989. Chemistry and micromorphology of aggregation in earthworm casts. *Geoderma*, **45**: 357–374

Six, J., Elliott E.T., Paustian K., and Doran, J.W., 1998. Aggregation and soil organic matter accumulation in cultivated and native grassland soils. *Soil Sci. Soc. Am. J.*, **62**: 1367–1377.

Six, J., Bossuyt, H., Degryze, S., and Denef, K., 2004. A history of research on the link between (micro)aggregates, soil biota, and soil organic matter dynamics. *Soil Till. Res.*, **79**: 7–31.

Soil Survey Staff, 1993. Soil Survey Manual. U.S. Department of Agriculture, 437 pp.

Tisdall, J.M., and Oades, J.M., 1982. Organic matter and water-stable aggregates in soils. *J. Soil Sci.*, **62**: 141–163.

Cross-references

Aggregate Stability to Drying and Wetting
Flocculation
Humic Substances
Microhabitats
Microstructure, Engineering Aspects
Physical Chemistry
Soil Structure
Sorption Phenomena
Tillage

AGRICHEMICAL

Pertaining to the various chemicals used in agriculture to fertilize crops, manage weeds and pests, or which are produced from agricultural crops. Examples: fertilizers, herbicides, biofuels such as ethanol.

Bibliography

Hester, R.E., and Harrison, R.M., eds., 1996. *Agricultural Chemicals and the Environment.* Cambridge, UK: Royal Society of Chemistry, 127 pp.

AGROECOLOGY

Agroecology is the attempt to apply ecological principles to agricultural systems, with the objective of sustaining those systems in an environmentally sound manner (Thomas and Kevan, 1993).

Bibliography

Thomas, V.G., and Kevan, P.G., 1993. Basic principle of agroecology and sustainable agriculture. *J. Agric. Environ. Ethics*, **5**: 1–18.

Cross-reference

Ecology

AGROECOSYSTEM

An ecosystem that has been modified by the practice of agriculture. This will involve the replacement of native species by domesticated plants and animals, and the application of fertilizers, pesticides and other agrichemicals, in order that the domesticates may compete successfully with wild species.

Bibliography

Newton, P.C.D., 2007. *Agroecosystems in a Changing Climate.* Boca Raton, FL: CRC/Taylor & Francis, 364 pp.

AGROGEOLOGY

Agrogeology, a subdiscipline of geology, is the scientific study of the origin, nature, composition, distribution and utilization of soils from a geological viewpoint. Geology is the scientific study of the Earth, and defines the soil as the uppermost geologic layer, or substratum, that supports plant life on the Earth's land surface. Critical data have been drawn together from several fields of natural science disciplines to provide an understanding of the cycling of elements and minerals in the course of time and explain the complexity of the terrestrial system.

The continental part of the Earth's crust – the lithosphere, comprises about one third of the Earth's surface and is composed of various rocks. The Earth's crust was formed throughout its 4.5 billion-years history. The principal materials in the crust (minerals, rocks, soils and water) on or near the surface of the Earth have been created and destroyed by numerous physical, chemical and biological processes. These processes are collectively referred to as the geological cycle, which comprises of a group of subcycles, including the rock, hydrolic and geochemical cycles.

The rock cycle is a sequence of processes that produces the three rock families: igneous, sedimentary and metamorphic. These migratory processes could be discussed in terms of the processes of magmatism, sedimentation and metamorphism and belong to the fields of geochemistry, mineralogy and petrology. In the lithosphere, the rock cycle begins with the initial crystallization of magma, proceeds with the alteration and weathering of the igneous rocks and the transport and deposition of the sediments. It then continues with the diagenesis and lithification of sedimentary rocks followed by their metamorphism to successively higher grades until eventually, through melting, magma is regenerated. The geochemical cycle involves the migration and distribution of elements during geological changes encompassing the chemistry of lithosphere, asthenosphere, hydrosphere, atmosphere and biosphere. The rock and geochemical cycles are closely related to one another and intimately related to the hydrolic cycle, which provides water necessary to many chemical and physical processes and supports life on Earth.

Intimate interactions between the rock and hydrolic cycles produce weathered rock materials that are the basic ingredients of soils. As opposed to the forces of tectonism and volcanism, which tend to build up the landscape, there are other processes that tend to wear it down. These subtle destructive processes are called weathering processes. Weathering is usually divided into physical disintegration or mechanical breakdown of rocks without chemical alterations; chemical weathering or decomposition of minerals with, often irreversible, chemical change; and biological weathering which is affected by the growth and movement of plants and animals.

Weathering can therefore be defined as the disintegration and alteration of rocks and minerals by physical, chemical and biological processes. The nature and rate of weathering depend of several factors such as: rock type, climate, topography and time. Physical weathering processes involve the disintegration of rocks and minerals by mechanisms of brittle fracture and subsequent decrease in the size of their particles without chemical alteration. The major factors in physical weathering environments are temperature, water, ice and wind, while the main activating agents are unloading, thermal processes (thermoclasty), growth and expansion of materials in pore space such as ice (gelification) and various salts (haloclasty).

Chemical weathering is the decomposition and alteration of minerals, and is a consequence of crystal structure breakdown at the molecular scale a leading to the formation of new minerals of completely different chemical composition, such as secondary oxide and hydroxide minerals, or clay minerals. The most important chemical agents involved in the weathering of minerals are water supplied by rainfall and CO_2 from root respiration and microbial degradation of organic matter. Temperature, rainfall and humidity are known by the term climate.

Hydrolysis, or the effect of water containing active hydrogen protons, is the most important and widespread process and is generally the method by which feldspars and micas are chemically weathered. There are also several other processes: carbonation, a reaction of carbonate and bicarbonate ions with minerals associated with hydrolysis of feldspars; hydratation, which involves the adsorption of water; solution, a reaction in which calcite or dolomite are altered to soluble bicarbonates; and oxidation and reduction reactions which involve the transferring of electrons.

Biological processes play a major role in rock and mineral weathering either as living organisms or dead soil organic matter, and have a significant effect on weathering and soil genesis. To recognize the importance of organisms and organic matter in weathering and soil formation two types of processes are distinguished: biological and biochemical weathering. Biological weathering occurs with the participation of live organisms. Tiny cracks in mineral crystals could be penetrated by bacteria, algae, fungal and lichen hyphae. Live roots growing into the cracks of minerals and rocks could contribute to physical weathering process.

Biochemical weathering is related to reactions of primary minerals with chemical compounds exuded by plant roots or microbial secretions as well as interactions with decomposition products of organic matter. Microorganisms cause precipitation and dissolution of minerals and control the distribution of elements in diverse environments at and near the surface of the Earth. The effect of chelation on mineral dissolution by organic (humic, fulvic, oxalic, acetic, salicylic, citric, etc.) acids is assumed to be more effective than geochemical hydrolysis. Complex extracellular polymers (polysaccharides, siderophores, and proteins) produced by a variety of microorganisms are involved in the formation of organomineral complexes in soils.

The soil is product of the interplay of several variables including geological parent rock, climate, organic activity, topography and time. Soil forming processes tend to produce distinctive soil layering or horizons, which lead to profile development. The horizons and relative profile development are an important concept of soil classification. Soil scientists have developed two modern systematic classifications of soils known as the Soil Taxonomy with 10 orders, of the Soil Conservation Services of the United States and the World Soil Map with 26 orders, of the Food and Agriculture Organisation of UNESCO. These classifications are based on soil morphology, color, physical and chemical properties of the soil profile and are emphasized by generic terminology. They are especially useful for agricultural purposes and related land-use planning.

The most active mineral constituents in soils are clays. Clays have a high surface area comprised of fine particles and special structural conditions of certain clay minerals. Most of soils contain only a small percentage of organic matter and much higher amounts of clays or mineral particles in the fraction of less than 2 micrometers (μm) in diameter.

Argillogenesis, or the study of the ways and conditions of birth, development, variability and decay of clay minerals is so complex, that as a consequence it is increasingly approached by inter- or multi-disciplinary methods. Several methods are currently used in the study of soil mineralogy, but the X-Ray Diffraction (XRD) method remains the most favorable. As a geologist, one should keep in mind that microscopy as well as detailed field work must still be associated with the XRD laboratory analyses, and that other instrumental methods, such as: electron microscopy, infra-red spectroscopy, geochemistry, isotopic analyses etc., are also extensively practiced. They have improved the study of mineralogical and geochemical processes within the soil horizons during soil formation as well as understanding of soil properties.

The relation between landforms and geology has been recognized by engineers and geologists since the first geological map was produced in Great Britain. A change in landforms always reflects a change in subsurface conditions. The shape of the landform reflects the history of weathering of different rock types and so the recording of changes in landform distinguishes areas with different geological and geomorphological history. The factors controlling the development of the landscape are considered as the effects of process, geology and time. The main processes include weathering, erosion and deposition, and the distinction between erosional and depositional landforms is very significant in landform analysis. In addition to geomorphological history, the effect of time is important in relation to the processes that are essential in understanding landforms and the soils with which they are covered.

Soils and life have been intimately associated almost from the earliest periods of geological time. The paleosols are products of complex terrestrial ecosystems existing at that time. For a long geological time plants and animals and surface processes were involved in developing of the paleosoil. A great deal of evidence has been collected concerning evolution of factors of soil formation during the geological history, particularly during the Pleistocene. Paleosols, formerly the integral component of the landscapes, apart from characteristics of the epoch of their formation have inherited features that correspond to previous natural climatic conditions as well as indications of subsequent changes. Orbitally forced Milankovitch-type cycling can be detected in paleosol series in the Pleistocene loess in many places across the Northern hemisphere.

Today, the application of classic geological principles to soil mapping and modern landscape-analysis methods has been enhanced by sophisticated methods of remote sensing, GPS and GIS techniques. Information from detailed lithological and soil maps could be extremely useful for land use planning and environmental protection especially when considering land capability for particular land use such as: agriculture, forestry, engineering, urban practice, etc.

Nikola Kostic

Bibliography

Birkeland, P.W., 1999. *Soils and Geomorphology,* 3rd ed., New York: Oxford University Press, 430 pp.

Chesworth, W., 1982. Late Cenozoic geology and the second oldest profession. *Geoscience Canada*, **9**: 54–61.

Hunt, C.B., 1972. *Geology of Soils; Their Evolution, Classification, and Uses.* San Francisco: W.H. Freeman, 344 pp.

van Straaten, P., 2006. Farming with rocks and minerals: challenges and opportunities. *An. Acad. Bras. Ciênc.*, **78**(4).

Cross-references

Biomes and their Soils
Fertilizer Raw Materials
Geography and Soils
Geology and Soils
Ice Erosion
Landscape and Soils
Neolithic Revolution

AGRONOMY

The management of land, particularly soil, in the production of crops.

Bibliography

Acquaah, G., 2004. *Principles of Crop Production: Theory, Techniques, and Technology.* Upper Saddle River, NJ: Pearson Prentice, 740 pp.

ALBELUVISOLS

Albeluvisols have a horizon of clay illuviation within a meter of the soil surface. This has an irregular upper boundary as a consequence of deep tongues of bleached soil material penetrating the clay horizon. This article is based on the descriptions in FAO (2001).

Connotation. From L. *albus*, white, and L. *eluere*, to wash out.

Synonyms. Podzoluvisols (FAO), derno-podzolic or orthopodzolic soils (Russia) and several suborders of the alfisols (Soil Taxonomy).

Definition. Within a meter of the surface, 'albeluvic tongues' occur in which a clay illuviation horizon is deeply tongued by bleached soil material from above so that the eluvial–illuvial boundary is broken and irregular.

Parent material. Mostly unconsolidated glacial till, materials of lacustrine or fluvial origin and of aeolian deposits (loess).

Environment. Flat to undulating plains under boreal taiga, coniferous forest or mixed forest. The climate is temperate to boreal with cold winters, short and cool summers, and an average annual precipitation sum of 500 to 1000 mm. Precipitation is evenly distributed over the year or, in the continental part of the Albeluvisol belt, has a peak in early summer.

Profile development. Mostly AEBtC profiles with a dark, thin ochric surface horizon over an albic subsurface horizon that tongues into an underlying brown clay illuviation horizon. *Stagnic soil properties* are common in boreal Albeluvisols.

Origin. Translocation of clay (*argilluviation* – see Luvisols) and various cool to cold climate factors play a role in the genesis of Albeluvisols. The characteristic albeluvic tonguing results from periglacial freeze–thaw sequencing at the end of the last glaciation. Movement of clay into a horizon of illuviation commonly causes poor drainage, such that periodic saturation produces redoximorphic characteristics (mottling, nodule formation, movement of Fe downwards and even out of the soil, for example). A fragipan is not uncommon at the interface between eluvial and illuvial horizons.

Use. Short growing season (frost!), acidity, low nutrient status, tillage and drainage problems are serious limitations of Albeluvisols. Most Albeluvisols are under forest; livestock farming ranks second; arable cropping plays a minor role. In Russia, the share of arable cropping increases towards the south and west of the Albeluvisol belt, especially on relatively nutrient-rich endoeutric Albeluvisols (see Figure A16).

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Acid Soils
Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles

ALISOLS

Alisols are strongly acid, generally unproductive soils, with accumulated high activity clays in their subsoils. Al dominates the exchange complex. The following is derived from FAO (2001).

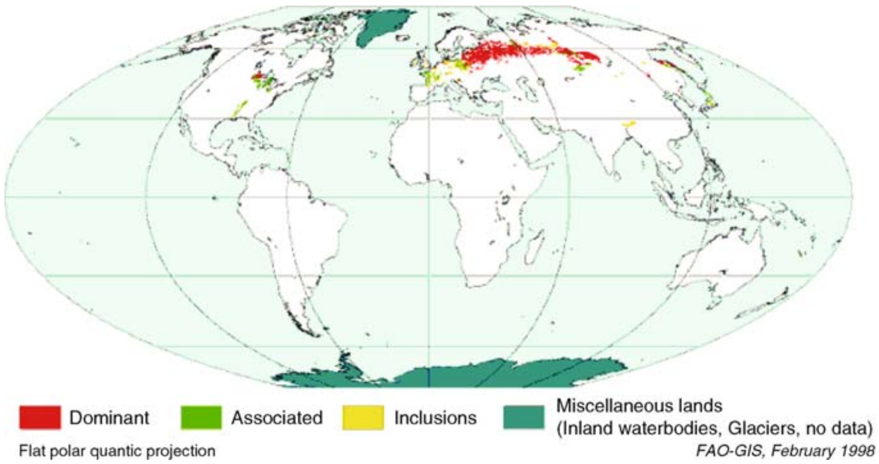
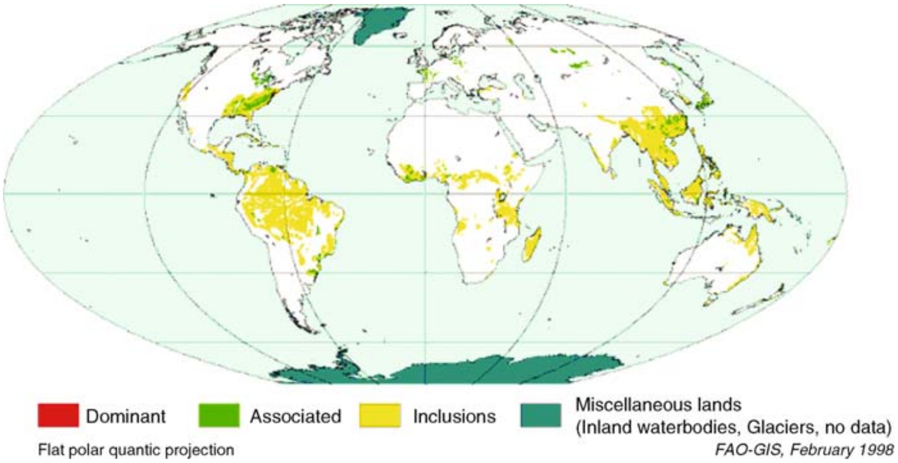


Figure A16 Distribution of Albeluvisols.



Flat polar quantic projection

FAO-GIS, February 1998

Figure A17 Distribution of Alisols.

Connotation. Strongly acid soils with subsurface accumulation of high activity clays that have more than 50% Al^{3+} saturation; from L. *aluminium*, alum.

Synonyms. 'Red yellow podzolic soils' with high-activity clays (Brazil), 'ultisols' with high-activity clays (Soil Taxonomy) and 'fersialsols' and 'sols fersiallitiques très lessivés' (France).

Definition. Defined by FAO (2001) as soils with

1. an argic horizon, which has a cation exchange capacity (1 M NH$_4$OAc at pH 7.0) of 24 cmol(+)kg^{-1} clay or more, either starting within 100 cm from the soil surface, or within 200 cm from the soil surface if the argic horizon is overlain by loamy sand or coarser textures throughout, and
2. alic properties in most of the layer between 25 and 100 cm from the soil surface, and
3. no diagnostic horizons other than an ochric, umbric, albic, andic, ferric, nitic, plinthic or vertic horizon.

Parent material. Alisols can form in a wide variety of parent materials having high-activity clay minerals such as vermiculite or smectite. Most occurrences of Alisols reported so far are on weathering products of basic rocks.

Environment. Most common in old land surfaces with a hilly or undulating topography, in humid (sub-)tropical and monsoon climates (see Figure A17).

Horizonation. ABtC profiles. Much of the variation among Alisols is related to the truncation of A horizons in eroded lands. The only diagnostic horizons present are ochric, albic, andic, ferric, nitic, plinthic, or vertic; and the following subclasses are recognized:

a. Plinthic Alisols: with plinthite in the top 125 cm
b. Gleyic Alisols: water saturation produces gleyic properties in the top 100 cm
c. Stagnic Alisols: standing water produces stagnic properties within 50 cm of the surface
d. Humic Alisols: with a mollic or umbric A horizon
e. Ferric Alisols: showing ferric properties
f. Haplic Alisols: all other Alisols

Origin. Alisols are found on old landscapes where weathering over the long term has essentially removed virtually all primary minerals except quartz. The clay fraction is dominated by high activity clays, which under appropriate, humid climate conditions, undergo hydrolysis with loss of silica, and alkaline and alkaline-earth cations by leaching, and with the release of Al. Three steps in the genesis of Alisols are recognized:

1. Weathering of bedrock to produce saprolite, which becomes the soil parent material. Most weatherable primary minerals are destroyed and secondary high-activity clays form. On basic and intermediate rocks these are predominantly smectitic, and on acid rocks, vermiculitic.
2. Movement of clay particles in the developing soil, either vertically (illuviation) or laterally. In the most acid soils (pH below about 5) the movement of fine clay tends to be impeded on account of the presence of a significant concentration of Al^{3+}, which causes flocculation. Step 2 may overlap the next step.
3. Weathering of secondary high-activity clay. These are unstable in highly leached environments depleted in silica and alkaline and alkaline earth cations. Their weathering liberates Al^{3+} into solution and, where primary ferromagnesian minerals were originally present, iron and magnesium are released from the octahedral inner layers of (2 : 1) clay minerals. Since the solum of an Alisol is an oxidizing environment Fe precipitates as a ferric hydroxyl phase and imparts a reddish color to some Alisols such as the Rhodic Alisols of the Caribbean region.

A common, further change is for a mature landscape to be truncated by surface erosion of the ancient landscapes on which these soils are found. Subsoil horizons then become exposed at the surface.

Use. Alisols contain low levels of plant nutrients (except for Mg^{2+} in some cases) whereas soluble inorganic Al is present in toxic quantities. If liming and full fertilization is no option, use of these soils is generally restricted to crops, which accommodate with low nutrient contents and tolerate high levels of free Al. Alisols are traditionally used in shifting cultivation and for low volume production of undemanding crops. In the past decades, Alisols have increasingly been planted to Al-tolerant estate crops such as tea and rubber, and also to oil palm.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Acid Soils
Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils

ALKALI

See *Acids, Alkalis, Bases and pH.*

ALKALINE SOILS

Alkaline soils are taken here to include all soils in which soil pH is generally higher than 7 throughout the solum. Other authors consider alkaline soils those that have pH > 8.5. This includes Calcisols, Gypsisols, saline and sodic soils, and those soils such as Chernozems and Kastanozems that have subsurface calcite, and which are generally found in sub-humid to semi-arid regions. It excludes those soils of the humid zone in which calcite may be present in sub-surface horizons and which are treated in the article on calcareous soils (Luvisols for example).

Ambient conditions

Alkaline soils so defined, are characteristic of the drier climates of the world, and tend to be concentrated in deserts and adjacent regions (Figure A18). The significant characteristic is that evapotranspiration exceeds precipitation for at least part of the year. Calcisols represent the least arid part of the spectrum and are found at the edges of the short grass prairie with a sparse vegetation of xerophytic shrubs and ephemeral grasses. With increasing aridity, Gypsisols, so called “desert soils”, become dominant. Where salts are present in the parent material or in groundwater, capillary uprise during a pronounced dry period can bring salt to the surface or at least to the upper part of the solum, and saline and sodic soils may form and encourage a halophytic vegetation.

In terms of Eh (pe)–pH conditions, the general field of the alkaline soils is shown in Figure A19.

Physico-chemical processes

Two physical processes dominate the genesis of alkaline soils. The first is the evaporation of water from the upper part of the solum during dry periods, and the second is the consequent capillary uprise of water from depth. The resulting chemical changes in the soil depend on the chemistry of parent materials and hydrological sources, both of which are highly variable. Generally speaking, the dominant aqueous species that accumulate in soil waters undergoing evaporation are Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-} and $H_4SiO_4^0$. As a first approximation, the sequence of precipitates that might be expected, following their relative solubilities, is calcium, followed by magnesium, and followed by sodium salts, as evaporation proceeds. In detail a good deal of variation is found in nature, and a concise way to explain this is as a consequence of what Eugster and Hardie (1978) call “chemical divides”.

Figure A20 demonstrates the way in which a sequence of chemical divides may lead to the formation of the commonest types of saline soil waters during the process of evaporation. The critical factor is the initial composition of the water. Specifically, this dictates the relationship between carbonate alkalinity ($mHCO_3^- + mCO_3^{2-}$) and the concentration of Ca^{2+} and Mg^{2+} ions.

Figure A21 is a magnified section of Figure A19 showing the usual sequence of alkaline soils found in sub-humid to arid climates, with pH and salinity both increasing with aridity.

Ward Chesworth, Felipe Macías, and Marta Camps Arbestain

Bibliography

Eugster, H.P., and Hardie L.A., 1978. Saline lakes. In Lerman, A., ed., *Lakes – Chemistry, Geology, Physics,* New York: Springer-Verlag, pp. 237–293.

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. Soils of the World. Heidelberg, Berlin: Springer-Verlag, 130 pp.

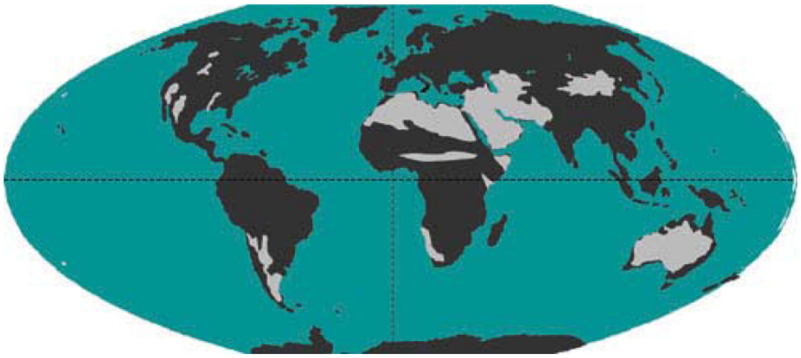


Figure A18 Major zones of occurrence of alkaline soils. These coincide essentially with regions of arid and semi-arid climate.

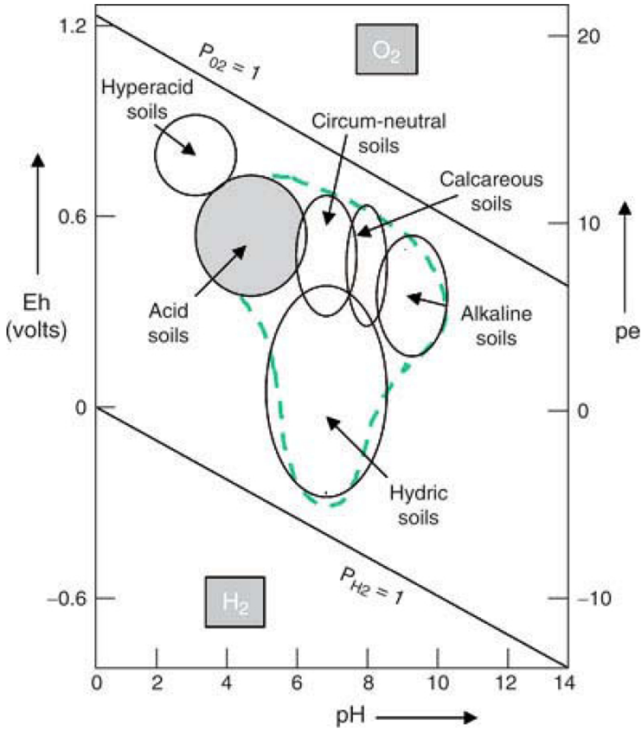


Figure A19 Alkaline soils defined in terms of the parameters Eh (pe) and pH. The heavy dashed line is the approximate field of the common mineral soils.

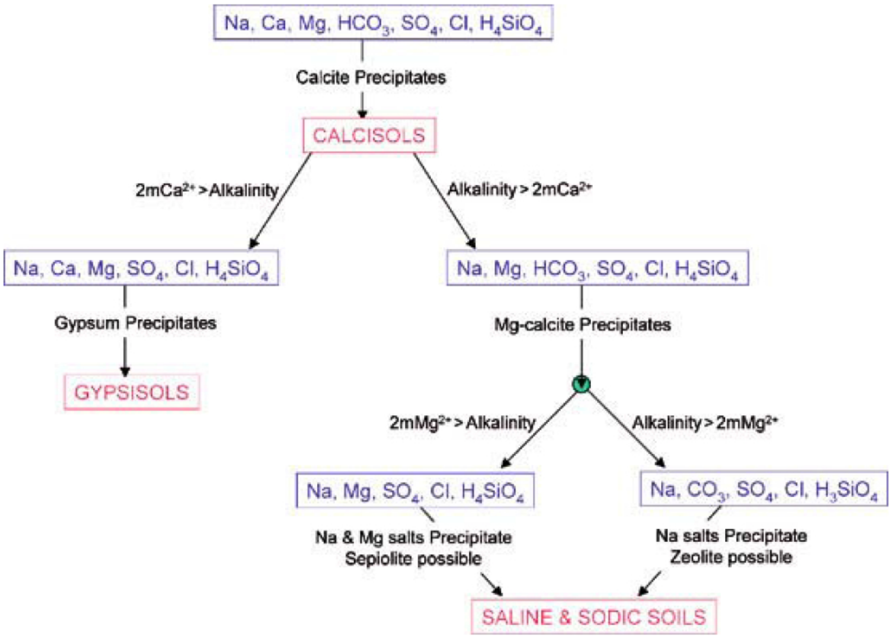


Figure A20 Chemical divides and the genesis of alkaline soils. The diagram shows the dominant ions in the soil solution at each stage of

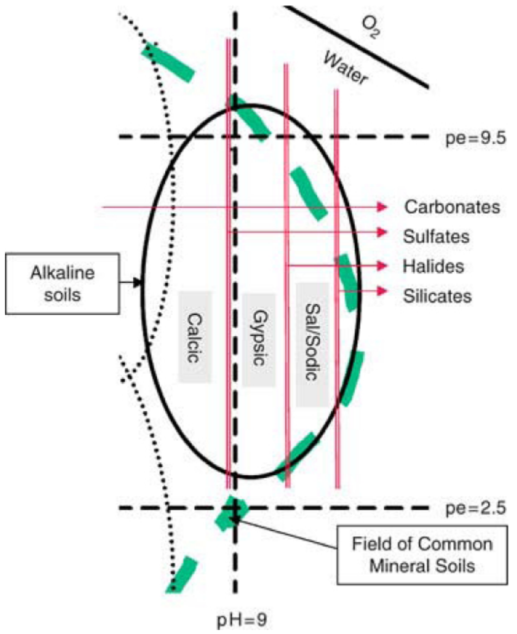


Figure A21 The alkaline soils field of Figure A19, magnified to show the approximate ranges of precipitation of carbonates, sulfates, halides and silicates in soils. The pH of an evaporating soil solution depends mainly on the concentrations of carbonate species in the system. The precipitation of neutral salts such as gypsum and halite is not pH dependent. The lower pH limits of sulfate and halide precipitation ranges shown in the diagram are based simply on empirical observation. A good deal of variability is possible depending principally on the initial composition of the soil solution.

Cross-references

Calcisols
Gypsisols
Solonchaks
Solonetz

ALKALIZATION

Generally used for processes which increase the pH of soils such that they become alkaline (pH greater than 7) or alkali (pH greater than 8.5). Synonym: alkalinization. McBride (1994, p. 274) states that mineral dissolution and the release of ions into solution are invariably involved in the generation of alkalinity.

Bibliography

McBride, M.B., 1994. *Environmental Chemistry of Soils.* New York: Oxford University Press, 406 pp.

ALLITIZATION

An advanced stage of weathering in which Al and Fe accumulate at the expense of other ions and species such as the alkalis, alkaline earths and silica, which are removed from the soil in the aqueous phase (Pedro, 1983, table 1).

Bibliography

Pédro, G., 1983. Structuring of some basic pedological processes. *Geoderma*, **31**: 289–299.

ALLOGENIC

Describes components transported into the soil from some external place of origin. Equivalent to the geological term allochthonous. See *Authigenic*.

ALLUVIUM

Alluvial sediment deposited from flowing water; or pertaining to a deposit formed in that way. The parent material of alluvial soils.

Bibliography

Gerrard, J., 1987. *Alluvial Soils.* New York: Van Nostrand Reinhold, 305 pp.

ANDOSOLS

Introduction

Andosols are soils of active volcanic areas. They exhibit unique soil properties that place them apart from other soils. The term 'andosol' is derived from Japanese, 'an' meaning dark, and 'do' connotating soil (Figure A22). Andosols are also found outside active volcanic regions when environmental conditions favor their formation. Andosols have a limited extent (1–2%) of Earth's land surface, but many such areas are densely populated.

The discussion of this entry follows the terminology of the World Reference Base for Soil Resources (WRB, FAO, 1998). Andosols are termed slightly different, or andisols according to the U.S. Soil Taxonomy (Soil Survey Staff, 1998). The soils discussed in this entry include tephra-rich soils, many of which are not considered Andosols, according to the WRB or Soil Taxonomy, but have various notations in international soil literature, such as vitrisols, (Iceland), vitrandosols (France), Pumice Soils (New Zealand), and vitrons (FitzPatrick's system).

Andosols were the subject of a book edited by Shoji et al. (1993a), which is the most comprehensive discussion of Andosols to date. Other publications devoted to Andosols include three special issues of scientific journals (Fernandez Caldas and Yaalon, 1985; Bartoli et al., 2003; Arnalds and Stahr, 2004), overview chapters, for example by Wada (1985) and Kimble et al. (2000), a monograph by Dahlgren et al. (2004), and a compilation of benchmark papers about Andosols (Tan, 1984).

The concept of Andosols

The development of the concept of Andosols has roots in the U.S. Soil Taxonomy, first presented as the andept suborder of inceptisols (Smith, 1986), but from 1990 as andisols, based on a work of international working group (ICOMAND), as was reviewed by Parfitt and Clayden (1991). The concept of the Andosol soil group, as used in the WRB, is similar to that of Soil Taxonomy (see Shoji et al., 1996).

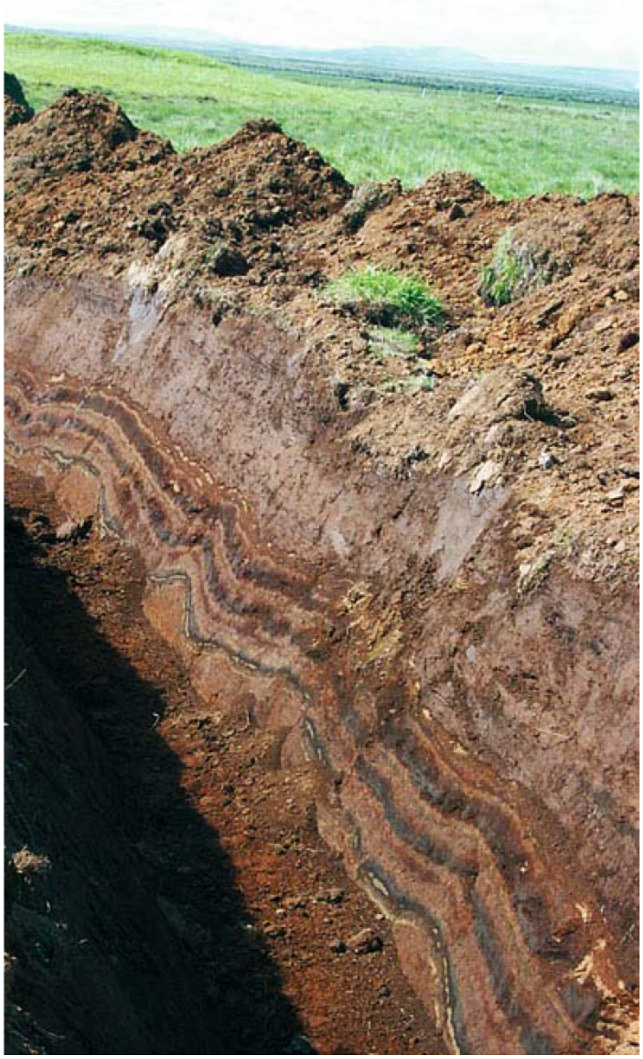


Figure A22 Andosol in Iceland. The profile is about 190 cm thick. Many distinct tephra layers are evident, disturbed by cryoturbation. Basaltic and andesidic tephras are dark, but thin light colored rhyolitic tephras are also seen near the middle and near the bottom of the profile. The soil contains considerable carbon in most horizons, also at depth.

The concept of andosols is tied to soils that develop in volcanic ejecta. The rapid weathering of volcanic tephra results in precipitation of short-range order minerals and/or metal–humus complexes, a process that is sometimes referred to as 'andosolization' (e.g., Duchaufour, 1977). These colloidal constituents provide the soils with properties that distinguish Andosols, such as low bulk density, variable charge characteristics, thixotropy, and strong phosphate retention. The measure of Andosol colloidal constituents is used for the identification of Andosols. However, the term not only reflects products of soil genesis, as vitric parent materials are also used as a diagnostic criterion for these soils according to the WRB and Soil Taxonomy.

Mineralogy and metal–humus complexes

The parent materials

The most common parent material of Andosols is *tephra*. It should be noted, however, that Andosols do form in other types of materials, as will be discussed later.

Tephra. This is a collective term for all airborne volcanic ejecta, regardless of morphology, size, and composition. Volcanic ash is tephra which is <2 mm in diameter (MacDonald, 1972). The nature of tephra materials varies substantially according to the nature of the volcanic eruption that produces the tephra and it can be differentiated on several criteria. *Volcanic glass* is a term commonly applied to tephra but strictly speaking it refers to the part of the tephra that has cooled rapidly. The term *vitric* refers to glass (from Latin 'vitr' = glass) and it is used as a diagnostic criterion for poorly developed Andosols/Andisols (FAO, 1998; Soil Survey Staff, 1998), and to coin the terms such as vitrisols and Vitric Andosol. It should be noted that Andosols form in the bulk of parent materials, not only in the Vitric component. Fisher and Schmincke (1984) and Heiken and Wohletz (1985) provided discussion on tephra materials.

Composition. The differentiation of tephra by silica content is perhaps the most useful division of the tephra (basalt, andesite, dacite, rhyolite) and is widely used in geology. It affects weathering rates and the genesis of Andosols as discussed later.

Morphology and mineralogy. Many terms are applied to the morphology of tephra, such as glass, lapilli, cinders, and pumice. Grain size is an elusive term for tephra, as it is often quite porous and has a large active surface area. It is also difficult to determine the mineralogy of tephra because of microcrystallinity and/or non-crystalline nature of the materials. Such terms as colored glass (basaltic-andesitic and some dacite tephra) and non-colored glass (rhyolitic) are commonly used (e.g., Dahlgren et al., 1993).

Genetic mineral components

The dominant clay minerals in Andosols are allophane, imogolite, ferrihydrite, and halloysite. Notable publications on allophane and imogolite include those of Wada (1989), Harsh et al. (2002), Dahlgren et al. (1993), and Dahlgren (1994). These are not layered lattice clay minerals such as smectite and kaolinite, but are described by terms such as 'spherical', 'tubular' and 'gel-like'. Their crystallinity has been subject to debate and these constituents have been described as 'amorphous', 'X-ray amorphous', 'poorly crystalline', 'noncrystalline', and 'short-range order' .

The tephra parent materials of Andosols weather rapidly, resulting in high concentrations of Al, Fe, and Si. The poorly crystalline (short-range order) morphological forms of these minerals are the result of rapid crystallization of Al and Si (allophane and imogolite) and Fe (ferrihydrite) from such soil solution. However, these minerals are not exclusive to Andosols as they are also commonly found in Podzols, but to a lesser degree.

Allophane and imogolite

Allophane is an aluminum and silica mineral that forms hollow spherules which are about 5 nm in diameter. The ratio between Al and Si is somewhat variable, most commonly 1–2, but values <1 have been recorded (Parfitt and Kimble, 1989). These minerals have an extremely large surface area and a high negative charge that is pH-dependent (variable charge), which increases rapidly with pH. In addition, allophane has considerable anion exchange properties.

Imogolite is tubular and often appears thread-like viewed with a transmission electron microscope. It usually has an Al/Si ratio close to 2, but similar properties to allophane.

Ferrihydrite
Ferrihydrite is a poorly ordered Fe^{III} mineral (Schwertmann, 1985), consisting of well aggregated spherical particles (Bigham et al., 2002) which often appear with gel-like structure. Its structure has been debated and ideas about the nature of ferrihydrite are still evolving. Ferrihydrite is very common in Andosols, especially where the parent materials are rich in iron, as in Iceland. It has a large surface area and a pH dependent cation and anion exchange capacity (Bigham et al., 2002).

Halloysite and other clay minerals
Halloysite is a common mineral in Andosols, especially in Si-rich environments, and is often associated with dry environments (Dahlgren et al., 1993, 2004) with distinct dry season. Its morphology varies, but it is believed to be closely related to kaolinite (see White and Dixon, 2002). Halloysite is often reported as representing more weathered environment than allophane dominated soils (e.g., Ndayiragije and Delvaux, 2004). Other minerals are found in many Andosols, especially when Andosols become mature, with the Andosol minerals being transformed to other minerals, such as kaolinite, smectite and Al/Fe oxides and chloritized 2 : 1 minerals (e.g., Shoji et al., 1985). Opalline silica is also often reported in Andosols, especially under grassland vegetation (e.g., Shoji et al., 1993b).

Allophane–humus and metal–humus complexes

The original concept of Andosols ('an-do') reflects the dark color of many andosols, which mainly results from the accumulation of organic matter. Large contents of organic matter characterize well-developed andosols. Appreciable amounts of carbon are found at depths, and the distribution is often quite erratic. There are two main pathways of organic accumulation in Andosols: the formation of allophane–organic matter complexes and metal–humus complexes.

Allophane and organic matter form bonds that are relatively stable, which results in soils that commonly have >6% C in both A and B horizons. This effect is enhanced when Al^{3+} and Fe^{3+} form stable bonds with organic matter by ligand exchange (metal–humus complexes). This means of carbon accumulation is effective at a relatively low pH. Research has confirmed the stability of these constituents, which can be >100 000 yr old in Hawaii (Torn et al., 1997).

In some areas, other environmental factors can enhance the accumulation of organic materials in Andosols, such as poor drainage and cold climate resulting in OC 12–20% (Arnalds, 2004).

Genesis

The rapid weathering of tephra constituents is perhaps what distinguishes the genesis of Andosols the most. It leads to a soil solution oversaturated with regard to Al, Si, and frequently Fe or organic molecules, which results in the precipitation of the colloidal Andosol constituents. The nature of the parent materials (most often tephra) and climate, which influences the rate of weathering and therefore the release of Al, Fe and Si, are the dominant factors shaping the formation of Andosols. Humid climate enhances the weathering of tephra and the majority of the world's Andosols are therefore found under humid conditions, but <10% under aridic or xeric moisture conditions (Wilding, 2000).

Andosols are most commonly considered youthful soils. Soils on slopes of volcanoes often show a trend from less weathered vitric or andic soils at high elevations (young PM/cold/coarse tephra) to allophanic soils, metal–humus complex dominated soils, and finally to more weathered soils of other types, such as Vertisols (warm, less tephra inputs, fine tephra). A range of soils can develop from Andosols, including Podzols, Mollisols, Vertisols, and Oxisols, (e.g., Dahlgren et al., 2004; Yerima et al., 1987). However, if the climate is dry and especially when the parent materials are silicious, vitric characteristics may dominate for a long time. Andosols also form in tephra redistributed by wind long distances away from where the volcanic materials were originally deposited, as in Iceland (Arnalds et al., 1995).

The nature of Andosols implies that these soils often become buried by new volcanic materials, both tephra and lava.

Allophanic, vitric and metal–humus complex andosols

Vitric (*vitrandic*), allophanic (*silandic*) Andosols, and Andosols dominated by metal–humus complexes (*aluandic*) can be viewed as three 'end-members' of Andosols (Shoji et al., 1996). The rate of cation release and the pH of the soil solution largely determine whether allophanic Andosols or soils dominated by metal–humus complexes are formed. Allophane formation is favored by a high pH, while it does not form when pH is under 5 (Figure A23a). Under such acidic pH conditions, the formation of metal–humus complexes becomes a dominant process (Figure A23b). The 'aluandic' soils often contain considerable amounts of phyllosilicates, such as chloritized 2 : 1 minerals (Shoji et al., 1985), under a variety of climatic conditions, which contribute to their physical and chemical behavior (see also Ndayiragije and Delvaux, 2003).

The weathering of basaltic tephra is rapid, resulting in areas of high chemical denudation (Stefansson and Gislason, 2001), rapid formation of allophane and ferrihydrite. The surface area of basaltic tephra can be quite high or $>10\ m^2\ g^{-1}$ (Wolff-Boenisch, 2004). Young basaltic tephra soils, which appear to have not been subjected to much weathering, can therefore meet criteria for Andosols (Arnalds and Kimble, 2001).

The weathering of basaltic or andesitic tephra releases an abundance of cations, which maintain the pH. The system can be continuously recharged with cations by weathering of new materials deposited by repeated volcanic eruptions. If not, the soil pH will eventually become low with depletion of tephric materials, and the formation of metal humus complexes becomes a dominant process.

Weathering rates of silicious (rhyolitic) tephra are slower than in basalt with less abundance of cations released to maintain the pH. Weathering often results in more acidic soils, especially in humid-wet areas. Dry climates can alternatively result in relatively unaltered parent materials.

The formation of metal–humus complexes becomes dominant at pH < 5, when humic substances form bonds with Al and Fe (predominantly). Their formation is influenced by the rapid release of Al (and Fe), as in the formation of the mineral colloids (allophane, imogolite and ferrihydrite). In Iceland, both mineral colloids and metal humus complexes seem to form when pH is 5–6 (Agricultural Research Institute, unpublished data). Metal–humus complexes have been shown to be quite stable against biodegradation (e.g., Nanzyo et al., 1993), and more stable than allophane–

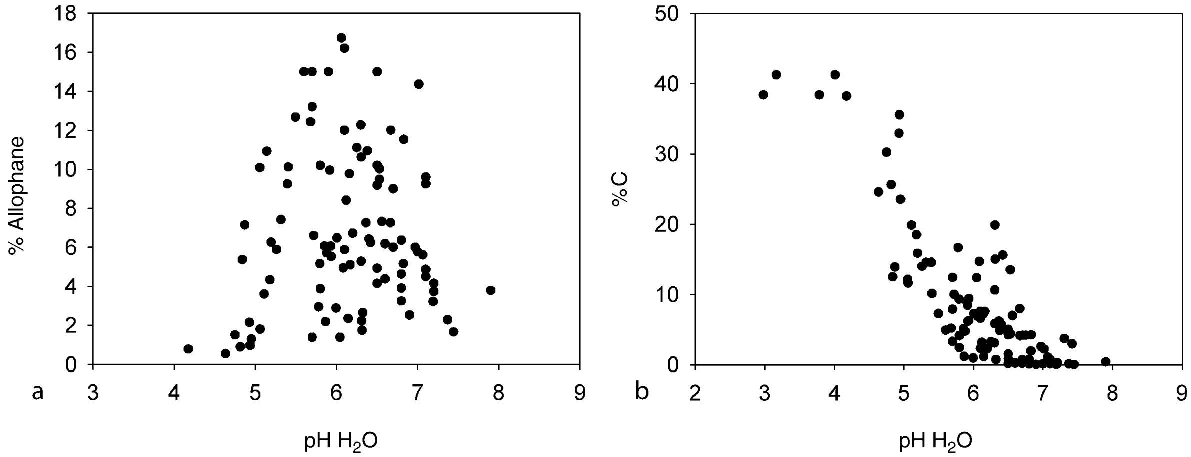


Figure A23 Allophane and organic carbon as a function of soil reaction in Icelandic Andosols and Histosols (surface horizons). Allophane does not form when pH becomes lower than 4.9 (**a**) and reaches a maximum around pH 6. Organic content rises rapidly with decreased pH, which also represents less tephra input in Iceland (**b**). With less tephra, there is less release of cations by weathering to maintain the pH. The gradient continues into Histosols, which have >20% organic carbon (figure based on O. Arnalds, unpublished data).

humus complexes (Boudot, 1992). Metal–humus complexes can be stable for >20 000 yr, and even >100 000 yr as exemplified by old soils in Hawaii (Torn et al., 1997).

The effect of vegetation on Andosol formation is often emphasized (e.g., Shoji, 1988), with darker soils rich in organic matter (melanic horizons) forming under grassland vegetation, but lighter colored fulvic horizons under woodlands.

Formation in redistributed volcanic rocks and other parent materials

Andosols have been reported to form in other materials than volcanic when environmental conditions result in a weathering environment characteristic of andosols. Andosols have formed in gabbros and amphibole parent materials in Galicia, Spain (Garcia-Rodeja et al., 1987), in low-activity clay regolith in India (Caner et al., 2000), in granite in Austria (Delvaux et al., 2004), and in non-volcanic materials in Nepal (Baumler and Zech, 1994). Old volcanic rocks, often reworked by glaciers or redistributed as sediments, can also serve as parent materials for Andosols, such as reported in Washington (Hunter et al., 1987) and France (reviewed by Quantin, 2004).

Properties

Morphology

When considering the horizonation and morphology of Andosols, it is important to bear in mind that the soil environment is characterized by deposition of parent materials, with the youngest materials on top, gradually or repeatedly being buried under new fresh vitric materials. However, some Andosols also form in volcanic bedrocks that for example have been reworked by Quaternary glaciers (see Quantin, 2004).

Andosols are usually dark soils rich in organic matter, but the morphology varies considerably according to the type of andosols. The color of Vitric Andosols is partly determined by the nature of the tephra materials, which range from black basaltic to light colored rhyolitic materials.

Horizonation typically follows an A–Bw–C sequence, but often with buried sequences due to repeated deposition events. Argillic horizon is usually not present. Clear tephra layers result in abrupt horizon boundaries. Tephra layers are sometimes distinct and can be important markers for dating.

While the surface horizon commonly has well expressed granular structure, the structure of the B horizon is usually poorly developed and difficult to identify. Young or poorly developed Andosols can contain various types of coarse fragments, which are described by specific terminology such as ashy, pumiceous, and cindery (see Shoji et al., 1993c).

Andosols tend to be very friable when lacking phyllosilicates, and non-plastic. Roots often extend far into the soils. However, hard-pans are also common under moist climates, which impede both root growth and water transport.

Physical properties

The many peculiar physical properties characterize Andosols such as strong silt sized aggregation and thixotropic nature, as was reviewed by Maeda et al. (1977). Vitric materials do not show these properties as clearly as allophanic or metal–humus Andosols, but their physical behavior depends on their type and degree of weathering (see Warkentin and Madea, 1980).

Aggregation and bulk density

Low bulk density is one of the diagnostic criteria for Andosols. Density of <0.9 g cm^{-3} is required. This low bulk density is a result of high organic content, aggregation of soil materials, and sometimes low density vitric materials. Icelandic research points to two main axes of influence, with density slowly decreasing with increased allophane content, but organic matter having more influence on bulk density with lowest values (0.2 g cm^{-3}) recorded in Histic Andosols (>12% C). The mineral colloidal fraction also forms stable silt-sized aggregates, which greatly influence the physical properties of Andosols (Maeda et al., 1977), and make conventional mechanical particle size determinations useless for Andosols. Drying can cause irreversible decrease in water retention and increase in bulk density.

Water retention and transport

Great water retention is one of the main characteristics of Andosols, hence the low bulk density. Common 1.5 MPa tension water contents are $>60\%$, but the term 'hydric' is used to describe Andosols when water retention is $>100\%$ at this tension based on dry weight of the soil. While allophane, imogolite and ferrihydrite contribute to this strong water retention, the effect of organic matter (metal–humus complexes, allophane–humus and humus alone) is much greater, following the two line pattern shown earlier for bulk density. Andosols have a large proportion of both large and intermediate pores, which allow for rapid water transport. Water infiltration, and both saturated and unsaturated hydraulic conductivity are rapid compared to most other soils (see Warkentin and Maeda, 1985; Basile et al., 2003). The silty aggregate behavior of the clay constituents and extremely high water retention leads to high frost susceptibility of Andosols (Arnalds, 2004).

Vitric materials can also have substantial water holding capacity, and extremely high infiltration rate and saturated hydraulic conductivity, enhancing their use for agriculture.

Atterberg limits and thixotropy

Andosols possess a special property, which has been called thixotropy. The soils can contain large amounts of water and yet appear relatively dry. When disturbed, the water is released. In other words, the soil can reach the liquid limit upon disturbance (Figure A24). This property is also expressed by very high liquid limits but a low range where the soil is plastic, resulting in very low plasticity index (often near 0). This property explains in part why andosols are quite susceptible to slope failures when disturbed.

Chemical properties

pH

Andosols can have a range of soil pH (H_2O). Metal–humus-dominated soils tend to be acid (<5) with low base saturation and they can show signs of Al toxicity. Soils dominated by allophane often have pH 5.5–6.5 (Nanzyo et al., 1993). If fresh basic parent materials are still present, pH is maintained by recharge of basic cations during weathering, which in Iceland sometimes leads to pH > 6.5 (Arnalds, 2004). Older, mature Andosols tend to have lower pH than younger soils, and can be quite acid. Soil reaction measured in KCl tends to be 0.5–1.5 units or more lower than the pH H_2O, the greatest difference between the two appears where metal–humus complexes are present (Nanzyo et al., 1993). Soil reaction measured in KCl provides important information about soil acidity in acid Andosols.

Soil reaction of Andosols rises rapidly when NaF is added to the soil solution, with F^- replacing OH^- from active surfaces. This is sometimes used to identify the presence of andic soil materials, both in laboratory and in the field.

Ion exchange

One of the most distinguishing features of Andosols is their pH-dependent charge. Allophane, imogolite, ferrihydrite and metal–humus complexes all have large reactive surface areas, but cation exchange capacity rises rapidly with increasing pH (see Wada, 1985). Determination of CEC is therefore very dependent on the pH used in any particular method and care should be taken when interpreting both CEC and base saturation values (see Madeira et al., 2003). Common CEC values reported for Andosols range between 10–40 $\text{cmol}_c\ \text{kg}^{-1}$. Andosols also exhibit anion exchange properties, which can be important for nutrient retention (e.g., Cl^-, NO^{3-}, SO_4^{2-}).

Exchange characteristics make Andosols susceptible to heavy metal and Cs^{137} pollution (e.g., Adamo et al., 2003) by retaining the pollutants quite effectively, especially when soils are not very acid (Nanzyo et al., 1993). Andosols often sustain dense populations, and pollution problems have been recorded in many areas, such as near Napoli, Italy (Adamo et al., 2003).

Classification

The development of early concepts and selection of classification criteria were reviewed by Parfitt and Clayden (1991) for Soil Taxonomy, and the subsequent evolution of the WRB criteria was discussed by Shoji et al. (1996). The colloidal constituents of Andosols, clays and metal–humus complexes, provide them with their distinctive characteristics. The identification of Andosols is therefore primarily based upon the measure of these constituents and their accessory properties.

Diagnostic properties

Identification of Andosols is based on the identification of an 'andic horizon' in WRB (FAO, 1998), but 'andic soil properties' according to Soil Taxonomy (Soil Survey Staff, 1998). Acid ammonium oxalate preferentially extracts the poorly ordered colloid constituents of Andosols and can be used to calculate the amount of allophane, imogolite and ferrihydrite (Parfitt and Childs, 1988; Parfitt and Wilson, 1985). The treatment also extracts Al and Fe associated with metal–humus

Figure A24 Thixotropy. Undisturbed clod is shown on to the left, but disturbed clod to the right. The soil reaches the liquid limit when disturbed with gentle pressure, even though the clod appears relatively dry. The soil is hydric andosol from the Azores (Portugal).

complexes. The primary diagnostic criteria for andic horizon is that it has $\geq 2\%$ oxalate extractable Al and ½Fe $(\mathrm{Al} + \frac{1}{2}\mathrm{Fe})_{o}$. Additional criteria used for identifying andosols are bulk density <0.9 g cm^{-3}, P-retention $\geq 70\%$, and thickness of ≥ 30 cm. WRB also defines a ‘vitric horizon’ , which is at least 30 cm thick, containing $>10\%$ volcanic glass in the fine earth fraction and has either $(\mathrm{Al} + \frac{1}{2}\mathrm{Fe})_{o}$ of $>0.4\%$, or bulk density >0.9 g cm^{-3}, or P-retention $>25\%$. Soil Taxonomy uses similar criteria for vitric materials, which are included with andic soil properties, by decreasing the requirements for $(\mathrm{Al} + \frac{1}{2}\mathrm{Fe})_{o}$ with increasing amount of vitric materials (0.4% $(\mathrm{Al} + \frac{1}{2}\mathrm{Fe})_{o}$ when vitric glass $>30\%$). In addition, tephric material (un-weathered) is defined by the WRB.

It should be noted that the tendency of Andosols to accumulate large amounts of organic matter is given special consideration by allowing andic soil horizons to have up to 20% C, while under other conditions $>12\%$ C (no clay) would normally result in Histosol classification (FAO, 1998). This breakpoint is at 25% C in Soil Taxonomy (Soil Survey Staff, 1998).

Andosols, subclasses

The WRB separates Andosols based on many criteria. Andic horizons are divided depending on whether they are allophanic (silandic), metal–humus complex dominated (aluandic) or vitric. Melanic and fulvic horizons are andic horizons with $>6\%$ C, but the melanic horizon is darker than the fulvic, but a distinction between the two is also based on the so-called melanic index (see FAO, 1998; Shoji, 1988). The term ‘hydric’ is used for Andosols with $>100\%$ water at 1.5 MPa tension. Andosols also include vitric and silic (allophane rich) subgroups. There is a range of other subunits of Andosols based on criteria common to other soil groups of the WRB, such as histic, mollic and gleyic. Tephric soil material is also used by the WRB for vitric soils.

Distribution

Andosols are found in volcanic regions, which are widespread on Earth, in all climatic regimes but more commonly in humid areas than dry (Wilding, 2000). Vitric soils are also widespread, but are not recognized as Andosols according to the WRB. Reviews by Kimble et al. (2000), Dahlgren et al. (2004) and FAO (2001) provided good accounts of aerial distribution of Andosols. They are common along the Pacific coast of the Americas, with notable areas are in Alaska (100 000 km^2, Kimble et al., 2000) the Pacific North-West USA, Mexico, Peru and Chile. Andosols are found in volcanic areas of Africa, e.g., Ethiopia, Rwanda, Kenya and Tanzania (FAO, 2001). Large areas are found in Asia, including the Kamchatka Peninsula (Russia), Japan, Indonesia and the Philippines, and New Zealand. Andosols are also found in active volcanic areas of mainland Europe (e.g., Italy, France). They are major soils of the volcanic islands in the Atlantic, including the Azores, Madeira the Canaries, and in Iceland. FAO estimate (2001) for global distribution of andic soils is 1.1 million km^2, but recent USDA-NRCS estimates are 1.2 million km^2 (Kimble et al., 2000) and 0.91 million km^2 (Wilding, 2000) (see Figure A25).

Areas affected by volcanic ash are much larger then the close vicinity of volcanoes, as volcanic materials can be transported long distances during eruptions or by aeolian/fluvial redistribution.

Andosols and land use

The low bulk density and lack of cohesion make Andosols susceptible to disturbance, such as made by heavy machinery. The soils are susceptible to failure when disturbed on slopes, which can cause them to reach the liquid limit (thixotropic property). Landslides are therefore common on slopes covered by Andosols, and this has caused many catastrophes in volcanic areas such as near Napoli, Italy in 1998 (e.g., Basile et al., 2003). Mantling of harder bedrock by andic soils and the platy character arising from tephra layers can form planes of failures. Considerable resources are spent on stabilizing Andosols (Figure A26).

Andosols are light and easy to plow, which favors their cultivation. The high water holding capacity and good hydraulic conductivites enhance their use for agriculture, but coarse layers of tephra can, however impede unsaturated water flow. Good quality products are often associated with Andosols, such as of wine and coffee. However, fertility varies greatly between Andosol types, especially between the acid metal–humus complex Andosols and the allophanic soils. Vitric soils are

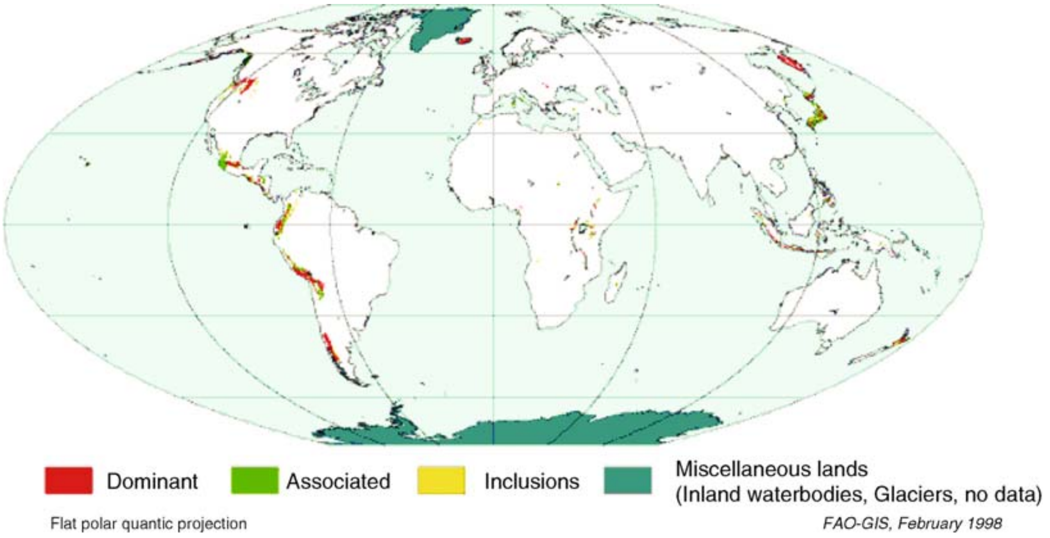


Figure A25 Andosols of the world.

Figure A26 Road construction in Hokkaido, Japan. Much effort is made to stabilize the slopes, but landslides are common in Andosol areas.

widespread, especially under dry temperature regimes (e.g., Africa, Mediterranean), and are successfully used for various crops, depending on local conditions, such as seasonal rainfall pattern and possible source of irrigation water.

Extreme examples of the value of Andosols and vitric materials for cultivation is the transport of andic soil materials to the lowlands of the Canary Islands for intensive cultivation (*sorriba*) (see Armas-Espinel et al., 2003) and the use of tephra as mulch for water conservation in the Canaries (Tejedor et al., 2003).

Hard pans commonly form in Andosols, which greatly affect their management possibilities, such as Mexico's *tepetates* (Servenay and Prat, 2003) and in the Azores (Pinheiro et al., 2004). Andosols have an especially strong tendency to retain phosphate, hence the P-retention classification criterion, and often require phosphorous additions for intensive crop production. Allophanic soils in the tropics are often heavily populated as a result of their fertility. Heavy land use can lead to pollution of these soils, enhanced by their colloid charge characteristics.

Much of the organic carbon in global cycling is retained in soils. The tendency of andosols to accumulate more carbon than other mineral soils (Eswaran et al., 1993) make them important in relation to the global carbon cycle and climate change, in spite of their limited distribution.

Olafur Arnalds

Bibliography

Adamo, P., Denaix, L., Terribile, F., and Zampella, M.,2003. Characterization of heavy metals in contaminated volcanic soils of the Solofrana river valley (southern Italy). *Geoderma*, **117**: 347–366.

Armas-Espinel, S., Hernandez-Moreno, J.M., Munoz-Carpena, R., and Regalado, C.M., 2003. Physical properties of "sorriba" – cultivated volcanic soils from Tenerife in relation to andic diagnostic parameters. *Geoderma*, **117**: 297–311.

Arnalds, O., 2004. Volcanic Soils of Iceland. *Catena*, **56**: 3–20.

Arnalds, O., and Kimble, J., 2001. Andisols of deserts in Iceland. *Soil Sci. Soc. Am. J.* **65**: 1778–1786.

Arnalds, O., and Stahr, K., 2004. Volcanic soil resources: occurrence, development, and properties. *Catena*, **56** (Special Issue).

Arnalds, O., Hallmark, C.T., and Wilding, L.P., 1995. Andisols from four different regions of Iceland. *Soil Sci. Soc. Am.* **59**: 161–169.

Bartoli, F., Buurman, P., Delvaux, B., and Madeira, M., 2003. Volcanic soils: properties and processes as a function of soil genesis and land use. *Geoderma*, **117** (Special Issue).

Basile, A., Mele, G., and Terribile, F., 2003. Soil hydraulic behaviour of a selected benchmark soil involved in the landslide of Sarno 1998. *Geoderma*, **117**: 331–346.

Baumler, R., and Zech, W., 1994. Characterization of andisols developed from nonvolcanic material in Eastern Nepal. *Soil Sci.*, **158**: 211–217.

Bigham, J.M., Fitzpatrick, R.W., and Schulze, D.G., 2002. Iron oxides. In Dixon, J.B., and Schulze, D.G., eds., *Soil Mineralogy with Environmental Applications.* Madison, WI: Soil Science Society of America, pp. 323–366.

Boudot, J.P., 1992. Relative efficiency of complexed aluminium, noncrystalline Al hydroxide, allophane and imogolite in retarding the biodegradation of citric acid. *Geoderma*, **52**: 29–39.

Caner, L., Bourgeon, G., Toutain, F., and Herbillon, A.J., 2000. Characteristic of non-allophanic andisol derived from low-activity regoliths in Nilgiri Hills (Southern India). *Eur. J. Soil Sci.*, **51**: 553–563.

Dahlgren, R.A., 1994. Quantification of allophane and imogolite. In Amonette, J.E., and Zelazny, L.W., eds., *Quantitative Methods in Soil Mineralogy.* Madison, WI: Soil Science Society of America Miscellaneous Publication.

Dahlgren, R., Shoji, S., and Nanzyo, M., 1993. Mineralogical characteristics of volcanic ash soils. In Shoji, S., Nanzyo, M., and Dahlgren, R.A., eds., *Volcanic Ash Soils. Genesis, Properties and Utilization.* Developments in Soil Science 21. Amsterdam: Elsevier, pp. 101–143.

Dahlgren, R.A., Saigusa, M., and Ugolini, F.C., 2004. The nature, properties and management of soils. *Adv. Agron.*, **82**: 113–182.

Delvaux, B., Strebl, F., Maes, E., Herbillon, A.J., Brahy, V., and Gerzabek, M., 2004. An andosol–cambisol toposequence on granite in the Austrian Bohemian Massif. *Catena*, **56**: 31–43.

Duchaufour, P., 1977. Pedology. Paton, T.R. (trans.). London: George Allen & Unwin.

Eswaran, H.E., Berg, Van Den E., and Reich, P., 1993. Organic carbon in soils of the world. *Soil Sci. Soc. Am. J.*, **57**: 192–194.

FAO, 1998. World reference base for soil resources. World Soil Resources Report 84. Rome: Food and Agriculture Organization of the United Nations.

FAO, 2001. Andosols. In Driessen, P., Deckers, J., Spaargaren, O., and Nachtergaele, F. eds., Lecture notes on the major soils of the world. World Soil Resources Report 94. Rome: Food and Agriculture Organization of the United Nations.

Fernandez Caldas, E., and Yaalon, D.H., 1985. *Volcanic Soils. Weathering and Landscape Relationships of Soils on Tephra and Basalt.* Catena Supplement No. 7. Amsterdam: Elsevier.

Fischer, R.V., and Schmincke, H.U., 1984. *Pyroclastic Rocks.* New York: Springer-Verlag.

Garcia-Rodeja, E., Silva, B.M., and Macias, F., 1987. Andosols developed from non-volcanic materials in Galicia, NW Spain. *J. Soil Sci.*, **28**: 573–591.

Harsh, J., Chorover, J., and Nizeyimana, E., 2002. Allophane and imogolite. In Dixon, J.D., and Schulze, D.G. eds., *Soil Mineralogy with Environmental Applications.* Madison, WI: Soil Science Society of America, pp. 291–322.

Heiken, G., and Wohletz, K., 1985. Volcanic Ash. Berkely, CA: University of California Press.

Hunter, C.R., Frazier, B.E., and Busacca, J., 1987. Lytell Series: a nonvolcanic andisol. *Soil Sci. Soc. Am. J.*, **51**: 376–383.

Kimble, J.M., Ping, C.L., Sumner, M.E., and Wilding, L.P., 2000. Andisols. In Sumner, M.E., ed.–in–chief, *Handbook of Soil Science.* New York: CRC Press, pp. E209–E124.

Macdonald, G.A., 1972. *Volcanoes.* Englewood Cliffs, NJ: Prentice-Hall.

Madeira, M., Auxtero, E., and Sousa, E., 2003. Cation and anion exchange properties of andisols from the Azores, Portugal, as determined by the compulsive exchange and the ammonium acetate methods. *Geoderma*, **117**: 225–241.

Maeda, T., Takenaka, H., and Warkentin, B.P., 1977. Physical properties of allophane soils. *Adv. Agron.*, **29**: 229–264.

Nanzyo, M., Dahlgren, R., and Shoji, S., 1993. Chemical characteristics of volcanic ash soils. In Shoji, S., Nanzyo, M., and Dahlgren, R.A., eds., *Volcanic Ash Soils. Genesis, Properties and Utilization.* Developments in Soil Science 21. Amsterdam: Elsevier, pp. 145–187.

Ndayiragije, S., and Delvaux, B., 2003. Coexistence of allophane, gibbsite, kaolinite and hydroxyl-Al-interlayered 2 : 1 clay minerals in a perudic andosol. *Geoderma*, **117**: 203–214.

Ndayiragije, S., and Delvaux, B., 2004. Selective sorption of potassium in a weathering sequence of volcanic ash soils from Guadeloupe, French West Indies. *Catena*, **56**: 185–198.

Parfitt, R.L., and Childs, C.W., 1988. Estimation of forms of Fe and Al: a review, and analysis of contrasting soils by dissolution and Moessbauer methods. *Aust. J. Soil Res.*, **26**: 121–144.

Parfitt, R.L., and Clayden, B., 1991. Andisols – the development of a new order in Soil Taxonomy. *Geoderma*, **49**: 181–198.

Parfitt, R.L., and Kimble, J., 1989. Conditions for formation of allophane in soils. *Soil Sci. Am. J.*, **53**: 971–977.

Parfitt, R.L., and Wilson, A.D., 1985. Estimation of allophane and halloysite in three sequences of volcanic soils, New Zealand. In Fernandez Caldas, E., and Yaalon, D.H., eds., *Volcanic Soils. Weathering and Landscape Relationships of Soils on Tephra and Basalt.* Catena Supplement No. 7. Amsterdam: Elsevier, pp. 1–8.

Pinheiro, J., Tejedor Salguero, M., and Rodriguez, A., 2004. Genesis of placic horizons in andisols from Terceira Island Azores, Portugal. *Catena*, **56**: 85–94.

Quantin, P., 2004. Volcanic soils of France. *Catena*, **56**: 95–109.

Schwertmann, U., 1985. The effect of pedogenic environments on iron oxide minerals. *Adv. Soil Sci.*, **1**: 172–200.

Servenay, A., and Prat, C., 2003. Erosion extension of indurated volcanic soils of Mexico by aerial photographs and remote sensing analysis. *Geoderma*, **117**: 367–375.

Shoji, S., 1988. Separation of melanic and fulvic andosols. *Soil Sci. Plant Nutr.*, **34**: 303–306.

Shoji, S., Toyoaki, I., Saigusa, M., and Yamada, I., 1985. Properties of nonallophanic andosols from Japan. *Soil Sci.*, **140**: 264–277.

Shoji, S., Nanzyo, M., and Dahlgren, R.A., 1993a. Volcanic Ash Soils. Genesis, Properties and Utilization. Developments in Soil Science 21. Amsterdam: Elsevier.

Shoji, S., Dahlgren, R., and Nanzyo, M., 1993b. Genesis of volcanic ash soils. In Shoji, S., Nanzyo, M., and Dahlgren, R.A., eds., *Volcanic Ash Soils. Genesis, Properties and Utilization.* Developments in Soil Science 21. Amsterdam: Elsevier, pp. 37–71.

Shoji, S., Dahlgren, R., and Nanzyo, M., 1993c. Morphology of volcanic ash soils. In Shoji, S., Nanzyo, M., and Dahlgren, R.A., eds., *Volcanic Ash Soils. Genesis, Properties and Utilization.* Developments in Soil Science 21. Amsterdam: Elsevier, pp. 7–35.

Shoji, S., Nanzyo, M., Dahlgren, R.A., and Quantin, P., 1996. Evaluation and proposed revisions of criteria for andosols in the World Reference Base for Soil Resources. *Soil Sci.*, **161**: 604–615.

Smith, G., 1986. *The Guy Smith interviews: Rationale for Concepts in Soil Taxonomy.* SMSS Technical Monograph No. 11. Boston, MA: Cornell University.

Soil Survey Staff, 1998. *Keys to Soil Taxonomy*, 8th edn. Washington DC: USDA, NRCS.

Stefansson, A., and Gislason, S.R., 2001. Chemical weathering of basalts, southwest Iceland: effect of rock crystallinity and secondary minerals on chemical fluxes to the ocean. *Am. J. Sci.*, **301**: 513–556.

Tan, K.H., 1984. Andosols. *Benchmark Papers in Soil Science Series.* New York: Van Nostrand Reinhold Company.

Tejedor, M., Jiménez, C., and Díaz, F., 2003. Volcanic materials as mulches for water conservation. *Geoderma*, **117**: 283–295.

Torn, M.S., Trumbore, S.E., Chadwick, O.A., Vitousek, P.M., and Hendricks, D.M., 1997. Mineral control of soil organic carbon storage and turnover. *Nature*, **389**: 170–173.

Wada, K., 1985. The distinctive properties of andosols. *Adv. Soil Sci.*, **2**: 173–229.

Wada, K., 1989. Allophane and imogolite. In Dixon, J.B., and Weed, S.B., eds., *Minerals in Soil Environments,* 2nd edn. Madison, WI: Soil Science Society of America, pp. 1051–1087.

Warkentin, B.P., and Maeda, T., 1980. Physical and mechanical characteristics of andisols. In Theng, V.K.G., ed., *Soils with Variable Charge.* Lower Hutt, New Zealand: New Zealand Soil Bureau, pp. 97–107.

White, G.N., and Dixon, J.B., 2002. Kaolin–serpentine minerals. In Dixon, J.D., and Schulze, D.G., eds., *Soil Mineralogy with Environmental Applications.* Madison, WI: Soil Science Society of America, pp. 389–414.

Wilding, L.P., 2000. Introduction: general characteristics of soil orders and global distributions. In Sumner, M.E., ed., *Handbook of Soil Science.* New York: CRC Press, pp. 175–183.

Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., and Putnis, C.V., 2004. The dissolution rates of natural glasses as a function of their composition at pH4 and 10.6, and temperatures from 25 to 74°C. *Geochim. Cosmochim. Acta.*, 4843–4858.

Yerima, B.P.K., Wilding, L.P., Calhoun, F.G., and Hallmark, C.T., 1987. Volcanic ash-influenced vertisols and associated mollisols of El Salvador: Physical, chemical, and morphological properties. *Soil Sci. Soc. Am. J.* **51**: 699–708.

Cross-references

Acid Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils
Iron Oxides

ANTHROPOGENIC

Used of soils, landscapes, or ecological systems generally, to indicate modification by human activities. Recognized as the group Anthrosols in the WRB System of Soil Classification, in terms of diagnostic anthropogenic horizons:

A terric horizon (from L. *terra*, earth) results from addition of earthy manure, compost or mud over a long period of time. The terric horizon has a non-uniform textural differentiation with depth. The source material and/or underlying substrates influence the color of the terric horizon. Base saturation (in 1 M NH_4OAc at pH 7.0) is more than 50%.

An irragric horizon (from L. *irrigare*, to irrigate, and agricolare, to cultivate) is a light colored (Munsell color value and chroma, moist, both greater than 3), uniformly structured surface layer, developed through long-continued irrigation with sediment-rich water. Clay and carbonates are evenly distributed and the irragric horizon has more clay, particularly fine clay, than the underlying soil material. The weighted average organic carbon content exceeds 0.5%, decreasing with depth but remaining at least 0.3% at the lower limit of the irragric horizon.

A plaggic horizon (from Dutch plag, sod) has a uniform texture, usually sand or loamy sand. The weighted average organic carbon content exceeds 0.6%. The base saturation (in 1 M NH_4OAc at pH 7.0) is less than 50%. The content of P_2O_5 extractable in 1% citric acid is more than 0.25% within 20 cm of the surface (frequently more than 1%).

A hortic horizon (from L. *hortus*, garden) results from deep cultivation, intensive fertilization and/or long-continued application of organic wastes. It is a dark colored horizon with Munsell color value and chroma (moist) of 3 or less. The hortic horizon has a weighted average organic carbon content of 1% or more, and more than 100 mg kg^{-1} (0.5 M $NaHCO_3$ extractable) P_2O_5 in the fine earth fraction of the upper 25 cm layer. Base saturation (in 1 M NH_4OAc at pH 7.0) is 50% or more.

An anthraquic horizon (from Gr. anthropos, human, and L. *aqua*, water) represents a puddled layer or a plow pan. Characteristically, plow pans have a platy structure; they are compacted and slowly permeable to water. Yellowish-brown, brown or reddish-brown rust mottles occur along cracks and root holes. The bulk density of the plow pan is at least 20% greater than that of the puddled layer, whereas its porosity is 10 to 30% less than that of the puddled layer. Non-capillary porosity is 2 to 5%.

A hydragric horizon (from Gr. hydros, water, and L. *agricolare*, to cultivate) is a subsurface horizon with characteristics associated with wet cultivation:

- iron-manganese accumulation or coatings of illuvial Fe and Mn; or twice as much dithionite-citrate extractable iron than in the surface horizon(s), or more, or 4 times as much dithionite-citrate extractable manganese or more; or
- redoximorphic features associated with wet cultivation; and
- thickness of more than 10 cm.

ANTHROSOLS

Anthrosols are soils that have been significantly altered by the agricultural, horticultural, domestic and other activities of humankind. This article is based on the descriptions in FAO (2001).

Connotation. Soils with prominent characteristics that result from human activities; from Gr. anthropos, man.

Definition. FAO (2001) defines Anthrosols as soils that have been formed or modified by human activities such that

1. a *hortic*, *irragric*, *plaggic* or *terric* horizon 50 cm or more thick is present; or
2. an *anthraquic* horizon and an underlying *hydragric* horizon occur with a combined thickness of 50 cm or more.

Parent material. Virtually any soil material, modified through cultivation, excavation, or by addition of material.

Environment. Plaggic Anthrosols are most common in northwest Europe; hydragric Anthrosols in Southeast and East Asia, and irragric Anthrosols in the Middle East.

Profile development. The influence of *Homo sapiens* is normally restricted to the surface horizon(s); the horizon differentiation of a buried soil can still be intact at some depth. Qualifiers are used to indicate the type of anthropogenic modification that has influenced soil development. Common anthropedogenic horizons and the soils they occur in, are:

Plaggic Anthrosols – soils modified by additions of sods. Occur for example in areas of glacial sand and loess of Europe such as Arenosols and Podzols. The *plaggic* horizon (from Dutch *plag*, sod), uniform in texture, commonly sand or loamy sand.

Terric Anthrosols are most noticeable in wetland areas with Fluvisols, Gleysols and Histosols or with in regions of acid/unfertile soils such as Albeluvisols, Arenosols or Podzols. The *terric* horizon (from L. *terra*, earth) forms where there has been long-term addition of earthy manure.

Irragric Anthrosols are most common in sub-humid to arid regions, with Calcisols, Gypsisols, Solonchaks and Solonetz, as well as with Regosols and Cambisols. The *irragric* horizon (from L. *irrigare*, to irrigate and *agricolare*, to cultivate) is a light colored, with a uniform structure, developed where irrigation with sediment-rich water has been practiced over the long-term.

Hydragric Anthrosols are found in river systems with Gleysols and Fluvisols, in uplands with Alisols, Acrisols, Lixisols and Luvisols in upland areas, and in volcanic districts with Andosols. The *hydragric* horizon (from Gr. *hydros*, water, and L. *agricolare*, to cultivate) is a subsurface horizon with the redoximorphic features associated with wet cultivation.

Anthraquic Anthrosols occur particularly as modifications of clay to loamy-clay soils, Mollisols and Fluvisols for example, or of soils with a low bulk density such as Andosols. The

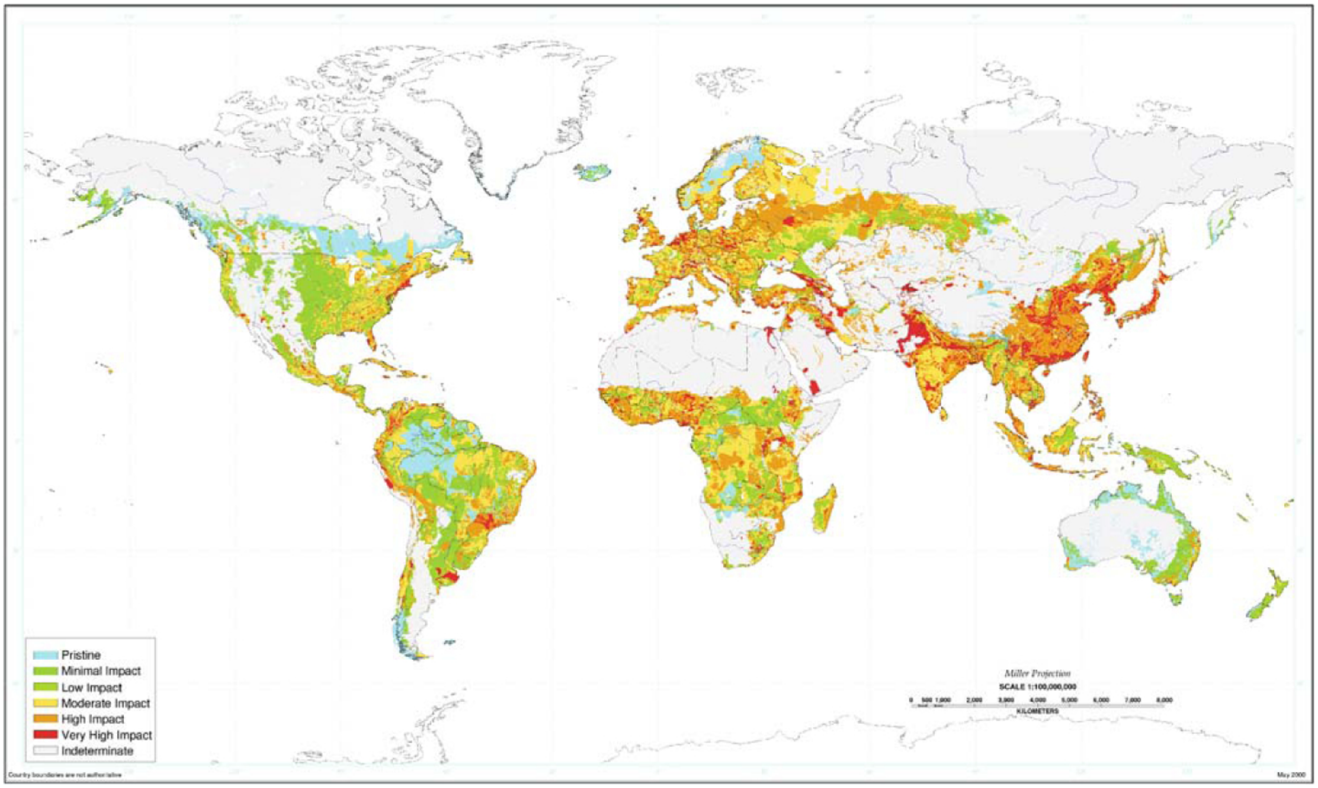


Figure A27 Anthropic landscapes. Courtesy USDA-NRCS, Soil survey division.

anthraquic horizon (from Gr. *anthropos*, human, and L. *aqua*, water) is a puddled layer or a plow pan, with low permeability.

Hortic Anthrosols can occur alongside virtually any reference soil group. The *hortic* horizon (from L. *hortus*, garden) is produced by deep cultivation, intensive fertilization and/or long-term application of organic wastes.

Origin

Human activities may modify a soil simply in terms of the activity itself (as in plowing), or by virtue of the addition of materials to the land surface (in land fills for example). In the latter case the material added, '*anthropogenic soil material*', is not itself an Anthrosol until pedogenetic change is evident. Typical '*anthropedogenic processes*' are

1. *deep working*, i.e., below the normal depth of tillage (e.g., in terraced lands in the Mediterranean Region, the Arab Peninsula, the Himalayas and the Andes);
2. *intensive fertilization* with organic/inorganic fertilizers *without* substantial additions of mineral matter (e.g., manure, kitchen refuse, compost, night soil);
3. *continuous application of earth* (e.g., sods, beach sand, shells, earthy manures);
4. *irrigation* adding substantial quantities of sediment;
5. *wet cultivation* involving puddling of the surface soil and human-induced wetness.

Use. European Anthrosols were traditionally grown to winter rye, oats, and barley but are now also planted to forage crops, potatoes and horticultural crops; in places they are used for tree nurseries and pasture. Irragric Anthrosols occur in irrigation areas where they are under cash crops and/or food crops. Hydragric Anthrosols are associated with paddy rice cultivation whereas hortic Anthrosols are (mainly) planted to vegetables for home consumption (see Figure A27).

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FAO, 2006. *World reference base for soil resources, 2006: A framework for international classification, correlation, and communication*. Rome: Food and Agriculture Organization of the United Nations. 128 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Anthropogenic
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Technosols

ARENOSOLS

Arenosols are sandy soils, developed on quartzose (and sometimes calcareous) sands of diverse origins, for example from residual materials remaining after the long term weathering of acid rocks, from aeolian deposits, or from fluviatile sediments including post glacial deposits. The following account follows FAO (2001).

Connotation. Sandy soils; from L. *arena*, sand.

Synonyms. Arenosols are equivalent to 'siliceous, earthy and calcareous sands' and various 'podzolic soils' (Australia), 'red and yellow sands' (Brazil) and the Arenosols of the FAO Soil Map of the World. In Soil Taxonomy Arenosols occur in part as Psamments and Psammaquents, and when deep, with an argic or spodic horizon within 200 cm from the surface, as 'grossarenic' subgroups within the alfisol, ultisol and spodosol orders. In France Arenosols correlate with taxa within the "Classe des sols minéraux bruts" and the "Classe des sols peu évolués".

Definition. Essentially sandy soils developed on sandy parent materials, formally defined by FAO (2001) as soils having:

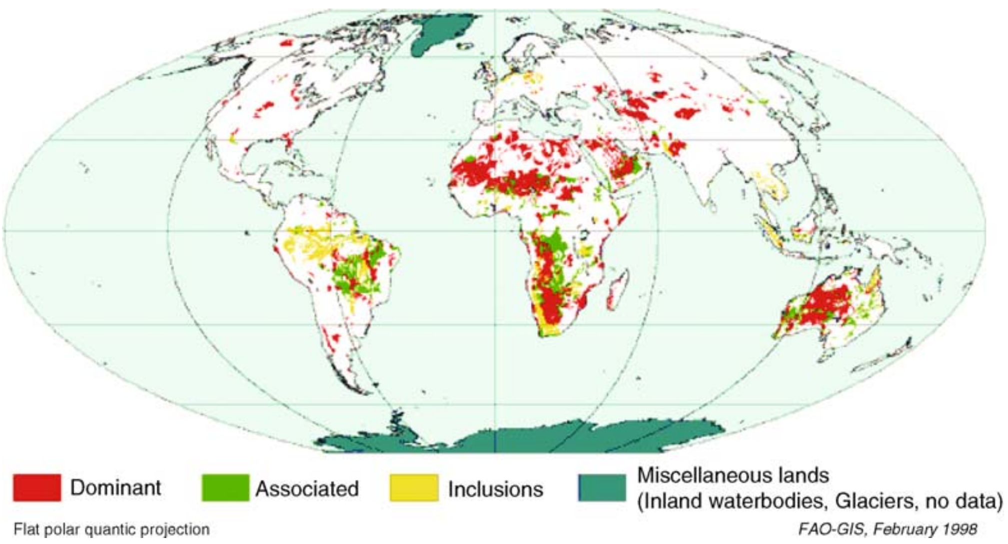


Figure A28 Distribution of Arenosols.

1. a texture, which is loamy sand or coarser *either* to a depth of at least 100 cm from the soil surface, *or* to a *plinthic*, *petroplinthic* or *salic* horizon between 50 and 100 cm from the soil surface; and
2. less than 35% (by volume) of rock fragments or other coarse fragments within 100 cm from the soil surface; and
3. no diagnostic horizons other than an *ochric*, *yermic* or *albic* horizon, or a *plinthic*, *petroplinthic* or *salic* horizon below 50 cm from the soil surface.

Parent material. Unconsolidated, in places calcareous, translocated sand; relatively small areas of Arenosols occur on residual sandstone or siliceous rock weathering.

Environment. From arid to (per)humid and from extremely cold to extremely hot; landforms vary from recent dunes, beach ridges and sandy plains under scattered (mostly grassy) vegetation, to very old plateaus under light forest.

Profile development. A(E)C profiles. In the dry zone, an *ochric* surface horizon is the only diagnostic horizon. Arenosols in the perhumid tropics tend to develop thick *albic* eluviation horizons; most Arenosols of the humid temperate zone show signs of alteration or transport of humus, iron or clay, but too weak to be diagnostic.

Origin. Under dry climates Arenosols have minimally developed profiles either because the parent materials are young, or because soil forming processes are relatively inactive during long droughty. In humid regions, the profile will be more mature, and in the limit achieved in the humid tropics, a giant Podzol may form with a thick albic E-horizon.

Use. Most Arenosols in the dry zone (see Figure A28) are used for little more than extensive grazing but they could be used for arable cropping if irrigated. Arenosols in temperate regions are used for mixed arable cropping and grazing; supplemental (sprinkler) irrigation is needed during dry spells. Arenosols in the perhumid tropics are chemically exhausted and highly sensitive to erosion. They are best left untouched.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin Springer-Verlag, 130 pp.

Cross-references

Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Soils of the Coastal Zone

ARGILLACEOUS

Describes geological materials rich in clay: shales for example. Not normally applied to soils, the roughly equivalent term in pedology being argillic, as in argillic horizon. Soils developed on argillaceous materials tend to be heavy, with clay minerals inherited or derived from sheet silicates in the parent rock. Where soils have developed on so-called "black" (i.e., organic-rich) shales, elements such as Cu, Mo, Ni, Zn, Cr, V, As and F, may be present in toxic amounts (e.g., Fang et al., 2001).

Bibliography

Fang, W., Hu, R., and Wu, P., 2001. Influence of black shales on soils and edible plants in the Ankang Area, Shaanxi Province, P. R. of China. *Environ. Geochem. Health*, **24**: 35–46.

ARGILLAN

See *Cutan*.

ARID

Adjective applied to climates with a low annual precipitation in the range 50 to 250 mm. Precipitation in the range 250 to 500 mm per year is considered to be semi-arid. In Soil Taxonomy an aridic moisture regime is recognized and is one of the diagnostic features of the aridisol order.

ARRHENIUS' EQUATION

Arrhenius' Equation is commonly expressed in the form shown in Figure A29. T is temperature in °Kelvin; R is the gas constant; E_A, is the activation energy, the minimum energy in joules per mole needed for the reaction to take place; e is 2.71828; and A is essentially constant over the small temperature range of typical soil systems, and is related to such factors as stericity, and the number of collisions between molecular particles.

The rate of a given reaction is a function of the rate constant and the concentrations of all reactants. For reactions under earth surface conditions, with activation energies of about 50 kJ mol^{-1}, the rate of reaction approximately doubles for a 10 °C rise in temperature.

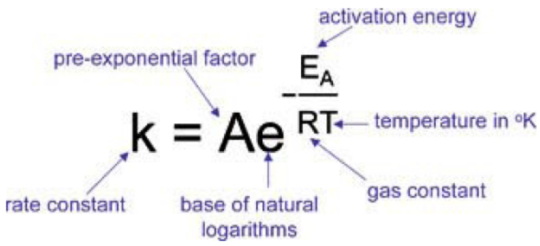


Figure A29 Arrhenius' Equation.

ASSOCIATION

A loose grouping of soils that occur together on a landscape, within a given ecological zone, or which develop on a particular parent material.

Bibliography

Dent, D., and Young, A., 1981. *Soil Survey and Land Evaluation*. London, Boston: Allen & Unwin. 278 pp.

AUGER

An instrument for boring into soil and obtaining a subsurface sample for examination. Commonly with a handle at right angles to the shank to facilitate penetration of the soil by manually twisting the instrument. Several varieties are used, a common one being the probe, which has a small chamber with a cutting edge at its lower end for retrieving the soil sample. (Tarnocai, 1993, 755–759).

Bibliography

Tarnocai, C., 1993. In Carter, M.R., *Soil Sampling and Methods of Analysis,* Chap. 71. Boca Raton, FL: Lewis Publishers, 823 pp.

AUTHIGENIC

Used to describe soil constituents that formed within the soil. The process is called neoformation. The equivalent term used by geologists is autochthonous, a word used in soil science only when referring to certain microorganisms. See *Allogenic*.

AZONAL SOIL

See *Order*.

B

B HORIZON

See *Horizon, Profile, Horizon Designations*.

BACKGROUND

Term applied to the general chemical composition of the soils or rocks of a region, against which the presence of anomalously high (or low) values may be gauged. Used especially in geochemical prospecting (Hawkes and Webb, 1962, p. 22–26).

Bibliography

Hawkes, H.E., Webb, J.S., 1962. Geochemistry in Mineral Exploration. New York: Harper & Row, 415 pp.

BADLANDS

Bare ground that has suffered extensive soil and sediment erosion by rain-wash, such that the land has been carved into an almost impassable surface of ridges, pinnacles, valleys and other shapes (Campbell, 1997). Particularly characteristic of arid and semi-arid regions. Contemporary erosion rates from about 3 to more than 80 mm per year.

Bibliography

Campbell, I.A., 1997. Badlands and badland gullies. In Thomas, D.S.G., ed., *Arid Zone Geomorphology.* Chichester: Wiley, pp. 261–291.

BARCHAN

See *Dune*.

Cross-reference

Wind Erosion

BARRENS

Originally barren grounds, applied particularly though not exclusively, to parts of the Canadian Shield where a combination of thin soils, rock exposure, cold climate and permafrost, result in a sparse vegetation. Now the newest geological source of diamonds (Krajick, 2001).

Bibliography

Krajick, K., 2001. *Barren Lands: An Epic Search for Diamonds in the North American Arctic.* New York: Times Books, 442 pp.

BASE

See *Acids, Alkalis, Bases and pH.*

BASE LEVEL

The level down to which running water flows on a landscape, and therefore the level that the landscape would be reduced to by erosion, if no other process intervened. The ultimate base level is sea level, though any part of the land surface where a stream-gradient is effectively zero, may act as a local, temporary base level. Planar landscapes formed by base levelling include some of the oldest land surfaces on earth (for example in the interiors of the Gondwanaland continents), and may have had continuous soil forming processes since the end of the Mesozoic (Adams, 1975).

Bibliography

Adams, G.F., 1975. *Planation Surfaces: Peneplains, Pediplains, and Etchplains.* Stroudsburg, PA: Dowden, Hutchinson & Ross, 476 pp.

Cross-references

Acrisols
Ferralsols

BASE SATURATION

Base saturation indicates the balance between acid and base cations adsorbed by the cation exchange complex (CEC) of a soil. The term is a partial misnomer because a base is a chemical compound that can react with an acid to form a salt; calcium hydroxide, $Ca(OH)_2$, is an appropriate example. In the present context, however, it is now understood to mean the *cation* of the base, that is, Ca^{2+}, as distinct from the cations H_3O^+ and $[A1(H_2O)_6]^{3+}$, which are acids.

If a neutral solution (that is, at pH 7) of a salt such as ammonium chloride percolates through a neutral soil, the leachate will contain an amount of cations equivalent to that in the initial solution, although the composition of the leachate will be different because of cation exchange; in particular, the leachate will be enriched in Ca^{2+}. If, on the other hand, the neutral salt solution passes through an acid soil, the leachate will be acid, and it will contain less base cations than the added solution because the base cations have been adsorbed by the soil to the extent that it was unsaturated.

Hissink (1925) introduced the concept of *degree of base saturation* and defined it as the ratio of the quantity of adsorbed base actually present in the soil to the total quantity the soil can adsorb. Hissink experienced difficulty in measuring total base adsorption because it increases almost indefinitely as a base is added to the soil; however, he was able to at least approximate the degree of base unsaturation from the amounts of $Ba(OH)_2$ that remained unreacted after addition to the soil.

Understanding of both cation exchange and soil *acidity* (*q.v.*) has improved considerably in recent years, and because these topics are intimately linked with base saturation, they will be discussed first.

Cation exchange

The origin of cation exchange lies in the negative electric charges on the colloidal clay and humus particles of the soil matrix. There are two main components of negative charge: a constant, or permanent, charge and a variable, pH-dependent charge.

The *permanent charge* is generated by partial isomorphous substitution within the lattices of clay-size layer silicates, and in particular, the substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet and of Mg^{2+} or Fe^{2+} for Al^{3+} in the octahedral sheet. The consequent deficiency in positive valency results in a crystal with an excess negative charge.

The *variable charge* is generated by the pH-dependent dissociation of hydroxyl groups, which may occur in *(a)* silanol groups located at the surfaces of aluminosilicate gels or the edges of layer-silicate crystals, *(b)* phenols, or *(c)* in carboxylic acids. Where appreciable amounts of organic matter are present such as in surface soils, the major part of the variable charge arises from proton dissociation by carboxyl and phenolic groups. Another mechanism contributing to pH-dependent charge is the "blocking" of negative charge by strongly adsorbed hydroxy aluminum cations. As the pH rises, these cations precipitate as aluminum hydroxide, and the negatively charged sites are then free to participate in cation-exchange reactions.

The adsorption of positively charged counterions (mainly Ca^{2+}, but also K^+, Na^+, NH_4^+, Mg^{2+}, Mn^{2+}, and Al^{3+}, depending on circumstances) by soil particles ensures their overall electrical neutrality. When a soil is suspended in or leached by a salt solution, the cations of the salt displace the freely diffusible counterions of the soil, producing cation-exchange phenomenon (see *Exchange phenomena*).

Acid soils

The nature of soil *acidity* was reviewed by Coleman and Thomas (1967). Soil acidity is a complicated field, but the main features can be illustrated by considering the reactions that occur when a base such as $Ca(OH)_2$ reacts with an acid soil.

- Free hydrogen ions (i.e., hydrated protons, H_3O^+) in solution are neutralized by the base:

$$H_3O^+ + OH^- \rightarrow 2H_2O \tag{1}$$

  It is important to realize that acid soils normally contain very little free hydrogen ion, except in very acid peat or muck soils, and that this reaction therefore accounts for very little of the base consumed.
- Aluminum ions, which balance in part the surface negative charges of acid soils, are desorbed by the cations of the base and are then precipitated as aluminum hydroxide by hydroxyl ions:

$$\begin{aligned} 2\text{soil Al} + 3Ca^{2+} &\rightarrow 3\text{soil Ca} + 2Al^{3+} \\ Al^{3+} + 3OH^- &\rightarrow Al(OH)_3 \end{aligned} \tag{2}$$

  The amount of surface charge is unaffected by these reactions. The components of acidity described under Equation (1) and Equation (2) are described as *exchange acidity* because they are acid cations displaced when the soil is leached by an unbuffered salt solution; they can be estimated by a direct titration of the leachate with a base.
- Acidic hydroxyl groups, which occur in a number of soil components as mentioned above, ionize and are neutralized by the base:

$$\begin{aligned} H_2O + R - OH &\rightarrow RO^- + H_3O^+ \\ H_3O^+ + OH^- &\rightarrow 2H_2O \end{aligned} \tag{3}$$

  This reaction is analogous to the neutralization of a simple weak acid, but the acid groups involved occur on soil surfaces rather than in solution. This component is described as *hydrolytic acidity.*

An important effect of reaction 3 is to increase the negative electric charge, which is then balanced by adsorption of cations from the base. This increase is the pH-dependent charge referred to above, and it is of considerable magnitude in surface soils because of the humus they contain.

The total acidity of the soil is the sum of the exchange acidity and hydrolytic acidity as defined above; i.e., it is the total base consumed in bringing the soil from its natural pH to the final pH attained after reaction with the base. The total acidity has also been called *titratable acidity*, and some authors have referred to it as *exchange acidity* (e.g., Peech, 1965).

Cation exchange capacity (CEC)

CEC measures the ability of a soil to adsorb cations in exchangeable forms. It corresponds to the negative charge of the soil and is expressed in milli-equivalents per unit mass of soil (mequiv kg^{-1}).

The negative charge, and hence the CEC, increases as pH rises. This was explained previously and is illustrated in Figure B1. The capacity of the soil to adsorb exchangeable cations cannot therefore be defined unless a standard pH for its measurement is agreed upon. Bradfield and Allison (1933) proposed that "a soil saturated with bases is one which has reached equilibrium with a surplus of $CaCO_3$ at the partial pressure of CO_2 existing in the atmosphere." This corresponds to a pH of 8.2–8.3 and provides a rational basis for the determination of both CEC and total acidity. A buffer (see *Buffers, buffering*) system containing triethanolamine and triethanolamine hydrochloride at pH 8.2, in 0.25 mol l^{-1} $BaCl_2$ solution has frequently been used for these determinations (Chapman, 1965; Peech, 1965).

The partial pressure of CO_2 in soils is generally greater than that in the atmosphere because of the respiration of soil fauna and flora so that the pH of a soil in equilibrium with $CaCO_3$ is lower than 8.2. This is one reason for the more common practice of measuring CEC at the neutral point, pH 7, using a 1.0 mol l^{-1} ammonium-acetate buffer solution.

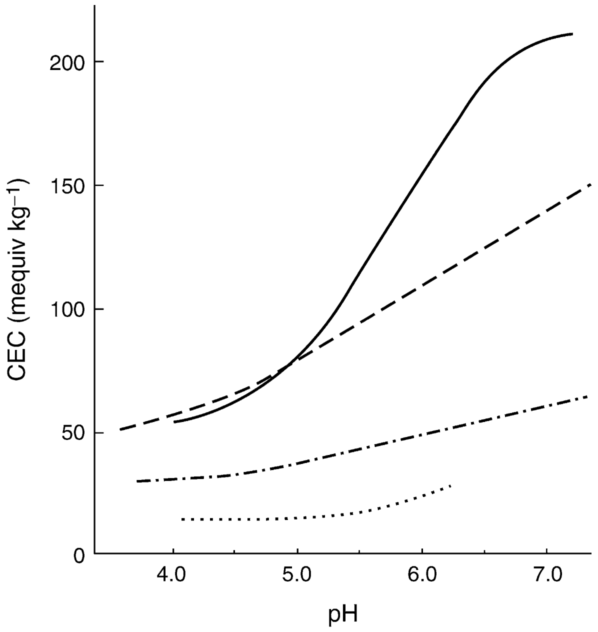


Figure B1 Effect of soil reaction (pH in 0.01 M $CaCl_2$ suspension) on CEC, for some contrasting soils adjusted to different reactions in the field. The effects are related mainly to the organic matter contents of the soils: 3.1% C; 1.7% C; 0.5% C; 0.3% C (subsoil).

A third approach in determining CEC is to leach soil with unbuffered salt solutions (1.0 mol l^{-1} KCl or NH_4Cl) that rapidly adjust to the natural reaction (pH) of the soil and displace only the exchangeable cations without generating extra pH-dependent charge. In this case CEC equals the sum of cations displaced from the soil, including Al^{3+} from acid soils of pH less than 5.2, as well as the base cation suite referred to previously.

Degree of base saturation

The degree of base saturation is defined simply as $(\Sigma M)/\mathrm{CEC}$, or when expressed as a percentage, $V = 100(\Sigma M)/\mathrm{CEC}$. Here ΣM refers to the sum of milli-equivalents per kilogram of exchangeable cations Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, and so on. It is clear from the previous discussion that when defining the degree of base saturation, the pH at which the CEC is measured must be specified. In the majority of soils literature, the CEC measured at pH 7 in ammonium acetate (NH_4OAc) solution is taken as the standard for base saturation, although the other methods mentioned previously are perfectly valid for different purposes.

The components that contribute toward CEC and that account for base saturation and unsaturation are related as follows:

$$\begin{aligned}\mathrm{CEC} = {} & \text{exchangeable base cations} \\ & + \text{exchange acidity (acid cations)} \\ & + \text{hydrolytic acidity} \qquad (4)\end{aligned}$$

The effect of different methods of expressing CEC on the apparent degree of base saturation is illustrated diagrammatically in Figure B2.

Base saturation and soil pH

Base-saturated soils are neutral in reaction while base-unsaturated soils are acid. Some relationship would therefore be expected between pH and the degree of base saturation.

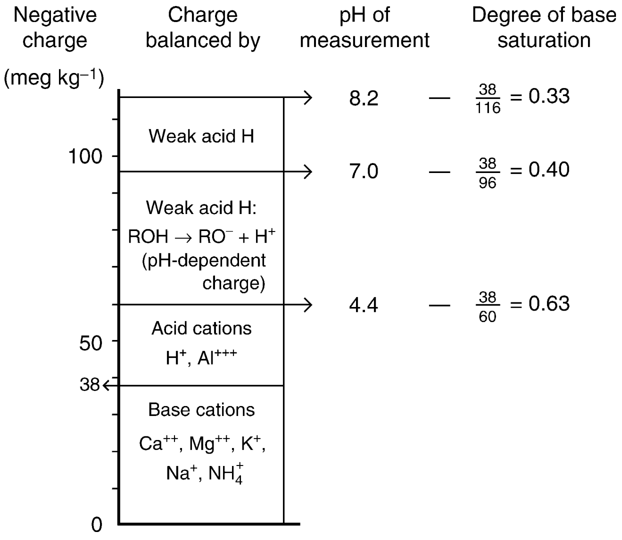


Figure B2 Diagrammatic illustration of components of negative charge and their relationship to degree of base saturation.

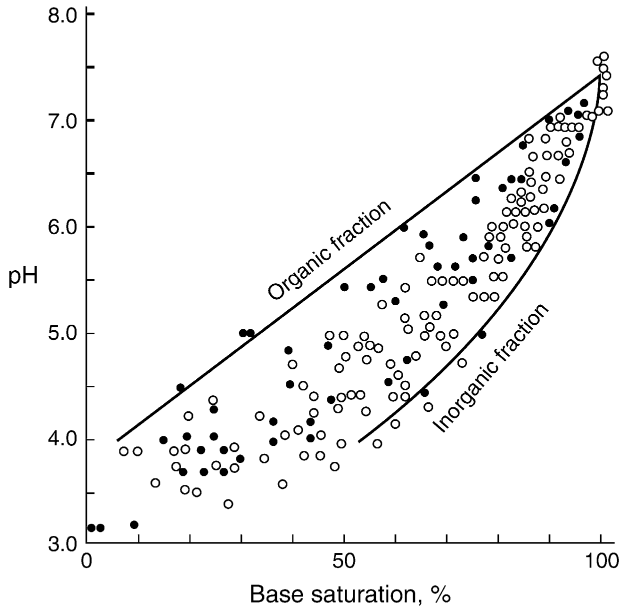


Figure B3 Relationships between soil pH (measured in 0.1 M KCl suspension) and degree of base saturation of some German soils, showing differing effects of organic and inorganic exchange sites (from Schachtschabel and Renger, 1966). Marsh soils $\not\subset$ parabrown earths.

A number of workers have sought such a relationship, but all have found that for different soils there is no simple direct relationship, although soils with more organic matter generally give higher pH values at a given saturation (based on CEC at pH 7) than similar soils with less organic matter. This is illustrated in Figure B3 by statistical regression lines for the contributions of the inorganic and organic fractions of some German soils.

Good regression lines for pH against base saturation were obtained by Blosser and Jenny (1971) when they separated soils from the same parent material according to vegetational type (considered to be a function of climate) and according to A and B horizons (reflecting differences in organic matter content). Limiting the study to the permanent charge components of CEC and expressing base saturation in terms of the balance between exchangeable calcium and aluminum, still gave considerable variation in the relationship with pH for contrasting soils (Turner and Clark, 1966; Bache, 1974).

Early workers in this field (Pierre and Scarseth, 1931) considered that differences between soils in this relationship originated in the amount and nature of the soil colloids and in the strength of the soil acids. These factors are expressed in modern terminology by the amounts and the dissociation constants of the humus acids, the amounts of clay, and the differences between different clay minerals in their selectivity coefficients for exchange of the cations H_3O^+, Al^{3+} and $(Ca, Mg)^{2+}$.

Base saturation and soil formation

Soil formation in a leaching environment is accompanied by a gradual loss of base cations, especially Ca^{2+}, from the cation-exchange complex. The soils thus become progressively unsaturated and increasingly acid. The hydrogen ions in solution, which cause this, originate either from the solubility of carbon dioxide:

$$2H_2O + CO_2 \rightarrow HCO_3^- + H_3O^+ \tag{5}$$

or from soluble acids that form during the decomposition of humus in the surface horizons of the soil. Soluble acids are particularly important where the vegetation is coniferous forest, and these acids may remove Ca^{2+} by the formation of chelate complexes as well as by hydrogen-ion exchange.

Cations are lost initially from the pH-dependent exchange sites, which acquire protons, the reverse of the reactions described previously:

$$(R\text{–}O)_2Ca + 2H_3O^+ \rightarrow 2ROH + Ca^{2+} + 2H_2O \tag{6}$$

As the pH drops below 5.2, in the more advanced stages of development, Al^{3+} ions begin to be released from the surfaces of soil minerals and are strongly adsorbed onto the exchange sites, displacing more Ca^{2+} into solution. The cations in solution are removed from the soil by leaching, either as bicarbonate or as organic-acid salts.

There appear to be few studies that relate modern concepts of base unsaturation to soil genesis and systematics, although Turner and Clark (1966) have done so for the Podzolic and Brunisolic orders of the Canadian soil-classification system. Degree of base saturation, based on CEC determined by ammonium acetate at pH 7, is used in modern classification systems to distinguish between mollic and umbric epipedons, and between eutric and dystric B horizons; in each case the second member of these taxonomic terms has less than 50% base saturation.

Bryon W. Bache

Bibliography

Bache, B.W., 1974. Soluble aluminium and calcium-aluminium exchange in relation to the pH of acid soils. *J. Soil Sci.*, **25**: 320–332.

Blosser, D.L., and Jenny, H., 1971. Correlations of soil pH and per cent base saturation as influenced by soil forming factors. *Soil Sci. Soc. Am. Proc.*, **35**: 1017–1018.

Bradfield, R., and Allison, W.H., 1933. Criteria of base saturation in soils. *Int. Soc. Soil. Sci. Trans. Commun.*, **II**(A): 63–79.

Chapman, H.D., 1965. Cation-exchange capacity. In Black, C.A., ed., *Methods of Soil Analysis,* Vol. 2. Madison, WI: American Society of Agronomy, pp. 891–901.

Coleman, N.T., and Thomas, G.W., 1967. The basic chemistry of soil acidity. In Pearson, R.W., and Adams, F., eds., *Soil Acidity and Liming.* Madison, WI: American Society of Agronomy, pp. 1–41 (additional bibliographic references may be found in this article).

Hissink, D.J., 1925. Base exchange in soils. *Faraday Soc. Trans.*, **20**: 551–556.

Peech, M., 1965. Exchange acidity. In Black, C.A., ed., *Methods of Soil Analysis*, Vol. 2. Madison, WI: American Society of Agronomy, pp. 905–913.

Pierre, W.H., and Scarseth, G.D., 1931. Determination of the percentage base saturation of soils and its value in different soils at definite pH values. *Soil Sci.*, **31**: 99–114.

Schachtschabel, P., and Renger, M., 1966. Beziehung zwischen V- und pH-Wert von Böden. *Z. Pfl. Dung. Bodenk.*, **112**: 238–248.

Turner, R.C., and Clark, J.S., 1966. Lime potential in acid clay and soil suspensions, *Int. Soc. Soil Sci. (Aberdeen) Trans. Commun.*, **II&IV**: 207–215.

Cross-references

Acidity
Buffers, Buffering
Chemical Composition
Exchange Phenomena
Leaching

BASEMENT

That part of the continental crust that has been anorogenic (i.e., not involved in mountain building activities, and therefore considered to be stable over the long term) since at least the early Paleozoic. Basement rocks are exposed as shields or cratons on all continents. Granitoid rocks dominate cratonic regions (e.g. Card and Poulsen, 1998) and constitute the parent materials of many of the acid soils worldwide, both on the deeply weathered basements of Africa, Australia and South America (e.g. ferrallitic soils), or on the young, granite-derived glacial deposits of the shield areas of the northern hemisphere (e.g. podzolic soils).

Bibliography

Card, K.D., Poulsen, K.H., 1998. Geology and mineral deposits of the Superior province of the Canadian shield. In Lucas, S., co-ord., *Geology of the Precambrian Superior and Grenville Provinces and Precambrian fossils in North America*, Vol. C-1. Geological Society of America, The Geology of North America, pp. 15–204.

BASIC

See *Acids, Alkalis, Bases and pH*.

BASIN

In geomorphology, a depression in a landscape, into which water drains from the surrounding higher ground. If the basin has an outlet it is said to be an open basin, otherwise it is considered closed. The geological usage relates to a circumscribed tectonic structure filled with sedimentary strata all of which dip towards the center of the structure. In hot, humid climates, upslope soils tend to have a clay mineralogy dominated by 1:1 clays or gibbsite, with smectite-bearing soils common downslope in basins or other depressions (Birkeland, 1999, p. 241).

Bibliography

Birkeland, P.W., 1999. Soils and Geomorphology, 3rd edn. New York: Oxford University Press, 430 pp.

BEACH

The shore of a sea, lake or large river, commonly covered by a deposit of sand or gravel. Arenosols commonly develop on old beaches.

Cross-reference

Soils of the Coastal Zone

BED

In geology, a coherent layer or stratum in a stratigraphical sequence of sedimentary rocks. In soil science a visually distinct layer of volcanic ash or windblown sand for example, within a profile. Tephra layers are particularly valuable in dating the soils of volcanic regions (Newton, 1996).

Bibliography

Newton, A.J., 1996. Tephrabase. a tephrochronological database. *Quatern. Newslett.*, **78**: 8–13.

Cross-reference

Andosols

BEDROCK

A rock body underlying a soil and its parent material. It may or may not be genetically related to the soil.

Cross-reference

Saprolite, Regolith and Soil

BENCH

A landscape feature representing a break in slope, where the inclination of the slope becomes quasi-horizontal.

BERM

In geology a remnant surface that predates the erosional episode which removed the rest of the surface. In engineering an artificial ridge or elongated mound of earth materials, including soil, constructed to enclose, completely or partially, a given area for erosion control, privacy or some other purpose.

BIODEGRADATION

The breakdown of a substance or material by the action of living organisms. The use of such organisms (especially bacteria and other microbial species) for that purpose. See *Bioremediation*.

BIODIVERSITY

A term in ecology to represent the total number of extant species in an ecosystem.

BIOGEOCHEMICAL CYCLES

A biogeochemical cycle describes the transfers of materials between an interconnected series of reservoirs, in and on the earth, and from scales ranging from the planet as a whole, to smaller units such as the soil. The soil itself is a critical component of all higher scale biogeochemical cycles, not only in the obvious case on land, but also as an important stage in the sedimentary cycle, to the marine environment.

The context

The idea of cyclical processes pre-dates science, and is found in Hindu, Buddhist and other ancient cosmogonies. In addition, the circle was considered to be an ideal form by Plato and a cyclic view of history appears in Book 8 of the *Republic*. During the Renaissance, the notion of cyclical history was developed by Vico, though in the history of science, the significant development was the Copernican model for the Solar System, which was confirmed and modified by Galileo and Keppler, and triumphantly explained by the celestial mechanics of Isaac Newton in the 17th century.

In the context of Earth science, the idea of cyclical processes is as old as scientific geology itself, with the publication of the *Theory of the Earth* by James Hutton in 1796. In effect, his idea of a continuous alternation of destructive and constructive events in Earth history is a perpetual motion machine that leads to the Rock Cycle (Figure B4).

The perpetual motion aspect of the idea ("no vestige of a beginning, no prospect of an end" in Hutton's words) did not survive the rise of thermodynamics, so that nowadays it is universally recognized that the cycles are not true cycles but have in fact evolved throughout geological time. For the much shorter time scale of the pedologist, this aspect of secular evolution may be ignored in general, though an important qualification to this last statement is that since the Industrial Revolution began some 250 years ago, anthropogenic effects have caused important modifications to take place in natural cycles.

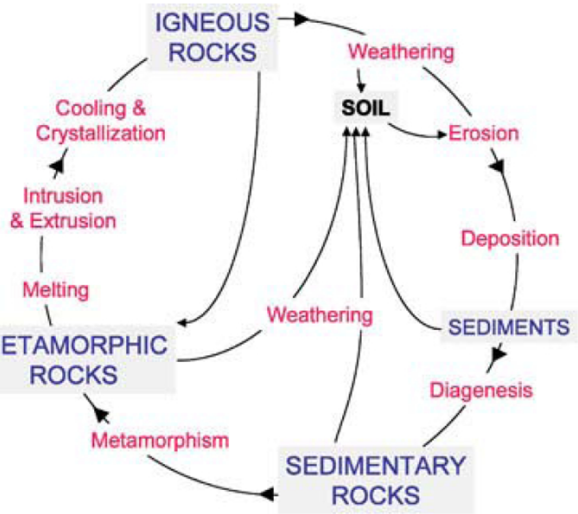


Figure B4 The rock cycle – a modern representation derived from James Hutton's 18th century classic of geology *Theory of the Earth*.

In detail, the rock cycle is made up of two divisions: an internal or endogenic cycle is distinguished from an external or exogenic cycle. Energy for the endogenic cycle comes from nuclear fission within the body of the Earth, and for the exogenic cycle, from the sun. Neither cycle is closed, though it is common to assume at least a high degree of closure, in determining mass balances within the external cycle. Interchange between the two cycles is brought about principally by the processes of plate tectonics (Figure B5).

The Exogenic Cycle contains within it, a series of nested material cycles, the most important of which in the present context is the Water Cycle (Figure B6). Water is the principal agent of transport of particulate and dissolved matter over the Earth's surface, and is the major influence in the differentiation and evolution of soils. As an absolute prerequisite to the maintenance of the biosphere, it is a ubiquitous component in all biogeochemical cycles.

Biogeochemical cycles and soil

Within, the closed (or quasi-closed) global cycles referred to above, the soil compartment is a completely open system in the thermodynamic sense of actively exchanging both energy and matter with its surroundings (i.e., the rest of the exogenic cycle). Figure B7 provides an example of the dynamics of carbon within the soil compartment of the global cycle of that element.

Two classic views that explicitly incorporate soil into the picture are shown in Figure B7 and B8.

Soil constitutes a reservoir of energy (in the form of organic matter), of water and nutrient elements, and of a microbial biomass that acts as the necessary intermediary in the redistribution of energy and materials throughout the terrestrial biosphere (Figure B9). As the focus of such redistributions, the soil is a choke point on the land surface where the terrestrial biosphere is particularly vulnerable to natural and anthropogenic change (Figure B10 and B11).

The global cycles of biologically active elements are fundamental to any consideration of biogeochemistry in Earth surface science, and are crucial in maintaining the integrity of the biosphere. For details of individual cycles see the articles *Hydrologic Cycle*, *Carbon Cycle*, *Nitrogen Cycle*, *Potassium Cycle*, and *Phosphorus Cycle*. Other examples appear in the companion volume in the Encyclopedia of Earth Sciences Series: the Encyclopedia of Geochemistry.

Ward Chesworth

Bibliography

Bashkin, V.N., 2002. Modern Biogeochemistry. London. Kluwer, 561 pp.
Chesworth, W., 2006. In: Lavigne, D.M., eds., Fink, S., associate ed., *Gaining Ground: in Pursuit of Ecological Sustainability,* Chap. 3. Guelph, ON: International Fund for Animal Welfare, pp. 31–42.
Garrels, R.M., Mackenzie, F.T., and Hunt, C., 1973. *Chemical Cycles and the Global Environment.* Los Altos, CA: Kaufman, Inc., 206 pp.
LaRoe, E.T., Farris, G.S., Puckett, C.E., Doran, and P.D., Mac, M.J., eds. 1995. *Our Living Resources: A Report to the Nation on the Distribution, Abundance, and Health of U.S. Plants, Animals, and Ecosystems.* Washington, DC., U.S. Department of the Interior, National Biological Service, 530 pp.
Martini, I.P., and Chesworth. W., 1992. *Weathering, Soils and Paleosols.* Amsterdam: Elsevier, 618 Pp.
Perel'man, A.I., 1967. *Geochemistry of Epigenesist.* N.N. Kohanowski (trans. from Russian with a foreword by Fairbridge, R.W. New York: Plenum Press, 266 pp.
Reeburgh, W.S., 1997. Figures summarizing the global cycles of biogeochemically important elements. *Bull. Ecol. Soc. Am.*, **78**(4): 260–267.

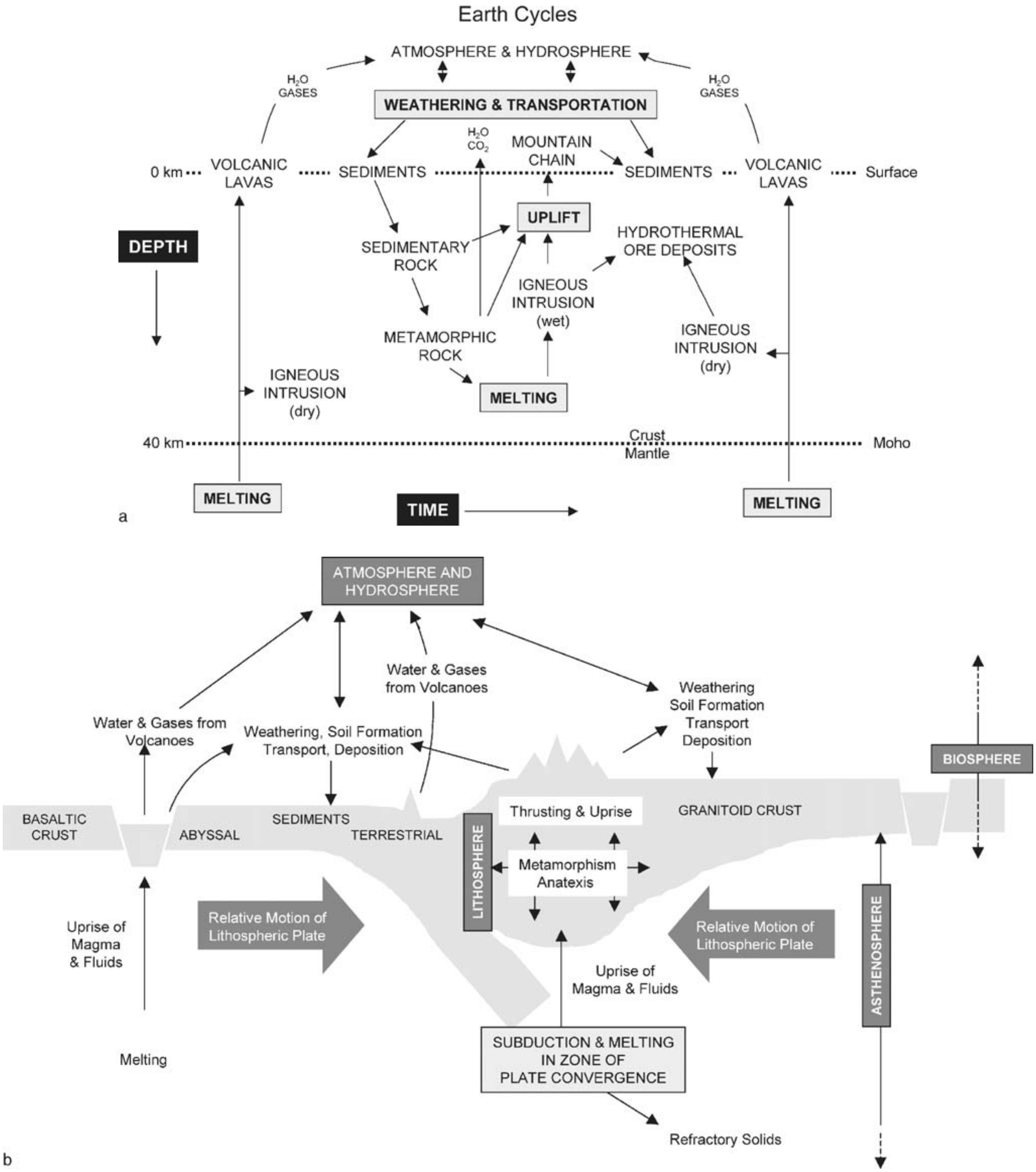


Figure B5 **(a)** Wyllie's (1971) representation of the rock (or geologic) cycle, the earliest to incorporate (implicitly) plate tectonic ideas. (**b**) A version in which the plate tectonic connection between endogenic and exogenic cycles is explicit. The plate tectonic mechanism connects the two major cycles by means of a conveyer system between constructive plate boundaries (oceanic rift systems) and destructive ones (subduction zones) connect these two major cycles – a distant echo of Hutton's theory of alternating destructive and constructive events.

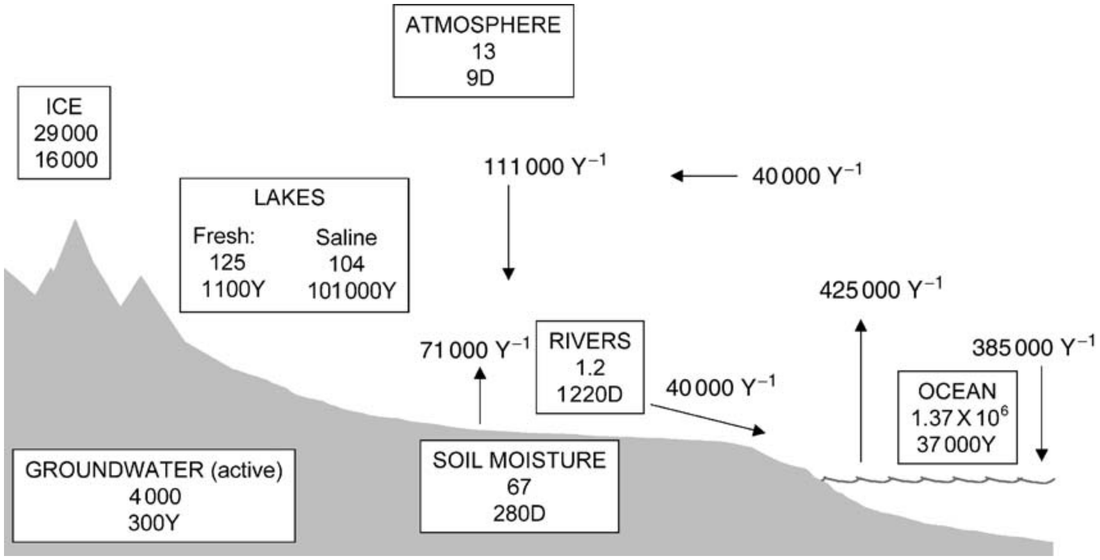


Figure B6 The water cycle. Major reservoirs are shown as boxes, with water content given in units of 10^3 km^3 and turnover times in years (Y) or days (D). Fluxes are given in km^3 yr^{-1}. The ocean reservoir makes up approximately 98% of the total mass of water, with soil water a mere 0.005%. Adapted from Reeburgh (1997).

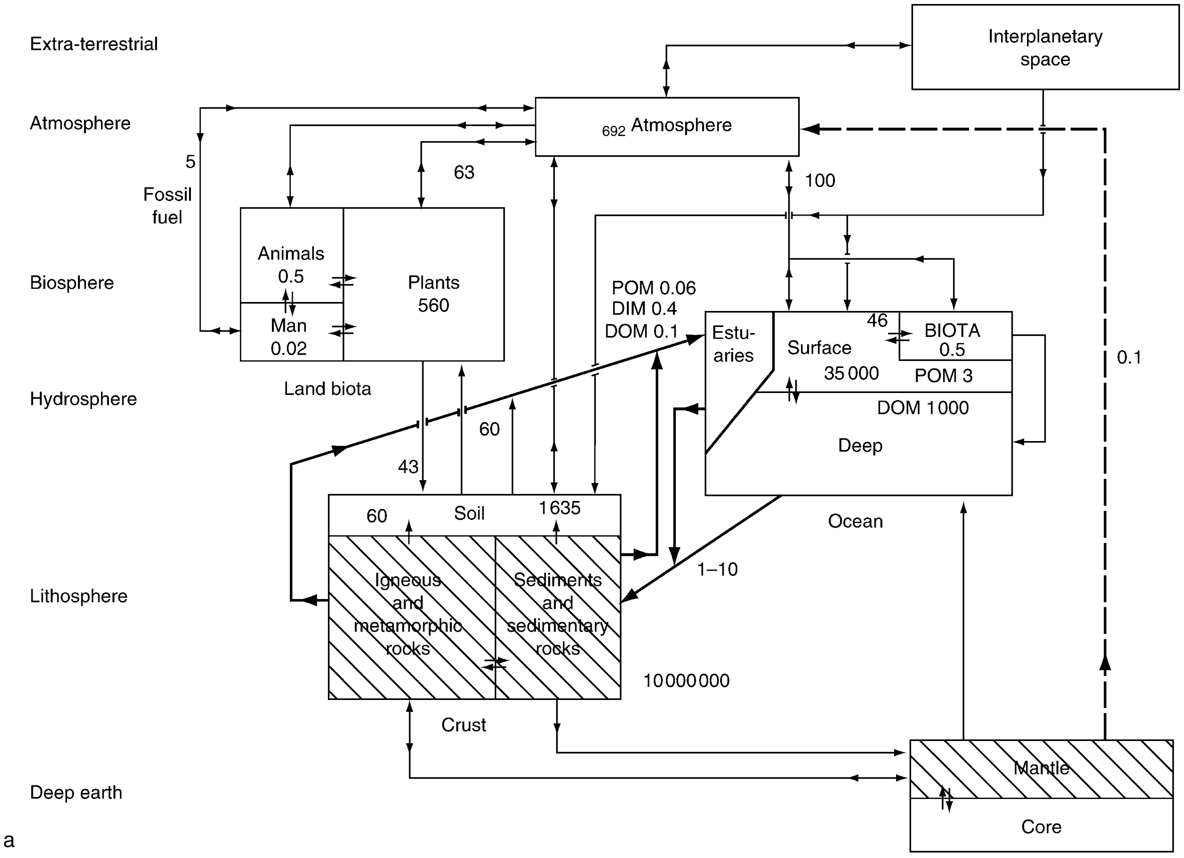


Figure B7 **(a)** The carbon cycle with reservoirs in boxes (billions tonnes) and fluxes and exchanges as arrows (billions tonnes per year). From Speidel and Agnew, 1982).

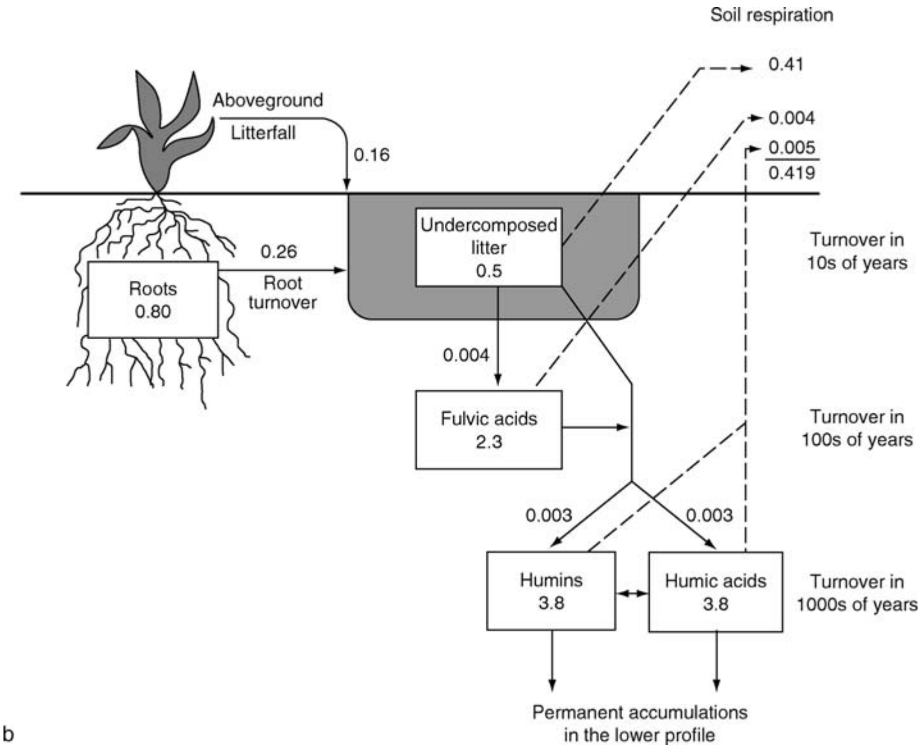


Figure B7 **(b)** Detrital C-dynamics in the upper 20 cm of a Chernozem. Carbon in reservoirs expressed as kg C m^{-2}, annual fluxes as kg C m^{-2} yr^{-1}. Total content of C down to 20 cm is 10.4 kg m^{-2}. (From Schlesinger, 1997).

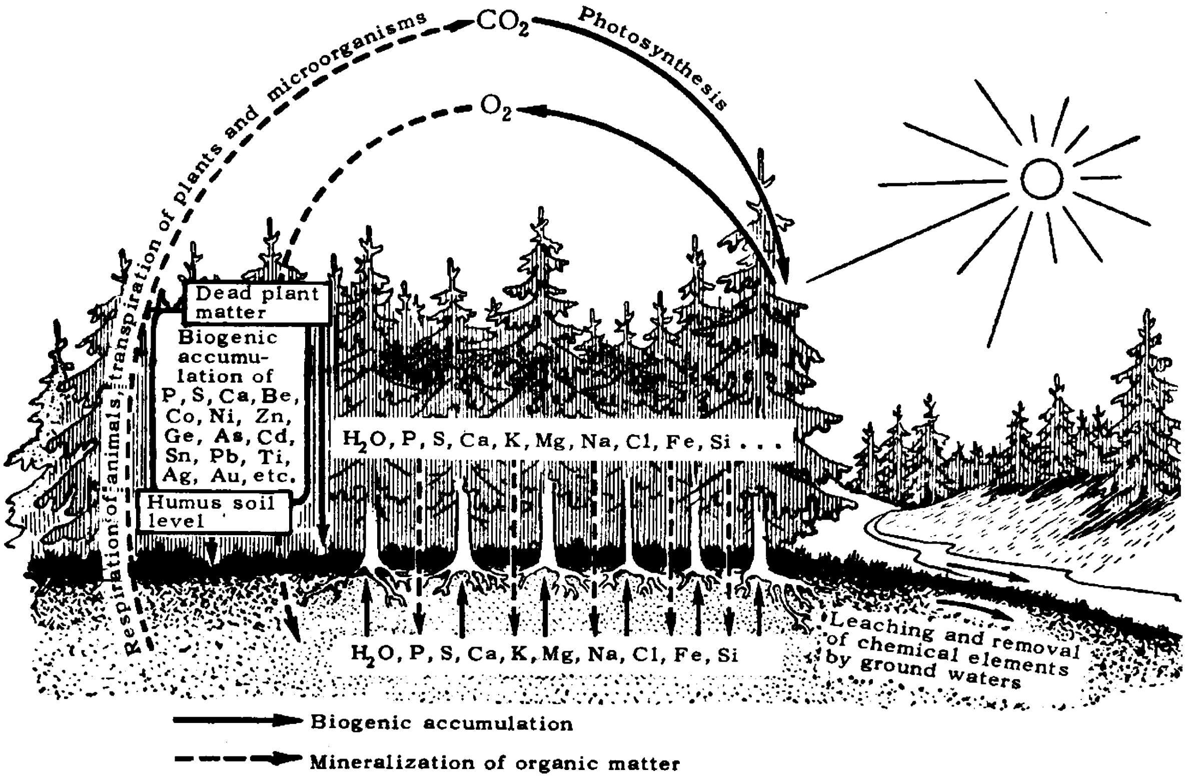


Figure B8 Qualitative view of the biogeochemical cycling of elements on taiga-like landscape. Perel'man (1967). Following Vernadskii in the 1920s a Soviet school of landscape geochemistry developed with Perel'man as one of the main contributors.

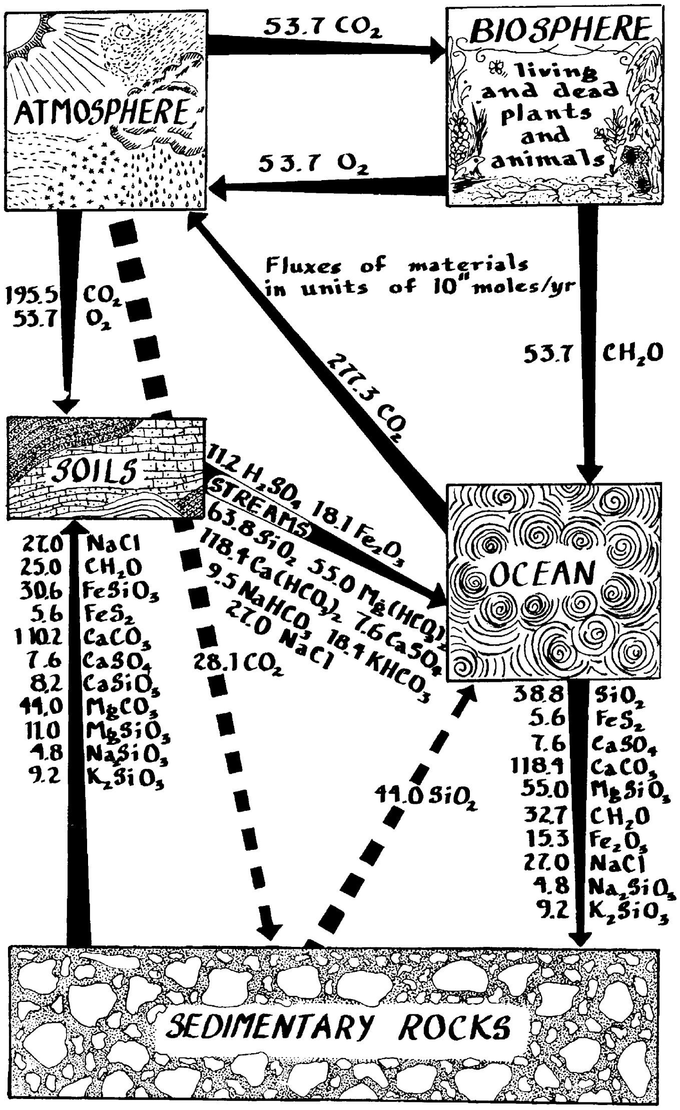


Figure B9 A pioneering attempt to balance the major chemical components circulating at the surface of the Earth. This classic work of Garrels et al. (1975) was developed as a means of assessing the human impact on the natural cycles.

Schlesinger, W.H., 1997. *Biogeochemistry: An Analysis of Global Change*, 2nd edn. San Diego, CA: Academic Press, 588 pp.

Speidel, D.H., and Agnew, A.F., 1982. *The natural geochemistry of Our Environment.* Coulder, CO: Westview Press, 214 pp.

Walker, B., Steefen, W., Canadell, J., and Ingram, J. 1999. *The terrestrial Biosphere and Global Change.* The natural geochemistry of Our Environment. Cambridge, MA: Cambridge University Press, 439 pp.

Cross-references

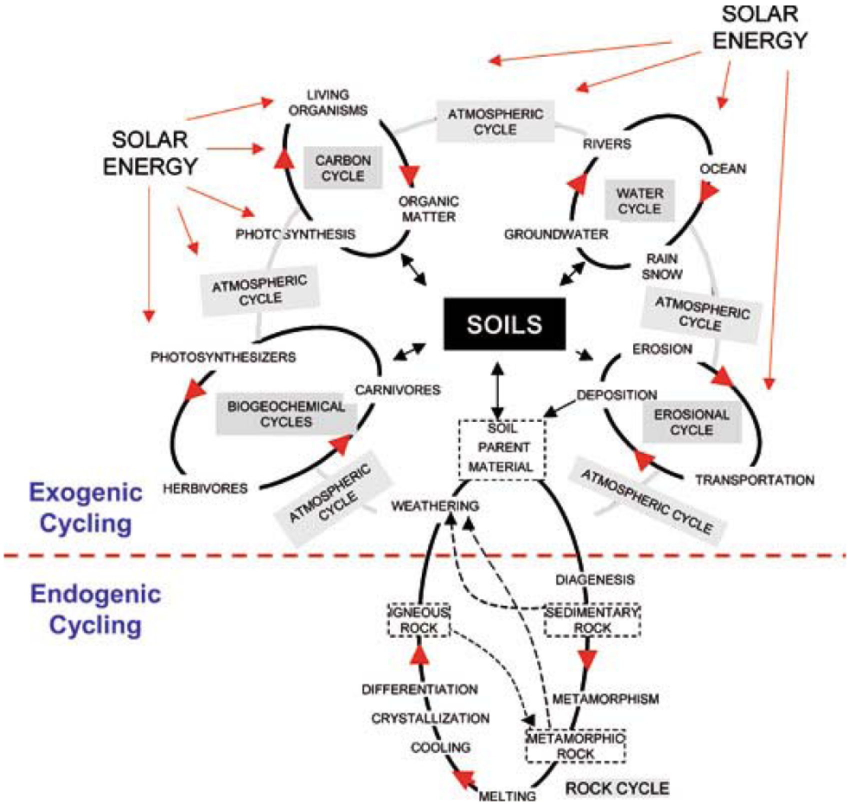
Carbon Cycling and Formation of Soil Organic Matter
Computer Modeling
Earth Cycles
Field Water Cycle
Nitrogen Cycle
Phosphorus Cycle
Potassium Cycle
Soil Microbiology
Sulfur Transformations and Fluxes

BIOMASS

The total weight of organisms living in all or part of an ecosystem. The standing biomass is that part of the total which is represented by above ground vegetation that is rooted in the soil.

BIOME

A community of plants and animals living together in one or other of the major types of habitat found on Earth, such as the temperate grassland, tropical forest, or freshwater habitats.



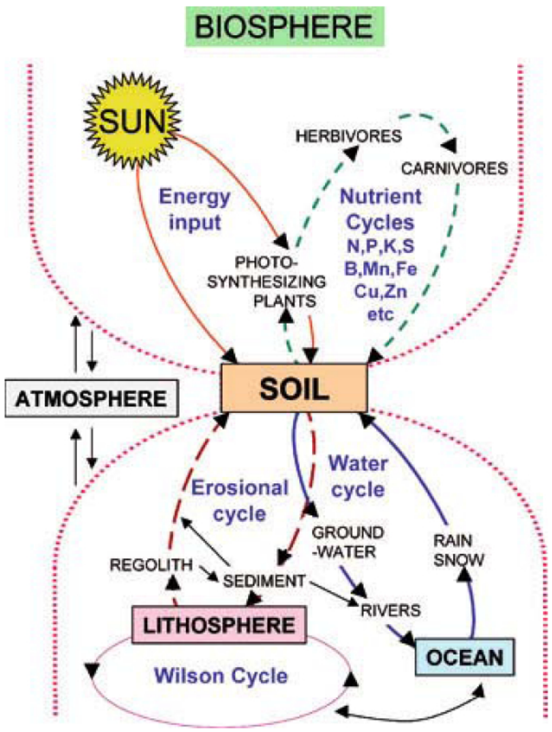


Figure B11 The hourglass paradigm: soil as a vulnerable choke point in the distribution of energy and material (Chesworth, 2006).

Specific soil types or associations develop and characterize terrestrial biomes (see Figure B12). The temperate grassland biome for example, tends to be dominated by chernozemic, kastanozemic and phaeozemic soils.

BIOMES AND THEIR SOILS

The word biome was first used by Clements in 1916 (Carpenter, 1939), and is currently used to mean a community of organisms living together and essentially typical of a particular climatic region on land or sea. Specific soil types or associations develop in, and are characteristic of, the terrestrial biomes. In Figure B13 these are classed into the following groups: Tundra, Forest, Grassland, Mediterranean, and Desert biomes. Table B1 provides a summary of salient characteristics. For an excellent recent treatment see Woodward (2003). The principal sources used here for information on soils of the major biomes are FAO (2001) and Zech and Hintermaier-Erhard (2007).

Soil formation has a long history (Retallack, 2000) and as biomes have evolved so has the soil. Microbial organisms were probably the first to colonize the land surface during the Precambrian, but it was not until the Silurian period that plants and arthropods began to occupy the land and modify the weathering surface into soils similar in a general way to modern soils. Modern soils are not notably affected by this distant history, but an outline of the abiotic and biotic changes in the

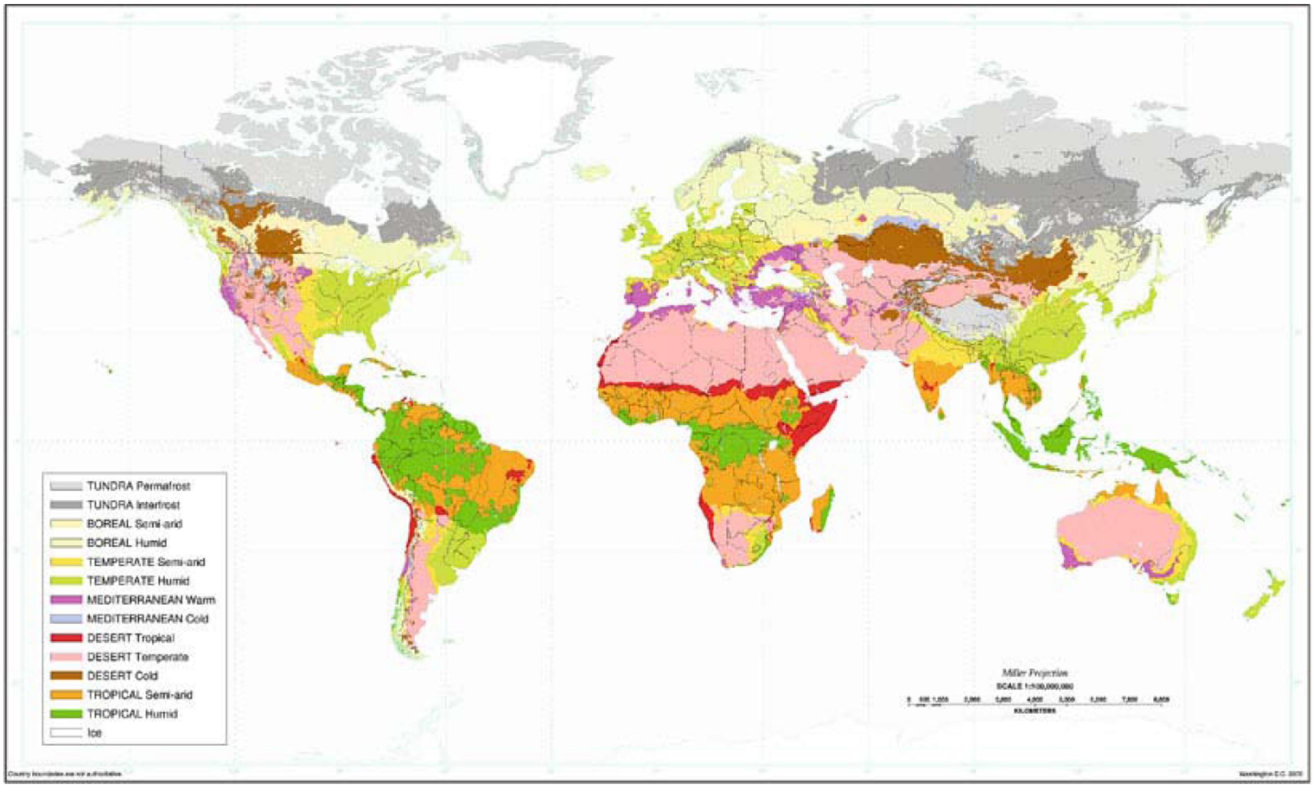


Figure B12 Major biomes. Courtesy USDA-NRCS, Soil Survey Division.

soil-forming environment over the last 30 million years is germane (Figure B14). During that time, major changes of significance to the diversity of soils have been the rise and decline of the Pleistocene glaciations, and the expansion of open, grassland habitats at the expense of continuous canopy forest. During the last 10 000 to 12 000 years, human activities have become paramount in modifying the soils in biomes amenable to the practice of agriculture. The clearance of forest in particular, has had a major effect not only on the modification of soil, but by releasing stored CO_2 into the atmosphere has also been a significant driver of global warming (Ruddiman, 2005).

Physical weathering is an important soil forming and soil modifying process in all biomes. In the more humid ones, hydrolysis is the important process of chemical weathering in soil genesis. In soils of the desert and tundra biomes, hydrolysis is much subdued and physical processes predominate.

Tundra biomes

Tundra is a Sami word used originally to mean the cold, treeless plain bordering the Arctic Ocean in Lapland. The Tundra biome stretches over a vast circum polar belt across northern Eurasia and North America (Arctic tundra), and a counterpart occurs as the highest and coldest zone of young fold mountains (Alpine tundra).

Arctic tundra

Arctic tundra stretches from the Arctic Ocean down to the Taiga zone. It is the coldest of the biomes (with a winter temperature of minus 35 °C or lower) and has the shortest growing season (50 to 60 days). Summer temperatures in the daytime may get into the 30s. Annual precipitation, mostly as snow, is low – typically less than the equivalent of 300 mm of rain. In the Köppen system of climate classification climate types are mostly ET, Dfc and Dfd.

About 5 million square kilometers of the Arctic tundra is polar desert with an annual precipitation of 250 mm or less and a mean summer temperature below 10 °C. Topographic relief is generally low, with bedrock and gravel plains as common landforms. Patterned ground is characteristic, and results from cryogenic processes caused by alternate freezing and thawing.

Biodiversity is low and population fluctuations are high. Mosses, lichens, sedges and grass species, with low, wind-adapted shrubs are typical. A varied fauna is supported e.g., polar bears, caribou, wolves, foxes, hares, migratory birds, a large number of insects, as well as salmon, trout, char and other fish species.

The Arctic tundra occupies a region of the globe that was glaciated during the Pleistocene. Consequently the parent materials available for soil are those that are typical of glaciated terrain: bare rock surfaces, and the materials of moraines, kames, eskers and drumlins, together with various outwash and wind-borne sediments derived from them. Till, gravel and sand are common. Because of low temperatures, chemical weathering is minimized in the Tundra biome, a fact displayed on old rock surfaces that still appear fresh with virtually unweathered striae, chatter marks and other stigmata of the ice that disappeared 10 000 or more years ago. The dominant soil-forming

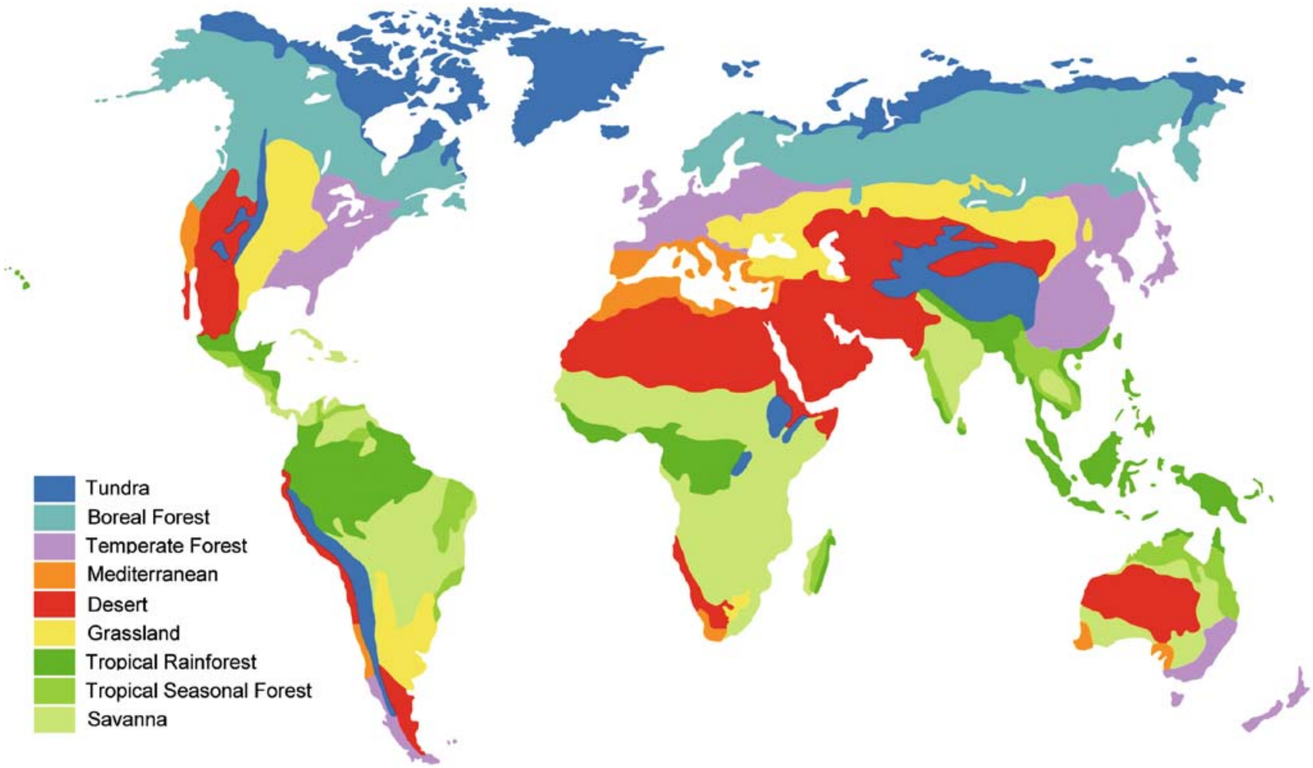


Figure B13 Major biomes of the world. From Daniels, L.D. (ed.) 2007. Explore the World's Biomes. Department of Geography, University of British Columbia, Vancouver BC. Accessed at http://www.geog.ubc.ca/~biomes. The original terminology has been slightly modified to be consistent with the text of the present article.

Table B1 Summary of the characteristics of the major biomes

Biome	Climate	Region	Vegetation
Forest	A, C, D		
tropical	Af, Am	Amazon, Congo, Indonesia, Malasia.	Evergreen rainforest, Deciduous in monsoonal regions.
temperate	Cfa, Dfa, (& Cfb in Europe)	Western Europe, Northeast & Northwest North America, Northern China, Korea, Japan.	Deciduous broadleaf forest.
boreal (taiga)	Df	Northern Canada, Scandinavia & Russia, Alaska.	Pine, Fir, Spruce
Grassland	A, B		
tropical (savannas)	Aw	East Africa, Sahel, Southern Brazil, Northeast Australia.	Isolated trees and bush in open grassland.
temperate	BSk, BSh	Midwest North America, Central Asia, Argentina.	Long and short grass prairies and steppes
Desert	B		
hot	BWh	Sahara, Namibia, Kalahari, Arabia, Southwest USA, Central Australia.	Negligible vegetation.
dry	BWk	Gobi, Central Asia, Southern Patagonia.	Xerophytic and halophytic vegetation.
Mediterranean	Csa, Csb, Cfb	Mediterranean, California, Iran, Southwest & South Australia, Cape region of South Africa, Central Chile.	Bushland
Tundra	E, ET		
polar		Northernmost North America, Europe and Asia; ice-free Antarctica.	Mosses, Lichens, Bush to the south.
alpine		American cordilleras, Alpine-Himmalayan fold belt	Similar with Bush downhill.

processes are physical. Typical are cryogenic processes, driven by soil water as it migrates towards the frozen front from warmer parts of the soil. These processes include freeze-thaw, cryoturbation, frost heave, cryogenic sorting, thermal cracking and ice segregation. Where the cryogenic activity has been weak, or has persisted for only a short time, gelic Leptosols and Regosols are found, but the defining soil of the tundra produced by these processes is the Cryosol. Diagnostic for the

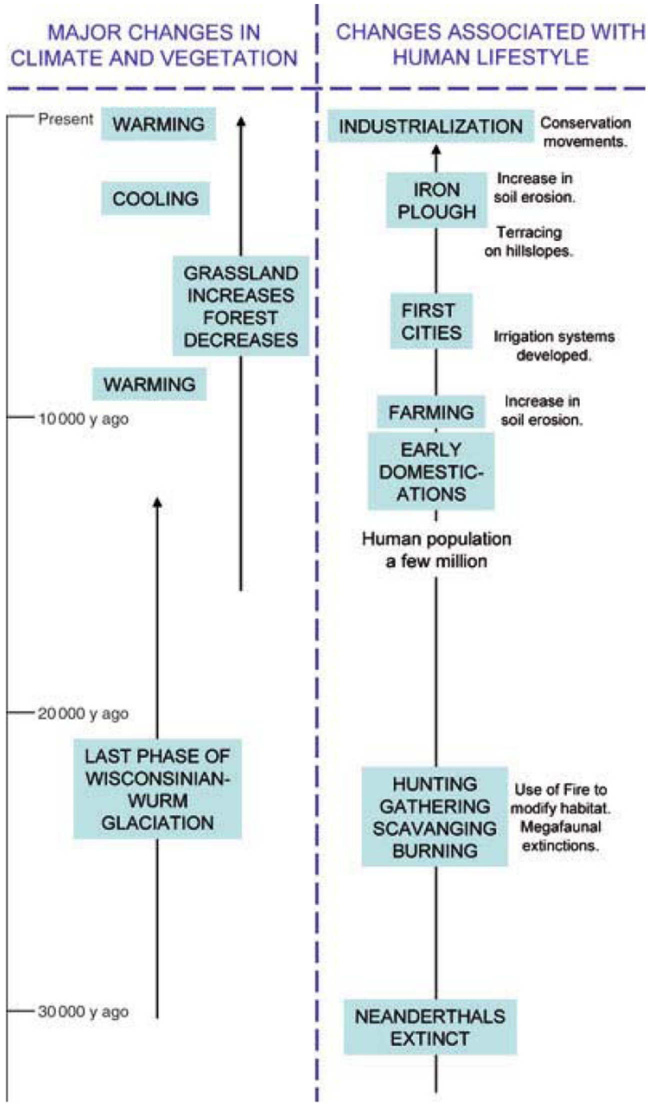


Figure B14 The historical and pre-historical context. Global change over the last 30 million years (adapted from Behrensmeyer et al., 1992).

Cryosol is a perennially frozen cryic horizon, which shows evidence of cracking, heaving and sorting, and has a characteristic platy and blocky texture.

Root systems in Cryosols are relatively shallow, since at depth, there is a perennially frozen layer of subsoil called permafrost, consisting mostly of badly sorted gravel and finer material. As a consequence drainage is poor with water saturation leading to the formation of Gleysols. Peat also accumulates in this environment so that Histosols are common.

The generally poor fertility of Tundra soil resides principally in the slowly decaying organic matter, with augmentation of N by biological fixation, P from particulates and K from aerosols in atmospheric precipitation.

Solifluxion is common in summer, when temperatures exceed the freezing point, and drier soils are subject to erosion by the sweeping winds that prevail in the arctic environment. Blowouts provide dramatic evidence for this in sandy soils.

Alpine tundra

Alpine tundra in effect is the Arctic tundra in microcosm. It is found above the tree line in the Mesozoic–Cenozoic mountain belts of the world, such as the Alps, Himalayas and Pyrenees of the Old World, and the Western Cordilleras of the New. The climate is generally not as extreme as the Arctic, and the growing season may be 100 days or more. Similar plants to the Arctic tundra are found in this biome, and the range of fauna includes mountain goats and sheep, bears (rare in Eurasia), grouse, partridge and insects.

Because of the prevalence of steep slopes and unstable surfaces, soils tend to be young (Leptosols, Regosols) or nonexistent. At the foot of slopes colluvium collects and is a common parent material of more developed mineral soils, including Cryosols. Where rainfall is particularly high and drainage restricted, Histosols are found, but unlike those of the Arctic tundra, Histosols of the Alpine variety tend to be well drained.

Forest biomes

There are three major types of forest biome: tropical, temperate and boreal.

Tropical forest

Tropical forests by the strictest definition occur within the area bounded by the tropics of Cancer and Capricorn at approximately 2 degrees 27 minutes north and south of the equator respectively. However, climatic regimes are no respecters of abstract lines on a map, so the tropical forest may extend into the subtropics. In Köppen's classification climate is of Af and Am types. Characteristically, average temperature ranges between 20 to 25 °C, with little variation month to month. Annual rainfall lies between 2 000 to 10 000 mm and is evenly distributed throughout the year in the typical tropical rainforest, though areas of seasonality of rainfall occur. Based on this seasonality and the increasing length of the dry period, the following subdivisions of tropical forest are recognized: *(a)* Evergreen rainforest: no dry season. *(b)* Seasonal rainforest: short dry period. *(c)* Semievergreen forest: longer dry season. *(d)* Moist/dry deciduous forest (monsoon). In Figure B13, this is simplified to tropical rainforest and tropical seasonal forest.

The forest has a highly diverse flora arranged ideally into three layers: an overstory of the largest trees, growing to heights of 75 m or more, accompanied by woody vines. An understory of immature trees and smaller tree species, epiphytes, vines and ferns, tolerant of lower light intensities, grow to heights between about 2 to 20 m. The third layer, the forest floor, is covered by fallen leaves, branches and trunks, with sparse living vegetation on account of the diminished intensity of light at this level. Fungi and microbial organisms however, are hyperactive agents of decay of the forest debris and litter, and help in the rapid and efficient recycling of plant nutrients that is a feature of tropical rainforest ecology.

There is a diverse fauna of mammals, reptiles, amphibians and birds, all commonly adapted to arboreal life. Raptors are the predominant predators of the upper story.

Being hot and wet, this is an environment where weathering is relatively rapid and leaching is intense. The resulting soils are typically ferrallitic (for example Ferralsols, Alisols and Plinthosols), with the bright red, orange or yellow colors characteristic of oxidized Fe. They are also nutrient-poor and acidic.

Accumulation of Fe and Al in the weathering zone (at the expense of Si) leads ultimately to the production of laterites and bauxites in this biome.

Soils and deposits of this type require long term weathering on very stable surfaces, for example those provided by the ancient granite–greenstone belts of the Precambrian Shield of Gondwana in South America, Australia and India. The greenstone belts (typically metamorphosed basalts) give rise to more fertile soils (Cambisols for example) than the granites.

The two largest areas of surviving rainforest are also the locations of two of the world's greatest river systems, namely the Amazon and the Congo. The river valleys are floored by alluvium predominantly of silt and clay sized particles. Consequently, Fluvisols, Vertisols and Gleysols are common in this environment.

The most fertile soils are found where recent volcanoes occur, for example in central Africa, Indonesia and the Philippines. Here is where Andosols develop, especially on glassy pyroclastic deposits. The most productive farmland in East Africa is found on the Andosols developed on volcanic ash associated with volcanic regions such as the Rungwe highlands of southern Tanzania, a massif that was originally an area formerly of tropical forest.

The area of rainforest in the world has steadily diminished throughout the late Cenozoic, a trend that has increased in the last 10 000 years with the clearance of forest for agriculture. It is estimated that more than half of the pre-farming, tropical forests have now been destroyed (Behrensmeyer et al., 1992).

Temperate forest

The Temperate Forest covers zones either side of the tropics where the climate is classified as Dfa, Cfa, and (in Europe, Cfb) in the Köppen system. Temperature varies between –30 and 30 °C, and precipitation amounts to 750 to 1500 mm. In general, rainfall is evenly distributed throughout the year, though some seasonality occurs.

In the northern hemisphere there are three major distributions of temperate forest: western and central Europe; eastern Asia; and eastern North America. Many genera are common to all three and were inherited from the circum polar flora of the Tertiary. The characteristic trees are broad leaved deciduous (for example species of oak, maple, beach, chestnut and elm) with an approximately six month growing season. Leaves are shed completely in the autumn as the trees enter a period of dormancy. In the southern hemisphere the analogous zone contains vegetation developed from the relict Gondwanaland flora. A needleleaf-broad leaf evergreen forest is characteristic.

In the northern hemisphere especially, the major areas of temperate forest are in regions profoundly affected by glaciation during the Pleistocene epoch. As a result, parent materials are commonly ice-contact deposits, or deposits arising during the process of deglaciation. Of particular importance is the wind-borne loess of Western Europe and northern China, especially in terms of wheat and rice production in current agriculture.

Cambisols and Luvisols are typical soils of the temperate forests of the northern hemisphere in the areas that were notably affected by the Pleistocene glaciations. Because of the glaciations, the soils are relatively young (10 to 20 000 years old). Both Cambisols and Luvisols have formed on the forested loess, and since calcite is usually present in this material, the soils generally have a pH between 7 and 8. The seasonal shedding of leaves provides the basis for a nutrient-rich humus, and results in soils with brown colored A and B horizons. Part of the temperate forest zone of the south east of the USA (as in Chile in the southern hemisphere), is dominated by Acrisols, with the red and yellow colors that are generally indicative of advanced weathering and long term leaching. This is a region that was not directly affected by the Pleistocene ice sheets, so that there has been a much longer period of pedogenesis here than further north. The resulting soils display a greater similarity to soils of the tropics, especially in terms of the colors imparted by ferric iron, and in the dominance of monosiallitization over bisiallitization.

In mountainous regions such as the western cordilleras of North and South America, temperate rainforest occurs, with precipitation exceeding 2 000 mm per year. Coniferous vegetation is common, and Podzols are the usual accompaniment. Where recent volcanism has produced pyroclastic parent materials, Andosols also occur.

In the old world especially in Europe and China, the temperate forest has been increasingly cleared since Neolithic times, and forest soils have been co-opted for agriculture. In the northeast of North America, the Luvisols were preferred by the early colonial farmers, as being easier to work than other soils of the glacially affected regions.

Boreal forest (or taiga)

The Boreal zone lies to the north of the temperate forest and extends from about 50° to 60° latitude, where it gives way to the tundra. Pleistocene ice affected the whole area, and coniferous forest dominates. This constitutes the largest of the terrestrial biomes, with approximately 500 million ha distributed in northern Canada, Eurasia, and Alaska. Pine, fir, and spruce species are common, and allow little penetration of light so that the understory is usually sparse. Temperature averages 10 °C in the summer and varies between about –40 to 20 °C in the course of a year. There are normally four to six frost-free months and the average growing season is about 130 days. Precipitation lies in the range 300 to 900 mm per year, though in more temperate regions may reach 2 000 mm.

The characteristic soil of the boreal forest is the Podzol, which has formed on various glacial materials but especially on coarse sediments and sands related to the fluvial processes that are important in deglaciation. Of particular importance to the process of podzolization are the organic acids and complexants formed by the microbial breakdown of pine needles. A pH as low as 3.5 is not uncommon in the A horizons of Podzols, and acidities at this level are sufficient to destroy (by hydrolysis) most ferromagnesian minerals present in the parent materials, with cations such as Al and Fe carried down to the B horizon as organo-metallic complexes. In the limit, the result is that a subsurface, bleached Ae horizon is produced overlying a darker Bs horizon where the transported organic material and cations are deposited. In the classic idea of a Podzol, the Ae horizon is composed almost entirely of quartz. In the boreal Podzol, alkali feldspar is an almost invariably accompanying mineral. This is a consequence of two factors. First, the ultimate parent materials of much of the glacially derived parent materials of the soil, are the predominantly quartzo-feldspathic rocks of the craton. Second, the 10 000 years or less during which the boreal Podzols have formed (i.e., the time since the ice sheets melted) is not sufficient to breakdown the alkali feldspars, which, next to quartz, are the most refractory of the felsic minerals during weathering.

Albeluvisols commonly accompany Podzols in the boreal forest, especially where the parent materials are water or wind deposited sands and silts. As the name suggests, Albeluvisols share features with both Podzols and Luvisols. In Western Europe where most Albeluvisols have been taken over for agriculture, they have been converted to Luvisols.

Water saturated regions of the Boreal forest, as is usual in other biomes, have resulted in the formation of Gleysols and Histosols.

The inherent fertility of Boreal forest soils is generally poor. This is because the granitoid materials worked and reworked by glacial, fluvial and aeolian processes to provide soil parent materials, are themselves low in plant nutrients; and even in the case of potassium, a plant nutrient that is a common major element of granites, the host alkali feldspar has not had sufficient weathering time to release the element.

Grassland biomes

Grasses, with large shrubs or trees absent or sparsely distributed, dominate grasslands. After the continental ice sheets withdrew at the end of the Pleistocene the climate became warmer and drier, and the grasslands increased to their present areas, latterly aided by the deforestation accompanying human activities.

The two main types are divided on the basis of climate: *(a)* Tropical grasslands or savannas. *(b)* temperate grasslands.

Tropical grassland (savanna)

Savanna is an open plain of grass, with scattered drought-resistant trees, characteristic of certain tropical and subtropical regions with distinct wet and dry seasons (Trumble et al., 2002). The largest areas of savanna are in Africa south of the Sahara, with significant areas also in Australia, South America, and India. In the Köppen classification of climates, savanna rates as Aw. The temperature range is similar to tropical forest, which gives way to savanna as precipitation falls off and becomes more seasonal. Annual rainfall is approximately 50 to 150 mm per year, though much drier and wetter conditions are known. It is concentrated into a rainy season lasting about half of the year. Grass fires occur during the dry season and are ecologically necessary in maintaining the savanna.

In addition to the savanna controlled by the climatic conditions stated above, some savanna is anthropic. It is produced by forest clearance followed by abandonment as soil fertility is exhausted by cropping.

The common soils of the savanna are highly weathered and leached soils such as Lixisols and Nitisols, with relict quartz as the dominant skeletal phase. Kaolinite and halloysite, goethite, hematite and possibly gibbsite may be present in the clay fraction. Graphite is usually present in A horizons, a legacy of grass fires, both natural and anthropogenic. In poorly drained topographic lows, Vertisols may form, otherwise the soils are usually sandy textured, with a thin Ah, and are well drained. Ferralsols, Arenosols, and Plinthosols are associated. Termitaria are conspicuous elements of the savanna landscape, and as bioturbators, termites are important agents of soil formation.

Where recent volcanic activity is found, the soils may be of high inherent fertility, though drought and high Al may present problems. Otherwise most of the soils of the savanna regions such as the Cerrado of the Brazilian Highlands, are of low fertility and acid reaction and plants adapted to high Al are common. Drought is a particular problem of the sandier soils, for example the pine savannas of Belize and Honduras.

Plinthosols are particularly characteristic of tropical forest. Where the trees have been removed by climate change (as in the Sahel) or by anthropic intervention (as in parts of the Cerrado), the surface soil may be eroded to expose the plinthic layer. Alternate wetting and drying hardens this to produce what was classically called a laterite. Laterite is commonly found as an ironstone cap on tropical landscapes, and is often an indication of an inversion of relief. The original plinthite formed in depressions where water collects, and on hardening became more resistant to erosion than the surrounding higher land. Hence the inversion as weathering and erosion proceeds.

Overgrazing is a particular problem of the savanna, and is partially implicated in the desertification of regions such as the Sahel, though late Pleistocene and Holocene climate change has undoubtedly played a greater role over the long term.

Temperate grassland

Temperate grassland is found in areas with climates rated Bsk, Bwk and Cfa in the Köppen system. Rainfall is generally between a semi-arid 250 mm to as much as 900 mm, and is seasonally distributed. An extreme temperature range (from as low as –40 °C in winter to 40 °C in summer) is characteristic. Various names are used locally for this biome, the two commonest being steppe in Eurasia, and prairie in North America. Others are pampas in South America, veldt in South Africa, and puszta in Hungary.

As the name suggests, grasses dominate the biome, and trees and large shrubs are absent. Tall grasses (2 m or more) with roots of equivalent depth grow in the wetter regions, while in drier areas, the grasses grow to about 20 cm and have roots extending about a meter down. As with savanna, fire and seasonal drought are important edaphic agents.

The temperate grassland fauna does not display a high biodiversity. Herbivores include bison, antelope and rodent species in the Old and New Worlds, and the wild horse in the steppes of central Asia. Carnivores are represented by badgers and weasels among others, and in North America, the coyote is a prominent omnivore. Curlews, eagles, hawks and other raptors, and scavangers such as ravens and vultures, are typical of the bird population.

The most characteristic soil parent material of the temperate grasslands is loess, which tends to be calcite bearing and inherently rich in plant nutrients. It originates by the aeolian erosion of glacial deposits, reworked as in Northern China and in the Mississippi watershed, by fluvial processes. Wind erosion carries coarse particles by saltation over short distances, building dunes and sand plains as in the Gobi desert. Silt and finer particles are carried over greater distances in suspension, and are the raw material of the vast loess deposits of the grasslands.

Typical soils of the loess (in sequence of decreasing annual rainfall) are Phaeozems, Chernozems and Kastanozems. Unlike savanna soils, the upper horizons of soils of the wetter areas (Chernozems in particular) are generally dark, humus rich and of a high inherent fertility. Phaeozems are also developed under the more humid climates and have a generally dark red color. Kastanozems are found in drier areas and are called chestnut soils on account of a brown solum. The soils normally have a good texture, held together by a well-developed system of grass roots. At the droughtier end of their range, temperate grasslands grade into desert and in this intermediate zone, soils typical of the desert biome make their appearance, Calcisols, Gypsisols, Solonetz and Solonchaks among them.

Since the invention of the steel plow, most of the major areas of temperate grassland have now been taken over for farming. The drier regions have become rangeland, and the wetter soils have been co-opted for arable agriculture. In the Mississippi watershed, 80% of the original grassland is now range or cropland, and the tall grass prairie has been all but obliterated. The well-established root system of the original grasses has been replaced by the shallower and less dense systems of crops such as corn and soybeans. A major result has been a decrease in humus content and a higher rate of wind erosion, including catastrophic episodes such as the dust bowl of the 1920s in midwestern USA.

Desert biome

For present purposes the desert biome will be taken to include areas of the land surface with Köppen climates of principally BWh and BWk types. This comprises deserts in the strict sense, with an annual precipitation of less than 50 mm, together with arid regions, where rainfall is normally between 50 and 250 mm per year. Most of the desert biome so defined occurs between 10° and 35° latitude (for example the Sahara and Kalahari Deserts), in the interior parts of continents (e.g., Australia, Mongolia) and in the rain shadow of young fold mountains as in parts of Peru and Nepal. Arid conditions also occur in the Arctic and in Antarctica and are considered under the tundra biome.

Hot deserts such as those of Australia have temperatures ranging from winter lows down to 10 °C, and summer extremes of 40 °C or more. The equivalent range in cold deserts such as the Gobi is about –25 °C to 20 °C.

Xerophytic shrubs, tolerant of extreme drought, are characteristic. Small burrowing mammals, lizards, snakes, and insects, with hawks and such animals as coyotes as the major predators, dominate the fauna. In the more vegetated areas of desert, antelopes are found, and in North Africa and Asia, two varieties of camel are native to the desert biome.

Physical characteristics and processes distinctive of the desert biome, and significant in the soil forming process are:

1. dominance of physical weathering over chemical,
2. development of internal drainage systems (including ephemeral streams) leading to salt lakes,
3. erosion principally by wind, but including an important component of water erosion during irregular, flash flooding,
4. evapotranspiration, which exceeds rainfall so that precipitation of carbonates, sulfates and/or chlorides may take place in the solum or at the soil surface.

The typical soil parent material in deserts is quartzose sand, much of which is in continual motion as active dunes and ergs. Where sand is sufficiently stable, Arenosols which now cover about 900 million ha (7% of the land surface) have formed. Since finer particles have been removed by aeolian erosion, the general texture is sandy, grading into coarser, more gravel-rich varieties. Because of the scarcity of soil water, horizonation is generally poorly developed.

Again, because of the scarcity of water, chemical weathering is not intense. Where it is noticeable, it leads to the precipitation of salts in the solum or at the surface of the soil. Calcite is the first and commonest precipitate, the soil forming process being known as calcification, with Calcisols as the soils produced. A calcite hardpan, also called caliche, may form at or near the surface. At the surface, it is also called calcareous duricrust.

With increasing aridity, the concentration of salts in the soil water reaches the solubility product of gypsum and a gypsiferous layer may form below the solum of a Calcisol. Where gypsum has precipitated in the solum, a Gypsisol may be the result. Gypsic duricrusts are produced by precipitation of gypsum at the surface. Sodium is one of the accumulating ionic components of soil water in the desert biome so that Solonetz and Solonchaks are also encountered in arid regions.

Arenosols are low in fertility, rapidly drained and have little potential for cropping. In parts of the desert biome with rainfall of 200 to 250 mm, exploitation as rangeland is possible. Where finer textured materials have accumulated, irrigation has been introduced to allow arable farming though long term irrigation increases the incidence of induced salinization.

Mediterranean biome

At about 3 million km^2, this is the smallest of the biomes. It occurs between 30 °N and 40 °S latitude, and has a climate classified as Cs on the Köppen scale. Winters are wet and summers are dry, a unique combination among climates of the world. Summer temperatures of 30 °C are common, with temperatures of 5 °C or less in winter. Rainfall is in the range 350 to 800 mm per year.

The characteristic vegetation is shrubland, which is known variously as maquis in the Mediterranean region proper, chaparral in California, matorral in Chile, fynbos in South Africa and mallee scrub in Australia. Other plant species vary in each isolated geographical location, but a common feature is adaptation to drought and fire. The plant population shows a high degree of endemism, presumably because of the unique nature of the climate to which they have adapted, as well as to geographical isolation brought about to some degree by marine and desert borders. The fauna of the various regions of this biome are also characterized by endemism.

Cambisols are common in the Mediterranean biome, and represent an early stage of weathering. They form in a weakly acid environment (pH about 6), where ferromagnesian minerals begin to show incipient hydrolysis. Fe is released from the primary mineral structures and precipitates as an amorphous iron hydroxy phase, which would normally age, to goethite or eventually to hematite. Sand, silt and clay particles become coated, and it does not need a particularly high iron content for the soil to acquire a reddish color (a process known as rubefaction). Gibbsite and alumino-silcate clays may also form, but reddening of the profile, together with an accumulation of organic matter in the A horizon, are the only macroscopic evidences of pedogenesis normally present. When the reddening reaches a Munsell hue of 7.5YR and a chroma greater than 4 in moist soil, the WRB qualifier chromic is applied. In fact chromic soils generally, are distinctive of the biome, Chromic Luvisols being as common as Chromic Cambisols (more common in Chile).

In the drier parts of the Mediterranean biome, soils that are characteristic of steppic or more arid, as well as more torrid climates, make an appearance, for example: Kastanozems, Calcisols and Solonchaks in the Mediterranean, Phaeozems and Acrisols in California, ferralitic soils and saline soils in Australia.

In limestone terrain karst phenomena occur. Indeed, the term karst comes from the Mediterranean region, and is derived (via the German) from the Serbo-Croat *Kras,* the high bare limestone region south of Ljubljana. Solution of the carbonates in the bedrock leaves behind a rubefied residual soil, rich in clay, to which the Latin term *Terra rossa* (red earth) is applied. There is a continuing debate about how much of the clay is autochthonous and how much allochthonous.

Much of the biome is mountainous in nature, so that soil erosion is endemic, bedrock surfaces are continually being exposed, and weakly developed soils such as Regosols and Leptosols are common. In anthropic terms, the Mediterranean region itself, is one of the most altered environments on Earth. Three thousand years ago it was well wooded with species of oak, cedar, pine, wild olive and carob, remnants of which remain. But, we know from classical Greek literature that even by 2 400 years ago, clearance of the land by fire, and grazing by sheep and goats, had made soil erosion a considerable problem in Greece. North Africa was famous as the "breadbasket" of the Roman Empire at its height. Now, much of its once productive farmland is underlain by soils truncated to the C horizon. Aridification is a further problem there, currently extending into southern Italy and Spain, as climatic zones move northwards with the globally changing climate.

A similar ecological history, though perhaps less emphatic, has affected the shrublands of California, where aboriginal burning and pre-conquest arable agriculture, was followed by livestock grazing from the time of the Spanish colonization onwards.

Other biomes

The word biome has also been used in somewhat questionable contexts and combinations. For example, in the failed experiment to construct an artificial microcosm of the biosphere in Arizona, Biosphere 2 (BERAC, 2003), an agricultural biome was identified. In the real world, agriculture does not constitute a biome, but is actually a set of technical processes by which human beings utilize a biome to produce food. So far over one third of the soils on land biomes as defined in this article, have been converted to this purpose.

The term mountain biome is also used (e.g., Endrödy-Younga, 1988), though mountain zones are in fact a collection of biomes with a vertical stratification. On a volcano such as Kilimanjaro in Tanzania the sequence is savanna, rainforest and tundra with increasing height, each miniature biome being an expression of the local climate at that elevation.

The term wetland biome also occurs in the literature (e.g., Gorham, 1979), perhaps more defendably, though again, wetlands are a feature of all biomes as the term has been used in this article. Of particular interest however, is the "mangrove biome" found in tropical salt marshes in the intertidal zone. The dominant organisms belong to about 60 salt tolerant plant species of the *Rhizophoraceae* family, mangroves in the broad sense (Plaziat, 2001). Their stilt roots, containing air sacs, are an adaptation to promote respiration in permanently waterlogged soils. The soils themselves are peaty Fluvisols or Histosols. Authigenic pyrite may be present in the highly reduced, water saturated part of the soil (specifically in Thionic Fluvisols), and where this has been exposed by drainage, or latterly by the careless and indiscriminate use of these soils in shrimp culture, the pyrite has oxidized to produce jarosite and other minerals typical of areas of high acidity and oxidization, waters of pH 3 or less, and a major problem of Al toxicity.

Ward Chesworth

Bibliography

Behrensmeyer, A.K., Damuth, J.D., DiMichele, W., Potts, R., Sues, H-D., and Wing, S.L., 1992. *Terrestrial Ecosystems through Time.* Chicago, London: University of Chicago Press, 568 pp.

BERAC. 2003. *An Evaluation of the Biosphere 2 Center as a National Scientific User Facility.* Washington, DC: U.S. Department of Energy Biological and Environmental Research Advisory Committee, 19 pp.

Carpenter, J.R., 1939. The biome. *Am. Midl. Nat.*, **21**: 75–91.

Endrödy-Younga, S, 1988. Evidence for the low-altitude origin of the Cape Mountain biome derived from the systematic revision of the genus *Colophon* Gray (Coleoptera, Lucanidae). *Ann. S. Afr. Museum*, **96**: 359–424.

FAO. 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

Gorham, E., 1979. Shoot height, weight and standing crop in relation to density of monospecific plant stands. *Nature*, **279**: 148–150.

Plaziat, J.-C., Cavagnetto, C., Koeniguer, J.-C., and Baltzer, F., 2001. History and biogeography of the mangrove ecosystem, based on a critical reassessment of the paleontological record. *Wetlands Ecology and Management:* **9**: 161–179.

Retallack, G.J., 2001. *Soils of the Past: an introduction to paleopedology.* Oxford: Blackwell Science, 404 pp.

Woodward, S.L., 2003. *Biomes of Earth: Terrestrial, Aquatic, and Human-Dominated.* Westport, CT: Greenwood Press, 435 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag 130 pp.

Cross-references

Climate
Geography of Soils
Geology and Soils

BIOREMEDIATION

A set of techniques employing the properties of living organisms, especially plants and bacteria, to ameliorate environmental problems caused by natural processes or human activities. See *Biodegradation*.

BIOSEQUENCE

A sequence of soils related in space and time and varying among themselves as a function of the dominant factor of the biology of the ecosystem of which they are a part. Biosequences have been used to study temporal changes in the standing biomass of mountainous regions in California and the Alps (e.g., Tinner et al., 1996), but whether the examples chosen are independent of other factors such as topography and climate, is problematical.

Bibliography

Tinner, W., Ammann, B., Germann, P., 1996. Treeline fluctuations recorded for 12,500 years by soil profiles, pollen, and plant macrofossils in the Central Swiss Alps. *Arctic Alpine Res.*, **28**: 131–147.

BIOSPHERIC ROLE OF SOIL

See *Soil*.

BIOSTASIS

An ecological steady state characterized by relatively little change in the quantity and quality of the biomass of a region over a term of perhaps tens of thousands to a few million years. The term was introduced by Erhart (1967).

Bibliography

Erhart, H., 1967. La genèse des sols en tant que phénomène géologique; esquisse d'une théorie géologique et géochimique, biostasie et rhexistasie, 2Paris: Masson, 177 pp. nd. edn.

BIOTIC

Pertaining to life and living organisms. The soil constituents and soil processes directly assignable to the influence of the biomass and of organic processes generally. Biotic potential is an index of the ability of a system to recover and regenerate after disturbance (Lomolino et al., 2006, p. 153).

Bibliography

Lomolino, M.V., Riddle, B.R., Brown, T.H., 2006. Biogeography, 3rd edn. Sunderland, MA: Sinauer Associates, 845 pp.

BISIALLITIZATION

A general term for the mineralogical transformations that result in the formation of clay minerals with a 2 : 1 sheet structure. (Pedro and Sieffermann, 1979, p. 42–46).

Bibliography

Pedro, G., Sieffermann, G., 1979. Weathering of rocks and formation of soils. In Siegel, F.R., ed., *Review of Research of Modern Methods in Geochemistry.* Paris: UNESCO, pp. 39–55.

BLACK COTTON SOIL

Synonym: regur. Dark colored soils developed extensively on the Deccan basalts of India. Calcareous and rich in expanding clays.

BLACK EARTH

Descriptive term commonly applied to chernozemic soils, on account of their black, humus-rich A horizon.

BLANKET

A uniform covering to a landscape. Used particularly to describe bogs that cover (or blanket) the highlands above the tree line in regions of humid climate.

Cross-reference

Mire

BLOWOUT

A hollow in soil or sand excavated by wind erosion.

Cross-reference

Wind Erosion

BOG

Bogs are sphagnum-dominated *wetlands* (*q.v.*). They are of low pH by virtue of the production of humic acids during the decomposition of organic matter.

Cross-reference

Mire

BOREAL FOREST

Or taiga: the belt of coniferous forest that encircles the polar regions of North America and Eurasia and that lies between the tundra, or barrens, to the north, and the temperate grasslands and deciduous forest to the south. The characteristic soil type is the Podzol.

Cross-reference

Biomes and their Soils

BOULDER

A weather worn mass of stone exceeding 60 cm across.

BRUNIFICATION

The production of a brown color in soil. The color represents a combination of iron in the ferric state together with darker organic matter. Clay-iron, and clay-iron-humic complexes are present in Brunisols (Soil Taxonomy) - soils produced by brunification (Gaucher, 1977 p 24).

Bibliography

Gaucher, G., 1977. Vers une classification pedologique naturelle basee sur la geochimie de la pedogenese. *Catena*, **4**: 1–27.

BUFFERS, BUFFERING

In the chemical sense of the word, buffers are those systems that tend to maintain a constant pH level despite the addition (within certain limits) of an acid or base or despite dilution. They usually consist of mixtures of either a weak acid and a salt formed from the acid and a strong base, or they consist of a weak base and a salt formed from the base and a strong acid. Many chemical reactions and all biological processes take place only at specific pH levels. If there is no buffer action, hydrogen-ion concentration may alter and cause the reaction to slow down until it stops, or produce products different from those required.

Theory

Using the case of an aqueous solution of acetic acid and sodium acetate – i.e., a mixture of a weak acid and its salt formed from a strong base – the dissociation equilibrium of the acid and the relative constant can be represented by

$$CH_3{-}COOH + H_2O \rightleftharpoons CH_3{-}COO^- + H_3O^+$$

$$K_a = \frac{[CH_3{-}COO^-][H_3O^+]}{[CH_3{-}COOH]} \qquad (1)$$

The hydrolysis equilibrium of the salt and the relative constant can be represented by

$$CH_3{-}COO^- + H_2O \rightleftharpoons CH_3{-}COOH + OH^-$$

$$K_i = \frac{[CH_3{-}COOH][OH^-]}{[CH_3{-}COO^-]} \qquad (2)$$

Considering that the concentrations $[CH_3{-}COO^-]$ and $[CH_3{-}COOH]$ indicated in Equations (1) and (2) are the same and that the values $[H_3O^+]$ and $[OH^-]$ are interdependent, because $[OH^-]\,[H_3O^+] = 10^{-14}$ at 25 °C $= K_w$, either Equation (1) or (2) can be rewritten in the form

$$[H_3O^+] = K_a \frac{[CH_3{-}COOH]}{[CH_3{-}COO^-]} \qquad (3)$$

Equation (3) shows that the concentration of hydrogen ions depends on the dissociation constant K_a and the ratio of the concentration of undissociated acetic acid to that of acetate ions.

If the value of $[H_3O^+]$ is expressed as pH, Equation (3) becomes

$$pH = -\log K_a - \log \frac{[CH_3{-}COOH]}{[CH_3{-}COO^-]} \qquad (4)$$

When

$$\frac{[CH_3{-}COOH]}{[CH_3{-}COO^-]}$$

equals 1, Equation (4) can be simplified into the form

$$pH = -\log K_a = pK_a \qquad (5)$$

Since the concentrations of undissociated acid and its anion can be identified by the analytical concentrations of the acid C_A and its salt C_S, the small fractions of dissociated acid and hydrolyzed salt can be ignored; and Equation (4) becomes

$$pH = -\log K_a - \log \frac{C_A}{C_S} \qquad (6)$$

that is,

$$pH = pK_a + \log \frac{C_S}{C_A} \qquad (7)$$

Similar reasoning can be applied to solutions of a weak base and its salt from a strong acid ($NH_4OH + NH_4Cl$), whereupon the following analogous expressions are obtained:

$$[OH^-] = K_B \frac{C_B}{C_S} \qquad (8)$$

$$pOH = pK_B + \log \frac{C_S}{C_B} \qquad (9)$$

Equations (3), (7), (8) and (9) are the basic relations that govern a solution buffer mechanism, and they are known as the *Henderson and Hasselbach Equations*.

Mechanism and efficiency of buffer solutions

The buffer action produced by a system results from acid–base equilibrium. If a small amount of strong acid (HCl) is added to an equimolecular solution of acetic acid and sodium acetate, some of the acetate ion is converted into acetic acid; if a strong base (NaOH) is added, some of the acetic acid is converted into acetate ion.

In other words, the strong acidity of the HCl is buffered by being converted into weak acidity, just as the strong base NaOH is buffered through the formation of its salt. Table B2 gives an idea of the effect obtained. The Henderson and Hasselbach Equations show that the greatest buffering effect is obtained when the pH of the buffer equals pK_a (or pK_b). In fact, under these conditions, variations undergone by the ratio

Table B2 pH Variation when HCl or NaOH are added to a buffered and nonbuffered system

	Composition	pH	Additions in equivalents	Resulting pH with:
			HCl–NaOH	HCl–NaOH
Buffered system	1 000 ml $CH_3{-}COOH$ 0.1 N $CH_3{-}COONa$ 0.1 N	4.74	10^{-3}–10^{-3}	4.73–4.75
Nonbuffered system	1 000 ml H_2O	7.00	10^{-3}–10^{-3}	3.00–11.00

C_S/C_A (or C_S/C_B) are minimal when acid or base is added; and so must be variations in pH. Further, the amounts of acid or base that can be buffered are restricted to the limits within which the ratio C_S/C_A may be considered constant. It can be calculated that the maximum amount of acid or base that can be added without overcoming the buffer action varies between 1/50 and 1/100 of the buffer components. This information is important in practice because it means that it is necessary to maintain fairly high total concentrations of acid (or base) and its salt to ensure a good buffer efficiency.

Thus one can say that when effecting a buffered reaction, the choice of buffer system components will be made according to the following criteria: (1) use a weak acid whose pK is as near as possible to the pH at which the reaction is to take place; (2) calculate the amount of conjugate base to mix with the acid from the opposite Henderson and Hasselbach Equation; (3) the ratio C_S/C_A must be within 0.1 and 10 to guarantee good efficiency. It follows that the pH range within which the buffer action is manifested has the limits of $pK + 1$ and $pK - 1$.

The salts of multi-proton-donating acids as buffers

Mixtures comprising the several salts of a weak multi-proton-donating acid likewise constitute buffer systems. For example, consider the neutralization reaction of H_3PO_4. Initially the monosubstituted salt is formed, then the bisubstituted one, and finally the trisubstituted

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 \qquad pK_{a1} \cong 2.00$$

$$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 \qquad pK_{a2} \cong 7.00$$

$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 \qquad pK_{a3} \cong 11.00$$

When the pH of the system equals pK_{a2}, the bisubstituted solution consists of an equimolecular mixture of mono and bisubstituted phosphates. This mixture constitutes a buffer system in which the acid–base equilibra that typify it are conceptually similar to those in the $CH_3{-}COOH/CH_3{-}COONa$ system. In fact, the mono and bisubstituted salts are completely dissociated, and the $H_2PO_4^-$ and HPO_4^{2-} ions are in equilibrium

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$$

The $H_2PO_4^-$ ion is the acid, and the HPO_4^{2-} ion is the conjugate base; thus Equation (7) can be applied

$$pH = pK_{a2} + \log \frac{C^{2-}_{HPO_4}}{C_{H_2PO_4^-}} \qquad (10)$$

Similarly, it can be shown that the mixture of bi- and trisubstituted phosphates is a buffer solution with maximum buffer action when the pH equals pK_{a3}.

Buffering in soil

Buffering in soil is defined as the resistance of the soil to variations in pH and is chiefly due to the colloidal humus and clay fractions. In soils containing appreciable amounts of phosphates and carbonates, buffering is also effected by these salts, as illustrated in the preceding section. As early as 1922 Arrhenius sustained that soils with strong buffer effects were very fertile and advised organic fertilization to increase the buffer action. That a soil does not undergo marked fluctuations in pH following additions of acids or bases or as a result of dilution is of considerable practical importance if the organisms living in it, particularly microorganisms and the higher plants, are to continue their various activities under those particular pedological conditions. A large change in pH means a radical modification in soil environment, which severely affects the availability of plant nutrients and alters the pedogenetic processes.

Compounds normally held in the *soil solution* (*q.v.*) may precipitate out, while others normally insoluble may to dissolve. This whole question is of interest not only in relation to plant mineral nutrition but also to the pedological characteristics and evolution of the soil.

Factors causing alteration in soil pH

Factors tending to modify soil pH can be divided into two groups:

1. those that bring about an increase in hydrogen-ion concentration tending to lower the pH;
2. those that produce an increased adsorption of exchangeable bases tending to raise the pH.

Acidity (*q.v.*) is principally encouraged by the decomposition of organic matter and the application of certain fertilizers. Both inorganic (H_2CO_3, HNO_3, H_2SO_4) and organic acids are found among the products of organic molecular decay, while nitric and sulfuric acids are formed by microbial action on fertilizers such as ammonium sulfate. The use of fertilizers like K_2SO_4 or KCl will also tend to lower the pH.

Alkalinity is usually encountered in arid regions where the colloidal complex of the soil is generally highly saturated with exchangeable bases, the degree of this alkalinity depending on the proportion of sodium. In these regions the weathering processes that liberate the alkaline cations from the soil minerals are helped by the extremes of temperature and by the fact that precipitation is limited to certain periods of the year. The low rainfall, moreover, means that these exchangeable bases are not leached away. Other factors conducive to alkalinity can be such agricultural processes as *irrigation* (*q.v.*), liming (see *Lime*), or fertilization (with superphosphates, Thomas meal, or $Ca(NO_3)_2$).

In theory, soil pH should not be affected by greater or lesser water content because variations dependent on the degree of dissociation of the various acids should be compensated by the variations in the degree of hydrolysis of the "salts". In practice, however, the soil pH does vary seasonally, but this is due not so much to dilution effects as to variations in biotic activities. In summer the fall in pH would seem to correspond to a greater microorganic activity with the contributing factor of an increased acid-exudate production by the plant roots; in winter a rise in pH value is often seen, probably due to the reduction in biotic activity.

The inorganic colloidal fraction as a buffer system

The colloidal soil complex functions as a slightly ionized acid or a slightly ionized salt of a weak acid. The acid character of clay was attributed to exchangeable aluminum. For a long time this theory was disputed, but it was finally accepted when Coleman and Harward (1953) demonstrated that hydrogen clay, prepared for treatment with HCl, tends to be spontaneously transformed into aluminum clay.

Acid soils are generally aluminum saturated and have the characteristics of a weak acid resulting from the hydrolysis of the adsorbed $Al(OH_2)_6^{3+}$ ion:

$$Al(OH_2)_6^{3+} + H_2O = Al(OH_2)_5(OH^-)^{2+} + H_3O^+$$

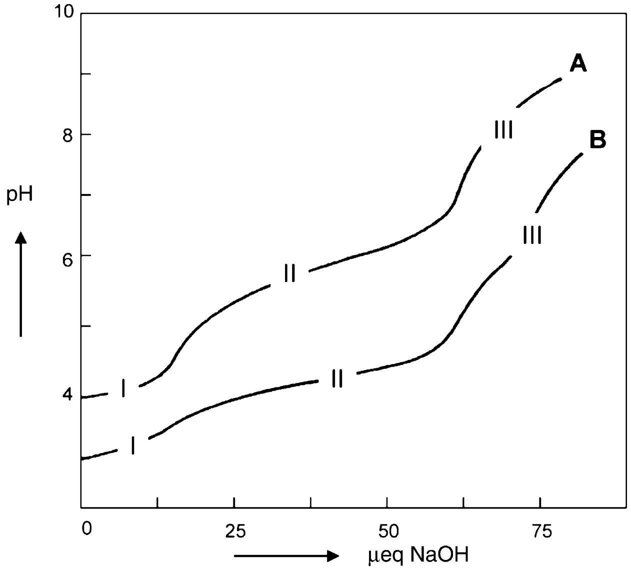


Figure B15 Potentiometric titrations of 0.1 g H:Al-bentonite in H_2O(A) and in NaCl(B).

But there are other weaker acid groups, present in the inorganic colloidal fraction, which create buffering at pH values higher than 5.5. They belong to two different types of "structural forms": the first has been identified as the aluminum interlayer, a hydroxy aluminum polymer, postulated as hexagon or multiple ring structure with a composition that may range from $Al_6(OH_{12})^{6+}$ to $Al_n(OH)_{3n}$; the second is considered to be of lattice origin and consists of silanol groups (–SiOH).

Figure B15 shows the potentiometric titration curves of a H-Al-bentonite from Sardinia in the absence and presence of electrolyte. The first buffer range (I) is due to the neutralization of the adsorbed H_3O^+ ions; the second (II) to the deprotonization of the Al^{3+} ions; and the third (III), which appears only in the presence of electrolyte, is due to the –OH lattice groups.

The spontaneous transformation of H-clay in Al-clay is a chemical mechanism through which the clay structure is slowly decomposed. This transformation also serves to increase the buffer capacity of the system by converting a strong acidity into a weak acidity.

The ability of soil silicates to oppose such acidification depends on the amount of cations and anions that are released into solution and it is related to their solubility.

The organic colloidal fraction as a buffer system

On the basis of current knowledge of humic acid structure, it can be held that the –COOH and phenolic –OH groups are chiefly responsible for the acidity in the organic fraction.

Figure B16 reproduces the titration curve of a humic acid extracted from a red brown earth (Posner, 1964). Based on the premise that "one of the major difficulties in the interpretation of titration curves of this type is the choice of the end point", Posner attributes the acidity between pH values 3.0 and 7.0 (zone I) to carboxylic groups, between 8.0 and 12.0 (zone III) to phenolic–OH groups, and between 7.0 and 8.0 (zone II) to the overlap of the either two groups as well as α-NH_2 groups. This interpretation is justified by the fact that the carboxylic acids and phenolic–OH groups have acidity constants around 10^{-5} and 10^{-10}, respectively. The validity of Posner's attribution is based "on absence of evidence to the contrary". He also showed that the CEC, average pK values, and range of pK values determined from the titration curves of humic acids vary with the method of extraction used.

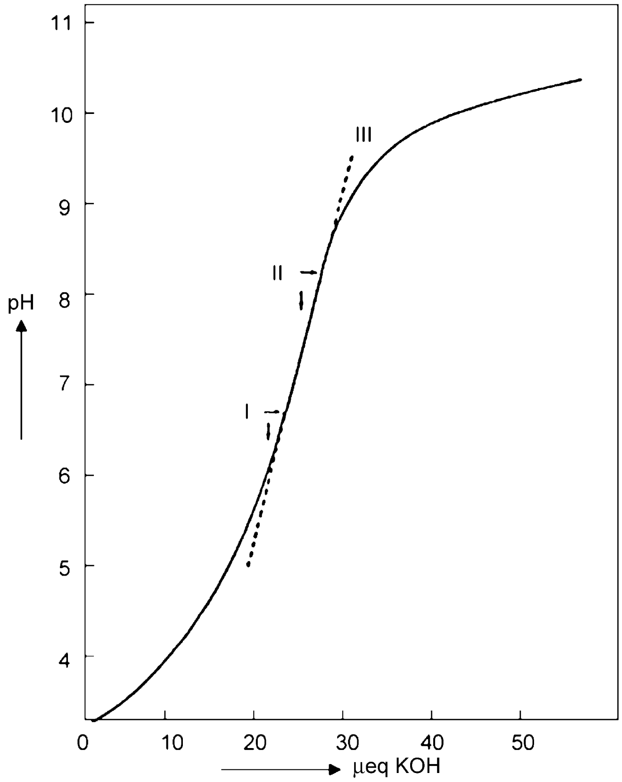


Figure B16 Potentiometric titration of 7.24 mg humic acid in 0.1 N KCl (adapted from Posner, 1964).

This observation is perfectly understandable since it is known that the acidity constant of a function is in strict relation to the structure of the vicinal carbon atoms and to the steric effect acting on them. Acid groups situated inside a "large humic molecule" can become more superficial and thus more active following extraction treatments.

The highly complex nature of humic materials suggests that a large number of sites are involved in proton binding: from titration data analyzed by bimodal Gaussian Distribution Model, mean pK values, distribution variances and total amount of humic acid sites can be calculated (Perdue and Lytle, 1983; Manunza et al., 1992; Gessa et al., 1994).

These parameters prove to be useful in differentiation of humic acids. The organic matter is the soil fraction with highest buffer power. However its contribution to soil buffering can vary in some extent as a consequence of partial neutralization of acid groups in the formation of stable metal-complexes and organo-mineral complexes (Manunza et al., 1995).

The soil solution as a buffer system

The soil liquid phase, in which gases (mainly CO_2), and organic and inorganic chemical species, acid in character are dissolved, constitutes a buffer system which operates over a wide range of pH. Ions and molecules – such as organic acids, H_2CO_3, metal ions – contribute buffering the soil pH according to the following equilibria:

$$A - H + H_2O \rightleftharpoons A^- + H_3O^+$$

$$M(H_2O)_x^{n+} + H_2O \rightleftharpoons [M(H_2O)_{x-1}OH]^{(n-1)+} + H_3O^+$$

The organic acids contain functional groups of different pK and mainly work between pH 4 and 8. The weak acid H_2CO_3 – produced by dissolution of CO_2 in H_2O – develops its buffer activity above pH 5.5 (p$K = 6.4$). Its efficiency depends on the partial pressure of the carbon dioxide of the soil atmosphere, which is produced mainly by the microorganisms present in the soil. In weakly acid and alkaline soils the CO_2 partial pressure often reaches 10^{-2} atm; consequently the acidity of the H_2O–CO_2 system has a considerable influence on the buffer capacity of these soils.

Soil buffering system – mechanism

Most of the acid groups of the colloidal complex become deprotonated between the pH values of 4.0 and 8.5. In this pH range, the soil passes from a state of maximum nonsaturation to that of maximum saturation. This situation can be represented as follows:

$$\text{micelle}\left|\begin{matrix}-H\\-H\\ \\-H\\-H\end{matrix}\right. \xrightarrow{+\,2B-OH} \left|\begin{matrix}-B^+\\-B^+\\ \\-H\\-H\end{matrix}\right. \xrightarrow{+\,2B-OH} \left|\begin{matrix}-B^+\\-B^+\\ \\-B^+\\-B^+\end{matrix}\right.$$

The acid form represented here is obviously a simplification; however, the hydrogen atoms shown should be considered as protons, which are released whatever the structural form they belong to since, as Jackson (1963) has observed, "fundamentally, all acidity groups depend on proton dissociation, that is exchangeable H^+, but differ only in the acidity strength of the functional groups". The weak-acid groups of the colloidal complex liberate protons into the soil solution; the state of equilibrium between undissociated and dissociated forms can be illustrated by:

$$\text{micelle H} + H_2O \rightleftharpoons \text{micelle}^- + H_3O^+$$

The addition of a base neutralizes the H_3O^+ ions and results in a further liberation of protons from the colloidal complex, leaving the pH more or less unvaried. When the acid function is partially salified, the colloidal complex can be compared to a mixture of a weak acid and its salt formed from a strong base, constituting exactly the form needed for acting as a buffer. In fact, buffering with respect to bases takes place through neutralization of the residual acid functions, while buffering with respect to acids is determined by the readsorption of protons into the colloidal micelle following a shift in the equilibrium of dissociation of the "weak acid" toward the undissociated form, with a consequent transfer of adsorbed exchangeable bases into the soil solution.

Buffer capacity of soil

Just as the efficiency of a buffer solution is assured by sufficiently high concentrations of acid (or base) and relative salt, so is the buffer capacity of a soil dependent on the percentage of its colloidal inorganic and organic constituent and in particular on the properties of their surfaces.

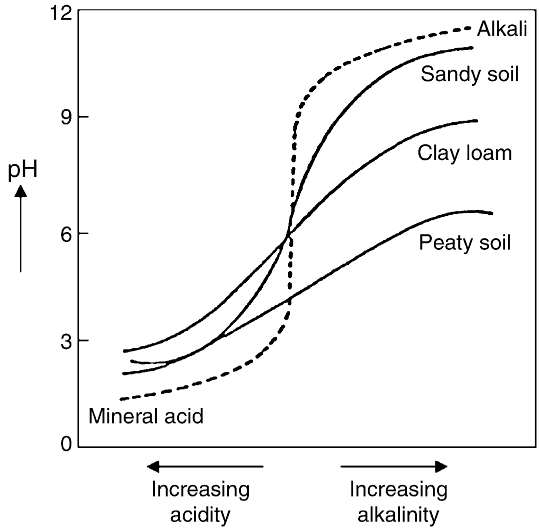


Figure B17 Buffering curves of different soils.

In agreement with Van Breemen and Wielemaker (1974) the buffer capacity can be defined by:

$$\beta^{ci}_{soil} = \frac{dCi}{dpH}$$

where β indicates the soil pH variation (eq.l^{-1} pH^{-1}) as a function of the amount of strong acid or strong base added.

Soils rich in organic matter have the most effective buffer capacity because their humic compounds have particularly high CEC values. Clayey soils have good buffer capacities, which, however, vary according to the composition of the clay fraction. Sandy soils have weak buffer capacities and undergo notable variations in pH for the same additions of acid or alkali (Figure B17).

Theoretically, the maximum buffering effect should be found when the colloidal complex is 50% saturated, that is, when the pH equals the apparent soil pK. It must be emphasized that soil pH is not directly proportional to the degree of base saturation, so different soils having the same degree of base saturation can have different values of pH. Therefore the pH at which the buffer capacity of a soil is maximum varies from soil to soil according to its apparent pK. Mehlich (1941, 1960) showed that pH values of kaolinitic and montmorillonitic soils at 50% neutralization were significantly different. For the former he determined apparent pK values of 6.5 and for the latter 4.5 to 5.0.

In general, it can be said that in mineral soils where the permanent charge is a high proportion of the total charge, the apparent pK values are fairly low compared to those in soils with a highly pH-dependent charge.

Carlo Gessa

Bibliography

Arrenhius, O., 1922a. The potential acidity of soil. *Soil Sci.,***14**: 223–232.

Van Breemen, N., and Wielemaker, W.G., 1974. Buffer intensities and equilibrum pH of minerals and soils: 1°, 2°. *Soil Sci. Soc. Am. Proc.*, **38**: 55–66.

Coleman, N.T., and Harward, M.E., 1953. The heats of neutralization of acid clays and cation exchange resins. *J. Am. Chem. Soc.*, **75**: 6045–6046.

Gessa, C., 1973. Interrelationships of third buffer range with pH-dependent and permanent charges in bentonite. *Geoderma*, **10**: 299–306.

Gessa, C., Melis, P., Bellu, G., and Testini, C., 1978. Inactivation of clay pH-dependent charge in organo-mineral complexes. *J. Soil. Sci.*, **29**: 58–64.

Gessa, C., Deiana, S., Maddau, V., Manunza, B., and Rausa, R., 1994. Binding of protons and metal ions in humic acid. Test of the bimodal Gaussian distribution model. *Agrochimica*, **38**: 85–90.

Hsu, P.H., and Bates, T.F., 1964. Fixation of hydroxy-aluminium polymers by vermiculite. *Soil Sci. Soc. Am. Proc.*, **28**: 763–769.

Jackson, M.L., 1963. Aluminium bonding in soils: a unifying priciple in soil science. *Soil Sci. Soc. Am. Proc.*, **27**: 1–10.

Manunza, B., Gessa, C., Deiana, S., and Rausa, R., 1992. A normal distribution model for the titration curves of humic acids. *J. Soil Sci.*, **43**: 127–131.

Manunza, B., Deiana, S., Maddau, V., Gessa, C., and Seeber, R., 1995. Stability constants of metal–humate complexes: titration data analyzed by bimodal Gaussian distribution. *Soil Sci. Soc. Am. J.*, **59**: 1570–1574.

Martin, A.E., and Reeve, R., 1958. Chemical studies of podzolic illuvial horizons. III. Titration curves of organic matter suspensions. *J. Soil Sci.*, **9**: 89–100.

Mehlich, A., 1941. Base unsaturation and pH in relation to soil type. *Soil Sci. Soc. Am. Proc.*, **6**: 150–156.

Mehlich, A., 1960. Charge Characterization of soils. *Seventh Int. Congr. Soil Sci. Trans.*, **2**: 292–302.

Perdue, E.M., and Lytle, C.R., 1983. Distribution model for binding of proton and metal ions by humic substances. *Environ. Sci. and Technol.*, **17**: 654–660.

Posner, A.M., 1964. Titration curves of humic acid. *Eighth Int. Congr. Soil Sci. Trans.*, **3**: 161–174.

Rich, C.I., 1960. Aluminium in interlayers of vermiculite. *Soil Sci. Soc. Am. Proc.*, **24**: 26–32.

Yuan, T.L., 1963. Some relationships among hydrogen, aluminium and pH in solution and soil systems. *Soil Sci.*, **95**: 155–163.

Cross-references

Acid Soils
Acidity
Nitrogen Cycle
Podzols
Sorption Phenomena
Sulfur Transformations and Fluxes
Thionic Soils

BULK DENSITY

Brady and Weil (2002) define *bulk density* as the mass (weight) of a unit volume of dry soil. Blake's (1965) definition states that this soil parameter is the ratio of the mass to the bulk, or microscopic volume of soil particles plus pore spaces in the sample. Therefore, the volume with which bulk density is concerned is that of the solid particles and pore space. Bulk density differs from *particle density* (*q.v.*) in that the latter concerns the relationship between the mass and volume of only the solid particles in the soil excluding the volume of pore space. Bulk density and particle-density values are used to compute *pore space* (see *Soil pores*) in a soil using the following relationship:

$$\%\,\text{pore space} = 100 - \frac{Db}{Dp} \times 100$$

where Db = bulk density, oven dry, Dp = particle density.

Bulk density is expressed as a ratio of grams per cubic centimeter (g cm^{-3}). Since the mass of a cubic centimeter of water is about 1 g, the bulk density of water is said to be 1 g cm^{-3} or 1. Soil usually has a bulk density greater than water. For topsoils a value of 1.1–1.3 g cm^{-3} is about normal. For subsoils bulk-density values are usually greater than those for topsoils and range from 1.3–1.7 g cm^{-3}. The bulk density of the substratum may be greater or less than that of the subsoil. These figures are necessarily approximate for the bulk-density value of a soil depends on many soil conditions such as the way the soil is managed, or cultivated. *Compaction*, *puddling* (*q.v.*), and a weakening grade of structure all relate to high bulk-density values. Any management practice that encourages these conditions to exist increases bulk density, thereby decreasing pore space and restricting gas diffusion and water movement in the soil. These conditions create soil zones where roots cannot penetrate and thus cannot derive water and nutrients.

Another use of bulk-density values in computing soil parameters is that of determining the *COLE* of the soil. COLE is the "coefficient of linear extensibility" and is therefore a measure of the potential volume change (PVC) of a soil as wetting or drying takes place and swelling or shrinking goes on (Buol et al., 2003). COLE is an expression of the shrink-swell tendency of the soil and is directly related to the change that occurs in bulk density as wetting or drying takes place. This relationship is shown by the following expression:

$$\text{COLE} = \sqrt[3]{\frac{Db_{\mathrm{d}}}{Db_{\mathrm{m}}}} - 1$$

where Db_d = bulk density, dry Db_m = bulk density, moist.

Because the COLE and related PVC are significantly critical to soil-use, soils with high COLE values have been separated from other soils at the subgroup level of generalization in some great groups in Soil Taxonomy (Soil Survey Staff, 1996). Soils with a COLE of 0.09 or greater are in the vertic subgroup. Even though these soils lack the intensity of shrink-swell necessary to place them in the Vertisol soil order, the amount of volume change that occurs on wetting and drying presents management problems that are serious enough to warrant setting these soils aside from others that lack a high shrink-swell tendency.

Bulk-density values are also often used to detect and describe dense layers such as fragipans and to give some indication as to the degree of development of these pans. In addition, they are used to detect appreciable amounts of volcanic ash, to determine the degree of alteration of *C horizon*s formed in saprolite, and to evaluate gains within and losses from various soil horizons if parent-material uniformity can be established (Buol et al., 2003).

David T. Lewis

Bibliography

Blake, G.R., 1965. Bulk density. In Black, C.A., ed., *Methods of Soil Analysis,* Vol. 1. Madison: American Society of Agronomy, pp. 374–390.

Brady, N.C., and Weil, R.R., 2002. *The Nature and Properties of Soils.* New Jersey: Prentice Hall, 960 pp.

Buol, S.W., Walker, M.P., and Southard, R.J., 2003. Soil genesis and classification, 5th edn. Ames, IA: Iowa State Press, 494 pp.
Grossman, R.B., Brasher, B.R., Franzmeier, D.P., and Walker, J.L., 1968. Linear extensibility as calculated from natural clod bulk density measurements. *Soil. Sci. Soc. America Proc.*, **32**: 570–573.
Soil Survey Staff, 1996. *Keys to Soil Taxonomy,* 7th edn. Washington D.C: U.S. Dept. of Agriculture, Natural Resources Conservation Service, 545 pp.

Cross-references

Aggregation
Particle Density
Soil Engineering
Soil Pores

BURIED SOIL

A fossil soil or paleosol preserved by being buried under sediment deposited by erosional processes.

C

C HORIZON

See *Horizon, Profile*.

CALCAREOUS SOILS

Calcareous soils as defined here are the soils that fall between the near neutral soils and the alkaline soils (Figure C1) in redox-pH space. They straddle the calcite fence of the pedogenic grid (Figure C2). The fence itself marks the pH zone below which calcite dissolves and above which it precipitates, by the reaction

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$

The deposition of calcium carbonate in soil takes place when the product of the activities of Ca^{2+} and CO_3^{2-} in the soil solution is $10^{-8.48}$ (Berner, 1976), and is commonly considered to be an inorganic process. However, evidence for the involvement of organisms (biomineralization) in the soil, especially bacteria, is accumulating (e.g., Goudie, 1996; Parraga et al., 2004).

Figure C3 shows a detail of Figure C2 with typical calcareous soils added: Calcic Luvisols, Calcaric Phaeozems, Chernozems and Kastanozems. Calcisols (considered also amongst the alkaline soils) have carbonates extending throughout the profile, though even in these soils, the surface pH may be too low to allow solid calcium carbonate to persist.

Calcrete (which is also sometimes termed caliche or calcareous duricrust when indurated) is in essence a variety of Calcisol. It has been defined as ‘a near surface, terrestrial, accumulation of predominantly calcium carbonate, which occurs in a variety of forms from powdery to nodular to highly indurated. It results from the cementation and displacive and replacive introduction of calcium carbonate into soil profiles, bedrock and sediments, in areas where vadose and shallow phreatic ground-water become saturated with respect to calcium carbonate’ (Wright and Tucker, 1991, p. 1). Calcretes may cover as much as 13% of the total land surface, being a prominent surface feature in arid and semi-arid climatic zones.

The pH range 5.5 to 7.0 in A horizons, covers a set of conditions too alkaline for notable amounts of Al^{3+} to be in solution,

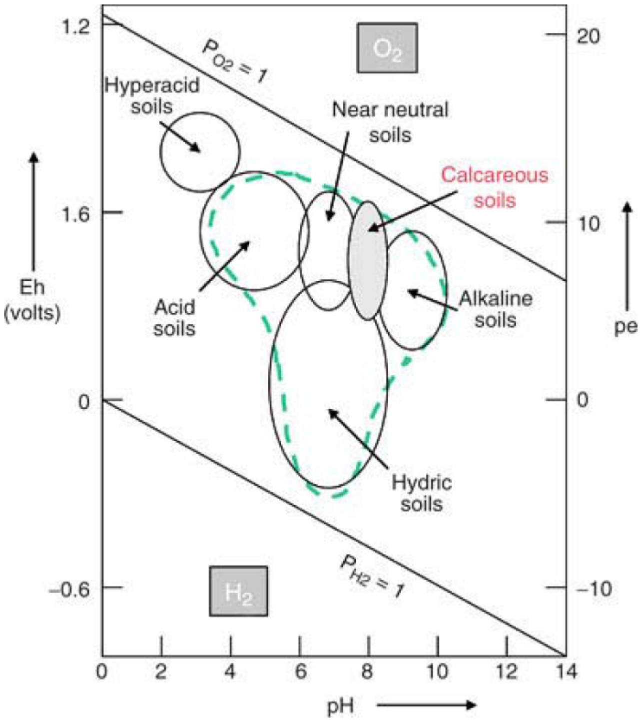


Figure C1 Approximate field of calcareous soil as defined in this article. The dashed envelope encloses the field of the common mineral soils.

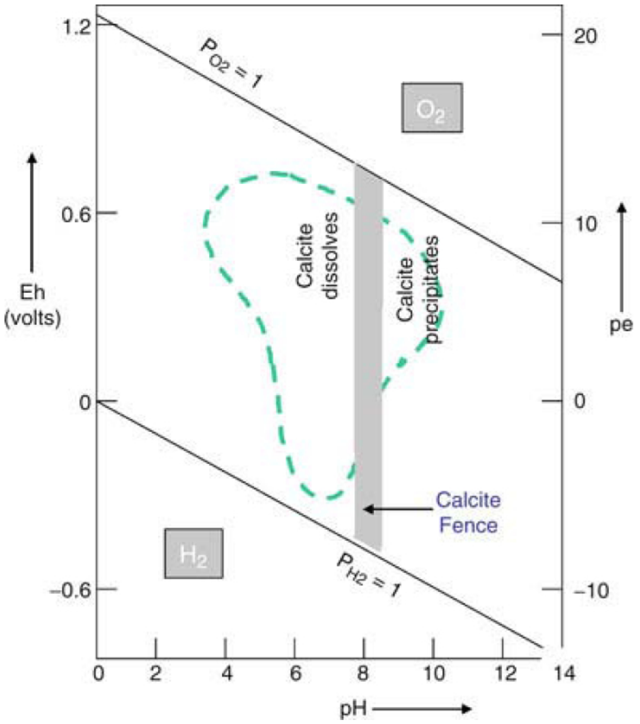


Figure C2 The calcite geochemical fence in relation to the common mineral soils.

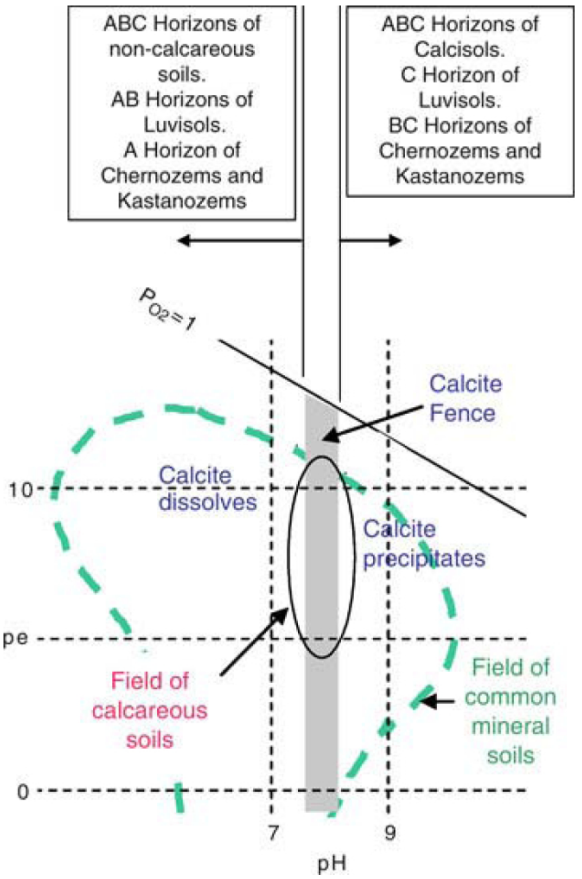


Figure C3 Detail of Figure C2 showing characteristics of the soils of Table C1 with respect to the presence or absence of calcite in their various horizons.

and too acid for Ca^{2+} (or Mg^{2+}) to reach saturation values with respect to carbonate phases. Clay can disperse under these conditions and be transported to the B horizon (illuviation), where a higher concentration of divalent cations in the soil solution will cause the clay to flocculate to form an argic horizon. Amongst the calcareous soils of Table C1, this is seen predominantly in the Luvisols (and Albeluvisols) and in luvic units of the other calcareous soils.

At the high end of the precipitation range of Table C1, the presence of calcite in soil is a benefit agriculturally as a pH buffer. Natural rainwater has a pH around 5.7, and a net addition of such precipitation to the soil system inevitably leads to acidification over the long term (more quickly if the rain is acidified by industrial and automobile emissions – as in the case of acid rain) As precipitation and consequent throughflow diminishes, the concentration of Ca^{2+} in the soil solution will increase to the level of calcite saturation (Figure C4). This is higher than the level for saturation with respect to the phosphate mineral apatite so that there will be a tendency for soil P to be fixed as apatite $Ca_5(PO_4)_3(OH, F, Cl)$, or as one of its precursors such as brushite $CaHPO_4 \cdot 2H_2O$ (Tunesi et al., 1999).

Ward Chesworth, Marta Camps Arbestain, and Felipe Macías

Table C1 Spectrum of soils that traverse the calcite fence of the pedogenic grid as climatic conditions change from cool to temperate humid. The pH indicated, is for the A horizon. In each of the soils referred to, pH also increases with depth (adapted from FAO, 2001)

Temp.	Precipitation (mm)	Vegetation	Soil group/Unit	pH
	>550	Deciduous forest	Luvisols, Albeluvisols	6.5–7
	500	Prairie and forest	Phaeozems	
Increases	500	Tall grass prairie	Luvic Chernozem	Increases
↓	450	Tall grass prairie	Haplic Chernozem	↓
	200–400	Short grass prairie	Calcic Chernozem, Kastanozem	
	<200	Open vegetation	Calcisols	7.5–8

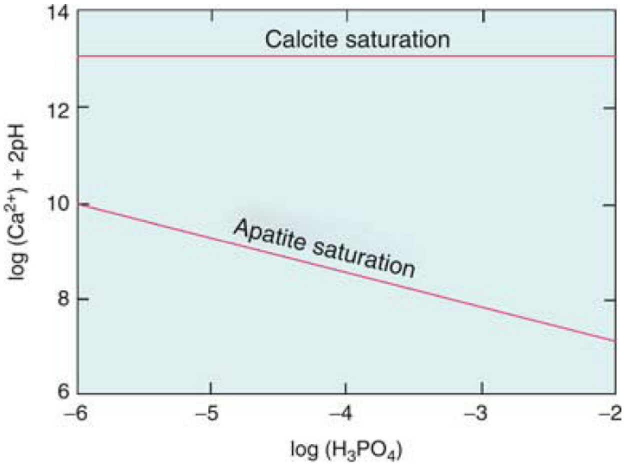


Figure C4 Calcite and apatite saturation in aqueous solution under a partial pressure of CO_2 of $10^{-3.5}$ bars (the normal atmospheric value) (adapted from Chesworth et al., 1987).

Bibliography

Berner, R. A., 1976. The solubility of calcite and aragonite at one atmosphere. *Am. J. Sci.*, **276**: 713–730.

Chesworth, W., van Straaten, P., Smith, P., and Sadura, S., 1987. Solubility of apatite in clay and zeolite bearing systems: application to agriculture. *Appl. Clay Sci.*, **2**: 291–297.

FAO. 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

Goudie, A. S., 1996. Organic agency in calcrete development. *J. of Arid Environments.* **32**: 103–110.

Párraga, J., Rivadeneyra, M., Martín- García, J., Delgado, R., and Delgado, G., 2004. Precipitation of Carbonates by Bacteria from a Saline Soil, in Natural and Artificial Soil Extracts. *Geomicrobiol. J.*, **21**: 55–66.

Tunesi, S., Poggi, V., and Gessa1, G., 1999. Phosphate adsorption and precipitation in calcareous soils: the role of calcium ions in solution and carbonate minerals. *Nutr. Cycl. Agroecosyst.*, **53**: 219–227.

Wright, V.P., Tucker, M.E., 1991. Calcretes: an introduction. In: Wright, V.P., Tucker, M.E., eds., *Calcretes.* Oxford: Blackwell Scientific, pp. 1–22.

Cross-references

Biomes and their Soils
Calcisols
Chernozems
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Duricrusts and Induration
Kastanozems
Luvisols

CALCISOLS

Calcisols are soils with a significant secondary accumulation of calcium carbonate resulting from precipitation from solution brought about by evaporation under arid or semi-arid conditions. The following summary is taken from FAO (2001).

Connotation. Soils with substantial secondary accumulation of lime; from L. *calcarius*, calcareous

Synonyms. Desert soil is a common international term.

Definition. Defined by FAO (2001) as soils having

1. a calcic or petrocalcic horizon within 100 cm of the surface; and
2. no diagnostic horizons other than an ochric or cambic horizon, an argic horizon which is calcareous, a vertic horizon, or a gypsic horizon.

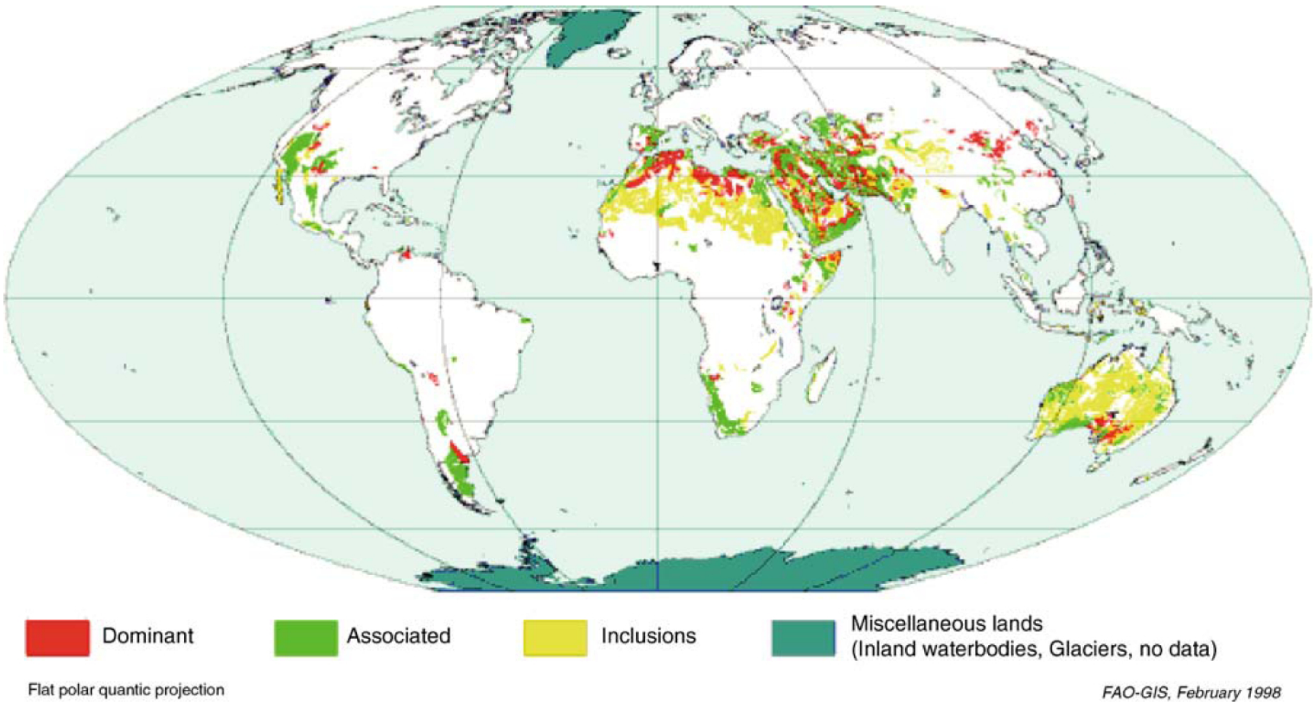


Figure C5 Distribution of Calcisols.

Parent material. Mostly alluvial, colluvial and aeolian deposits of base-rich, commonly calcareous, weathering material.

Environment. Level to hilly land in arid and semi-arid regions (see Figure C5). The natural vegetation is sparse and dominated by xerophytic shrubs and trees and/or ephemeral grasses.

Profile development. 'Typical' Calcisols have ABC or AB(t) C-profiles with a pale brown ochric surface horizon over a cambic or argic subsurface horizon. Finely textured subsurface horizons may develop some or all of the characteristics of a vertic horizon. Substantial secondary accumulation of lime occurs within 100 cm from the surface.

Origin. Solution and precipitation of calcite ($CaCO_3$) is the characteristic genetic process in Calcisols. The chemistry of this process is dealt with in the article on *Carbonates*. Commonly the surface horizon is wholly or partly de-calcified with calcite re-precipitated in a horizon of accumulation in the subsoil. Erosion, or the activities of burrowing animals, may lead to homogenization within the profile so that calcite may be re-introduced to the surface.

Use. Dryness, and in places also stoniness and/or the presence of a shallow petrocalcic horizon, limit the suitability of Calcisols for agriculture. If irrigated, drained (to prevent salinization) and fertilized, Calcisols can be highly productive under a wide variety of crops. Hilly areas with Calcisols are predominantly used for low volume grazing of cattle, sheep and goats.

Otto Spaargaren

Bibliography

FAO. 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Alkaline Soils
Biomes and their Soils
Calcareous Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles

CAMBISOLS

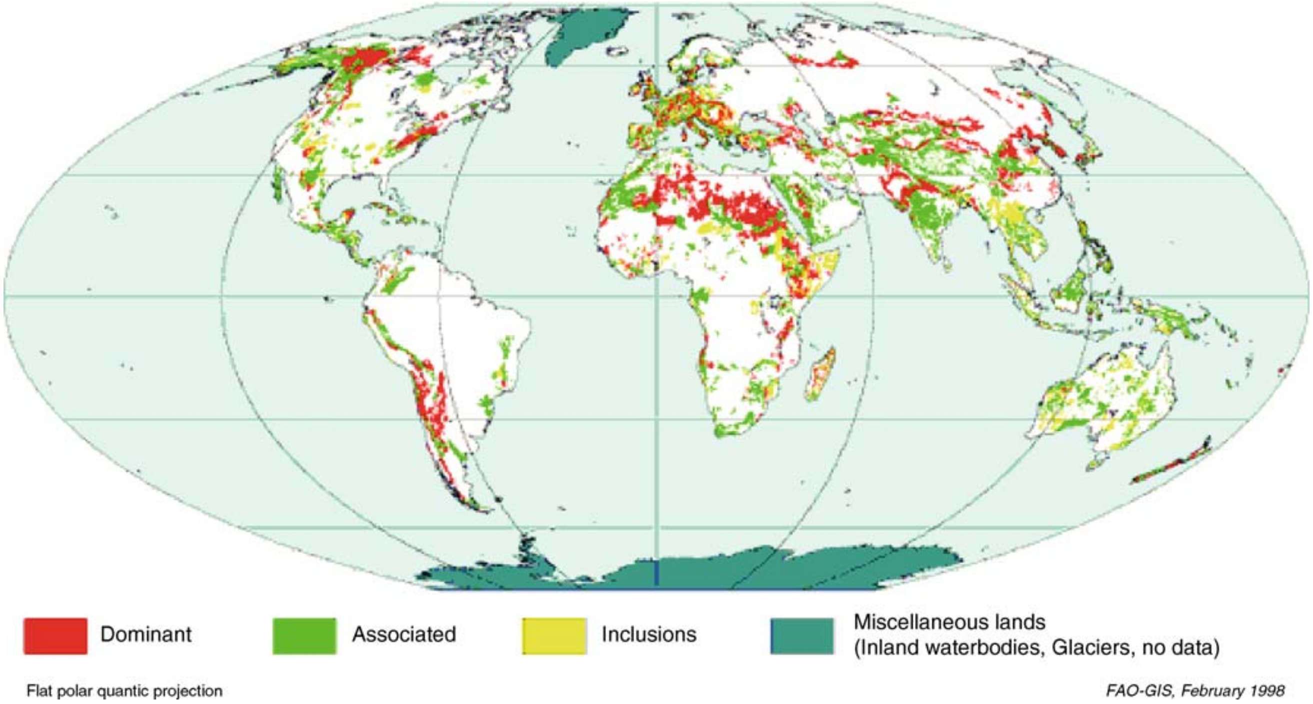
Cambisols are soils at an early (incipient) stage of soil formation. There is generally a brownish discoloration below the surface horizon, to mark the beginning of pedogenesis. The subsoil has a soil rather than a geological structure. This article is based on FAO (2001).

Connotation. Soils with beginning horizon differentiation evident from changes in color, structure or carbonate content; from L. *cambiare*, to change.

Synonyms. The name was first used in the legend to the FAO World Soil Map. The equivalent term in Soil Taxonomy is inceptisols. Other classifications use terms connoting brown soil e.g., 'Braunerde' (Germany), 'Sols bruns' (France), 'Brown soils'/'Brown Forest soils' (USA pre-Soil Taxonomy), and 'Brunizems' (Russia).

Definition. Cambisols are defined by FAO (2001) as soils having

1. a cambic horizon; or
2. a mollic horizon overlying subsoil with low base saturation within 100 cm depth; or
3. one of the following:



Flat polar quantic projection

FAO-GIS, February 1998

Figure C6 Distribution of Cambisols.

4. an andic, vertic or vitric horizon starting between 25 and 100 cm below the surface; or
5. a plinthic, petroplinthic or salic or sulfuric horizon starting between 50 and 100 cm below the soil surface, in the absence of loamy sand or coarser material above these horizons.

Soils at an incipient stage in their formation with a cambic horizon (in practice a section of the soil profile between an A horizon and a relatively unaltered C horizon, that has soil rather than a rock structure and that differs in color from that the C horizon).

Parent material. Medium and fine-textured materials derived from a wide range of rocks, mostly in colluvial, alluvial or aeolian deposits.

Profile development. ABC profiles. Cambisols are characterized by slight or moderate weathering of parent material and by absence of appreciable quantities of illuviated clay, organic matter, aluminum and/or iron compounds.

Origin. Weathering by hydrolysis is the characteristic process though it is not advanced and consequently appreciable quantities of weatherable minerals (feldspars and ferromagnesians for example) persist in the soil. Signs of incipient weathering will normally be present only in the case of primary ferromagnesian minerals, which may release iron and allow the formation of ferric hydroxides to color and coat other grains in the soil. Minor amounts of clay and gibbsite may also form, accompanied by minimal leaching of alkalies and alkine earths. Migration of Fe, Al, organic matter or clay will not be evident.

Environment. Level to mountainous terrain in all climates and under a wide range of vegetation types (see Figure C6).

Use. Used in arable farming, grazing and forestry. Cambisols are subject to the usual restrictions due to climate and topography, as well as to characteristics associated with early stages of soil formation such as shallowness, stoniness, or low base status.

Otto Spaargaren

Bibliography

FAO. 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. Soils of the World. Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles

CAPABILITY

The possibilities inherent in a soil or land in general, of being capable of conversion to a particular use. Many classifications of the capability of land for particular uses exist, and a large number are ‘pedocentric’ (Rossiter,

Otto Spaargaren

Bibliography

Rossiter, D.G., 1996. A theoretical framework for land evaluation (with discussion). *Geoderma*, **72**: 165–202.

CAPILLARY PRESSURE

Two fluids are *immiscible* if they retain a distinct phase identity when they are mixed. As a consequence of the different degrees of attraction between molecules of a different nature a tension exists at the interface, which is called *surface tension*. The surface tension σ has the dimension of a force per unit length of the interface edge (Figure C7).

If the interface between two fluids, e.g., water and air, in equilibrium is flat, the pressures (in the water and in the air) are equal. In contrast, if the interface is curved, as shown in Figure C8, there exists a pressure difference between the two phases. At equilibrium for a spherical bubble of air in water, it can be shown (e.g., Morel-Seytoux, 1969, p. 472 and Sumner, 2000, p. A69) from a consideration of balance of forces on a small element of interface (Figure C8) that

$$p_a - p_w = \frac{2\sigma}{R} \tag{1}$$

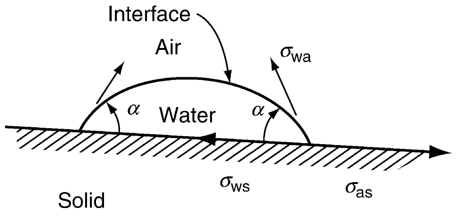


Figure C7 Surface-tension forces at fluid–fluid or fluid–solid interfaces.

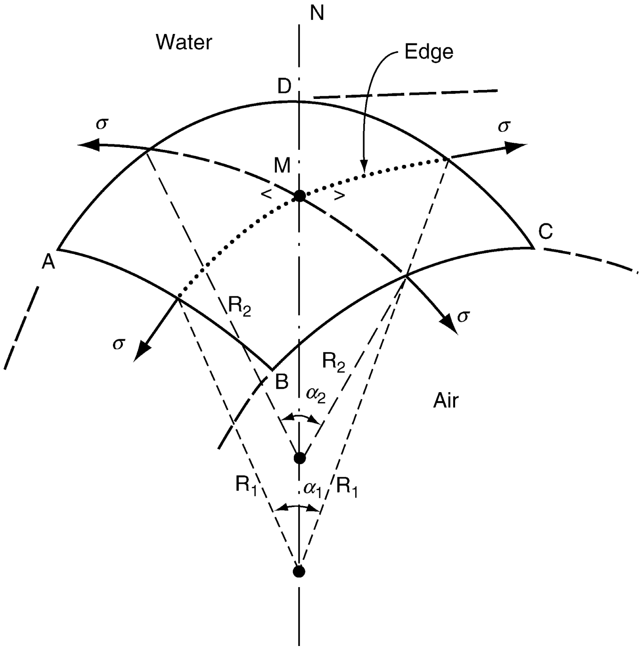


Figure C8 Capillary force equilibrium at an interface between two immiscible fluids.

where p_a is air pressure, p_w is water pressure, and R is the radius of the bubble. The difference in pressure between the fluid at the higher pressure and the fluid at the lower pressure is called the *capillary pressure* and is usually denoted by the symbol p_c. If the interface is not spherical in shape (see Figure C8), Equation (1) generalizes to a form, known as *Laplace's or Plateau's Equation*:

$$p_c = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{2}$$

where $(1/R_1) + (1/R_2)$ is the total curvature of the interface at point m, and R_1 and R_2 are the radii of the curvature of interface lines in any two mutually orthogonal normal planes at M (see Figure C8). The radii of curvatures R_1 and/or R_2 are algebraic quantities, which are positive if the center of the curvature lies within the phase at higher pressure and negative otherwise.

By definition, the capillary pressure is always a *positive* (or zero) quantity. The capillary pressure is often expressed as an equivalent water height, denoted h_c and called *capillary-pressure head*. The term "capillary pressure" is misleading because the definition of capillary pressure assumes in no way the presence of a solid wall, as introduced by a capillary. It does, however, assume the presence of two immiscible fluids. However, the presence of a solid wall may have a bearing on the *shape* of the interface and consequently a bearing on the *magnitude* of the capillary pressure.

Wettability

Just as there exists a surface tension between immiscible fluids, there exists a surface tension between a fluid and a solid. The surface tension between water and air, σ_{wa}, differs from that between water and solid material, σ_{ws}. A water drop on a glass plate tends to spread as shown in Figure C7. The contact angle α between the water–air interface with the solid at equilibrium fulfills the requirement of zero resultant force at the contact of the three phases, and consequently,

$$\cos\alpha = \frac{\sigma_{as} - \sigma_{wa}}{\sigma_{wa}} \tag{3}$$

Equation (3) is known as *Dupré or* Young's formula.

As α is less than $\pi/2$, water is said to be the *wetting* fluid while air is the *nonwetting* fluid. In contrast, the contact angle of the air–mercury interface is greater than $\pi/2$, (Figure C9), in which case air is the wetting fluid.

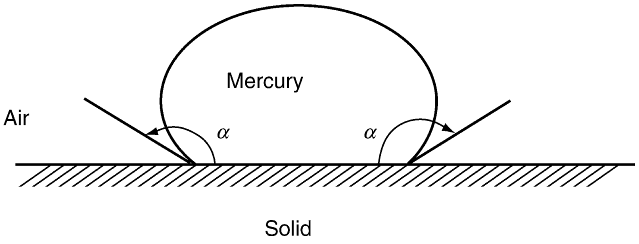


Figure C9 Contact angle of air–mercury interface.

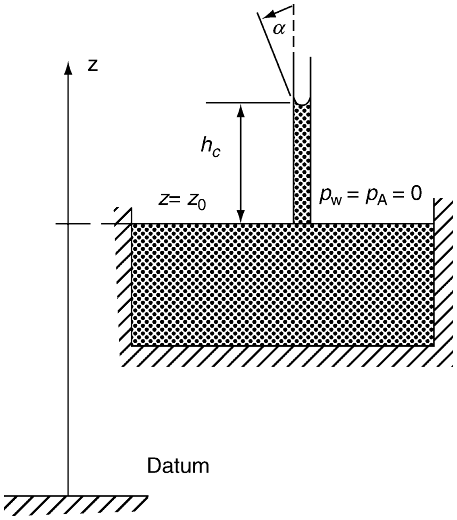


Figure C10 Capillary rise.

Capillary rise in a tube

Consider a cylindrical capillary tube with radius R vertically located in a water container in which the water level is at elevation $z = z_0$ (Figure C10). Because water wets the capillary, at equilibrium the air–water interface has the shape of a spherical meniscus concave toward the air, of total curvature $2(\cos\alpha/R)$, where α is the contact angle. According to Equation (1) since air pressure is atmospheric, the water pressure is

$$p_w = p_A - \frac{2\sigma\cos\alpha}{R}$$

where p_A is atmospheric pressure. If atmospheric pressure is used as a reference pressure, then the water (gauge) pressure at the interface is negative, i.e., less than atmospheric; in other words, the water is under *suction*. As a result of this imbalance, the water rises in the capillary tube up to an equilibrium level $h_c + z_0$. At hydrostatic equilibrium the total head of water must be constant; thus

$$\phi = \frac{p_w}{\rho_w\, g} + z$$

where ρ_w is specific mass of water, and g is the acceleration of gravity. As the water (gauge) pressure is zero at $z = z_0$, it follows that $\phi = z_0$ everywhere in the water phase. Consequently, at the meniscus level, one must have:

$$\frac{p_w}{\rho_w g} + z = -\frac{p_c}{\rho_w g} + h_c + z_0 = z_0$$

or

$$h_c = \frac{p_c}{\rho_w g} = \frac{2\sigma\cos\alpha}{R\gamma_w} \tag{4}$$

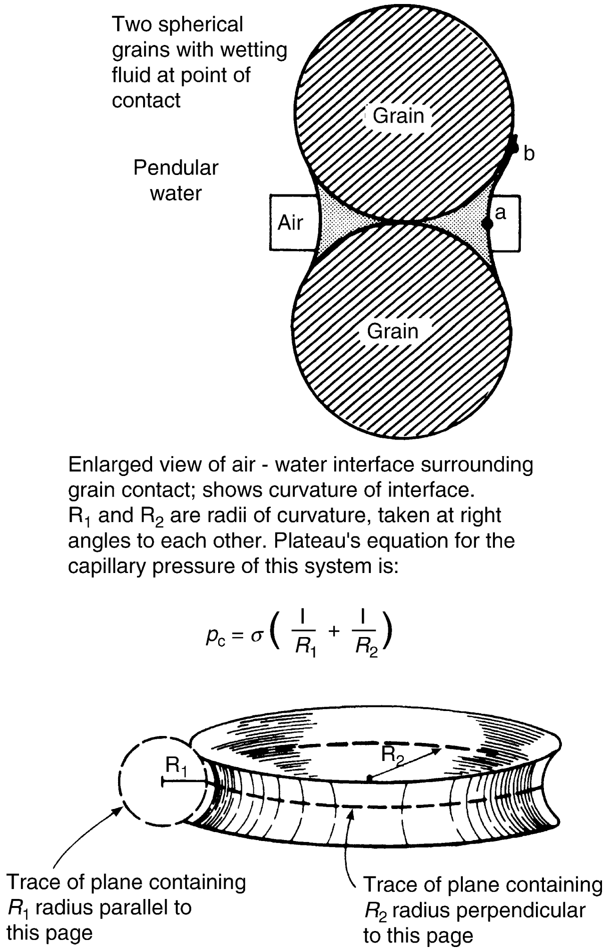
where $\gamma_w = \rho_w g$ is the specific weight of water. Equation (4) is usually referred to as the *capillary rise equation*.

Capillary head in unsaturated porous media

It is customary to view an unsaturated soil as consisting of capillary "pores" in which menisci separate the two phases. This viewpoint is usually valid in granular soils at sufficiently large moisture contents where forces in the water body other than those due to individual fluid pressure, surface tension, and gravity can be neglected. At equilibrium it is assumed that for a given (macroscopically uniform) water content, the air–water interfaces have the same constant total curvature throughout the porous medium. Soil scientists traditionally define this state by the *capillary head*, $\psi = -P_c/\gamma_w$ which is the *negative* of the *capillary pressure head* defined previously. The total (hydraulic) head is thus

$$\Phi = \psi + z \tag{5}$$

Clearly at low water contents and with soils of fine texture such as clays, the major fraction of the water content in the medium is distributed in thin films covering the solid matrix. In such cases the interaction between the water–air interface and the water–solid interface must be considered, and the simple *mechanical* model for capillary pressure is no longer valid. This latter conclusion can be understood visually from a description of the microscopic and macroscopic geometry (Figures C11 and C12). Consider two wetted soil particles covered with thin, yet observable, films of water (Figure C11). So-called pendular (Stallman, 1964) water exists between the two soils particles. In one region (point *a* of Figure C11), the total curvature is positive; hence p_c is positive. In another region (point *b*), the overall curvature is negative, yielding a negative value of p_c. At equilibrium the air pressure is constant, and based on the capillary geometrical mechanical model, the water pressure would be of different signs around each soil particle. As the water phase is continuous and in equilibrium, it is clear that *other* forces must compensate for this pressure difference in the water and maintain the equilibrium.



Enlarged view of air - water interface surrounding grain contact; shows curvature of interface. R_1 and R_2 are radii of curvature, taken at right angles to each other. Plateau's equation for the capillary pressure of this system is:

$$p_c = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Figure C11 Geometry of capillary equilibrium.

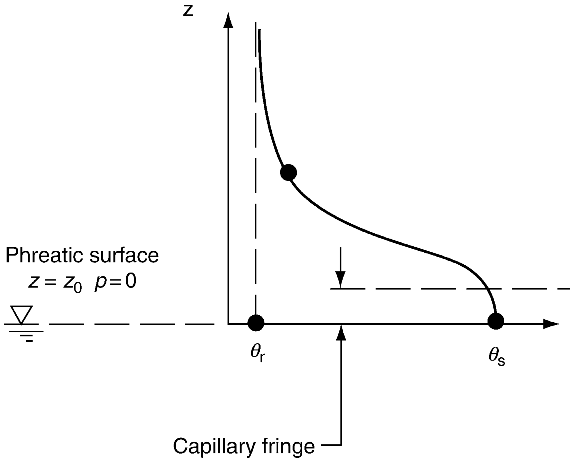


Figure C12 Capillary pressure versus water content.

Figure C12 displays a profile of water content θ above a water-saturated medium at rest. Above the water table (*phreatic* surface) at $z = z_0$, the water content gradually decreases with elevation. Immediately above the water table the rate of change of water content with elevation, $d\theta/dz$, is negligible. As elevation rises, $d\theta/dz$ gradually decreases to an inflection point and then increases again toward zero as the water content approaches θ_r, the *residual* water content. This low residual value of water content may be observed at more than several hundred meters above the phreatic surface. As water is in equilibrium throughout the soil, the total head Φ is also constant and equal to z_0. If Equation (2) were generally valid, then the pressure of water at the low water contents would be less than 10 atm. Actually, suction in water cannot exceed 0.7 atm, which shows that the mechanical model of capillary pressure is not generally valid. It is possible, however, to apply Equation (5) for the saturated–unsaturated soil profile with ψ representing the cumulative effect of pressure and other *unspecified* (though effective) factors. The value of ψ for a given equilibrium water content is determined from the total head equation, for Φ equals constant, yielding

$$\psi = -(z - z_0) \tag{6}$$

where z is the elevation of the given water content. For convenience, soil scientists continue to refer to ψ as the "capillary head."

The dependence of ψ on the water content – sometimes called the *water-retention* curve – is an important soil characteristic because it indicates physical properties of the soil such as texture and structure and determines the water availability for plants under various boundary conditions. Figures C13 and C14 show $\psi(\theta)$ curves for sands and silt loam and for heavy soils. The difference between the two extreme types is considerable: (1) the porosity generally increases as the soil texture gets finer. While sand particles function as independent units, fine-texture soils tend to develop structure with different

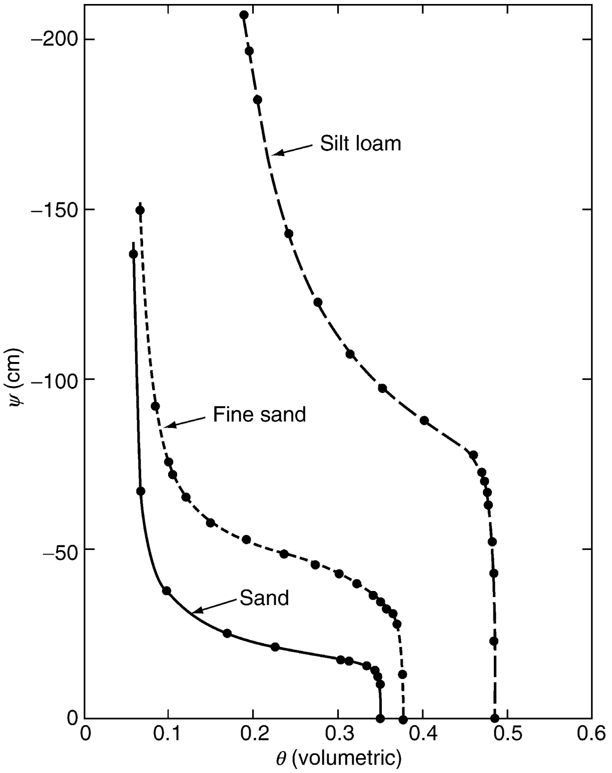


Figure C13 Water-retention curve for sand, fine sand, and silt loam (after Brooks and Corey, 1966).

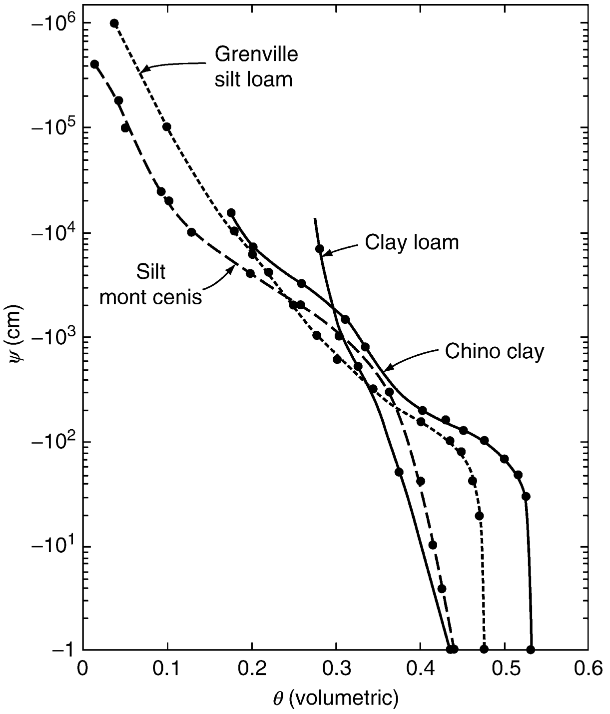


Figure C14 Water-retention curves for heavy soils: Grenville silt loam (Staple, 1965); Silt mont cenis (Vachaud, 1966); Clay loam (Bruce, 1972) and Chino clay (Gardner, 1959).

degrees of stability. Small particles adhere together with the aid of colloidal material to create greater particles, called *aggregates*, with greater pore space between them. Hence the observed water content at $\psi = 0$ in heavy soils is greater than in sandy soils. (2) Sands usually have a minimum critical value of ψ (in absolute value), which must be exceeded before a reduction in water content can be observed. Thus for $\psi_{\mathrm{cr}} \leq \psi \leq 0$, θ remains essentially constant at the saturated value, θ_{s}. At this value of $\psi = \psi_{\mathrm{cr}}$, air starts to penetrate into the soil, and for this reason it is also called the *air-entry value*. Soils of very fine texture have no clear air-entry value because reduction of the water content occurs first as a result of compression of the soil while it is still saturated with water. (3) The $\psi(\theta)$ curve of granular soils displays an abrupt drop in water content within a small range of decrease in ψ. It occurs at a relatively high value of ψ ($\psi > -100$ cm of water). From the mechanical capillary perspective, the implication is that sands have a narrow *pore*-size distribution (*q.v.*). On the other hand, for soils of fine texture the capillary pores represent only a small portion of the total void volume. Even at relatively high water contents, most of the water lies in thin films covering the solid particles. Strong forces hold this film water to the soil, and high energy is required to extract it. The rate of change of water content with ψ is very small, and the effective range of values of ψ may be as low or even lower than –150 m of water. The residual water content (also called the *irreducible water content*) at low values of ψ, where $\mathrm{d}\theta/\mathrm{d}\psi$ tends to zero, is much greater in heavy soils (as high as 20%) than in sands (usually less than 6%).

The shape of the $\psi(\theta)$ curve is affected by both soil and fluid properties. Beside the factors previously mentioned – namely, soil texture, structure, and interface contact angle – other factors play a significant role. These are: the type of soil minerals, the composition and amount of the organic fraction, the chemical components of the fluids considered, the temperature, and the history of the process. The process history is very important and is thus discussed thoroughly in a succeeding section headed “capillary hysteresis.”

The water-retention curves $\theta(\psi)$ are determined experimentally. No theory has yet been developed that is accurate or simple enough to derive analytically the $\theta(\psi)$ curve. There is, however, value in fitting the observed data by analytical expressions. Such analytical yet empirical expressions serve two purposes: (1) They permit solutions to unsaturated-flow problems in closed form, and (2) they eliminate the truncation errors introduced in the estimation of ψ and $\mathrm{d}\psi/\mathrm{d}\theta$ in numerical solutions. A variety of expressions have been proposed in the literature. The simplest one is the power function:

$$\psi = a\,\theta^{-n} \tag{7}$$

where a and n are adjustable parameters. Equation (7) can be modified to account for air-entry value and residual water content in the form

$$\begin{aligned} \theta(\psi) &= \theta_{\mathrm{s}} \qquad \text{for} \quad \psi > \psi_{\mathrm{cr}} \\ \psi &= S_{\mathrm{e}}^{-n} \qquad \text{for} \quad \psi < \psi_{\mathrm{cr}} \end{aligned} \tag{8}$$

where

$$S_{\mathrm{e}} = \frac{\theta - \theta_{\mathrm{r}}}{\theta_{\mathrm{s}} - \theta_{\mathrm{r}}}$$

is called the *effective saturation*. For $\theta(\psi)$ curves with monotonically decreasing slope, a similar expression is used:

$$S_e = \frac{a}{a + \psi^n} \tag{9}$$

Two other expressions are respectively of exponential nature, namely

$$\begin{aligned} \theta &= \theta_s & \psi &\geq \psi_{cr} \\ S_e &= e^{\alpha(\psi - \psi_{cr})} & \psi &< \psi_{cr} \end{aligned} \tag{10}$$

or logarithmic, namely

$$\begin{aligned} \theta &= \theta_s & \psi &\geq \psi_{cr} \\ S_e &= 1 - \frac{\ln(\psi - \psi_{cr} + 1)}{\ln(\psi_{15} - \psi_{cr} + 1)} & \psi &< \psi_{cr} \end{aligned} \tag{11}$$

Equation (11) mixes dimensional and dimensionless terms and as a result can be used only if ψ is expressed in centimeters of water.

None of these analytical curves except that defined by Equation (9) has an inflection point and can be accurately adjusted only to the experimental curves for a limited range of ψ or θ values. More flexible and realistic expressions can be derived such as

$$\psi = a\,\theta^n(\theta_s - \theta)^m \tag{12}$$

$$S_e = a\,\frac{\cos\,h\left[\left(\frac{\psi}{\psi_0}\right)^n + b\right] - c}{\cos\,h\left[\left(\frac{\psi}{\psi_0}\right)^n + b\right] + c} \tag{13}$$

where a, b, c, n, and ψ_0 are adjustable parameters (King, 1964), or any combination of the more elementary functions mentioned previously. These latter expressions are of limited value, however, as the amount of work required for adjustment is considerable, and they are too complicated to be used in the derivation of closed analytical solutions. The most commonly used soil water retention model was developed by van Genuchten (1980). For a detailed review and references, see Mualem and Dagan (1976) and Kosugi et al. (2002).

Experimental determination of capillary head

There are a variety of ways to measure the capillary head in a soil. One method determines directly the pressure difference between air and water and the corresponding water content in the soil. Suppose a rock (or soil) sample, completely saturated with water at atmospheric pressure, is placed in contact along a fraction of its surface with air. Pressure in the air phase is increased and remains constant. A certain volume of air penetrates the core and expels a corresponding amount of water, which is measured.

The air is retained in the porous medium by a semipermeable membrane that transmits the displaced water but not the air. Ultimately a no-flow condition is established. Due to the expulsion of a certain volume of water, the remaining water fills up only a fraction of the total pore space. (The fraction of the total pore volume occupied by water is called the *water saturation*.) Pressure in the air is increased again. When equilibrium is reached, a new and lower equilibrium water saturation prevails in the core. Ultimately, repeating the operation successively (and patiently), a curve of capillary head versus water saturation or water content is obtained (Figure C15). Because water was drained from the core in the procedure, the curve so obtained is labeled “drainage” or “drying curve.” Because the core was initially *fully* saturated (no air present at all), the curve is labeled “first draining curve.”

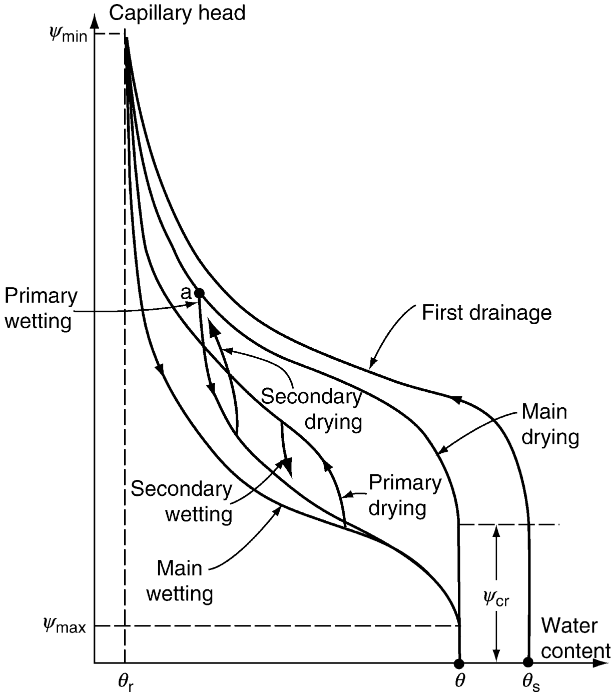


Figure C15 Nomenclature of capillary hysteresis.

It is found experimentally that a point is reached when even a tremendous increase in capillary pressure no longer induces a saturation change. The water saturation is said to have reached its irreducible, or residual, value. The concept of irreducibility is relative to the process. For example, the residual water saturation could be reduced further by placing the core in an oven at an elevated temperature.

Capillary hysteresis

Once residual water content has been established in the core by displacement by air, the *imbibition*, or *wetting*, curve can be obtained by letting the pressure drop stepwise and water imbibe back. *Imbibition* (*q.v.*), or wetting, are the terms used if the water content increases with time. However, a different curve is obtained (Figure C15), which implies that given a water content, several equilibrium states are possible depending on previous history. The capillary-pressure curve is said to display *hysteresis*. By the time the capillary pressure has returned to the zero value, all the air has not been expelled. A fraction of it has been trapped, the residual air content. This imbibition curve is referred to as the “main wetting curve.” If the soil is drained again, the main drying curve is described. If the process is reversed before the capillary head has reached the value ψ_{min} (point *a* on Figure C15), a primary wetting curve is described. But if the process is reversed only after the value ψ_{min} has been reached, then the main wetting curve is described again. The main drying and main wetting curves form the *main hysteresis loop*. Depending on the location of the reversal point in the process of successive wetting and drying, the described curves are referred to as “primary,” “secondary,” “tertiary,” etc.

The observed capillary hysteresis results from the cumulative effects of several factors. Probably the most important one is the geometry of the porous system. Let us adopt the mechanical capillary-pressure model discussed earlier. Under these conditions it is possible to depict different porous-matrix geometries that lead to hysteresis. They have in common the existence of cavities with converging and diverging walls. The isolated pores so constructed are connected by narrow channels, which permit *different* configurations of the interface at equilibrium for the *same* value of ψ. Figure C16 displays a pore with two degrees of filling, yet with the same curvature radius for the interface and consequently the same capillary head. Figure C17 displays another type of geometry that causes hysteresis (the "ink-bottle" effect), as the same curvature can exist with various degrees of filling of the void space.

A second effect is the hysteresis of the contact angle α. As stated previously in the discussion of the capillary rise in a capillary tube, the capillary pressure depends on the contact angle according to the formula

$$p_c = \frac{2\sigma}{r}\cos\alpha \qquad (14)$$

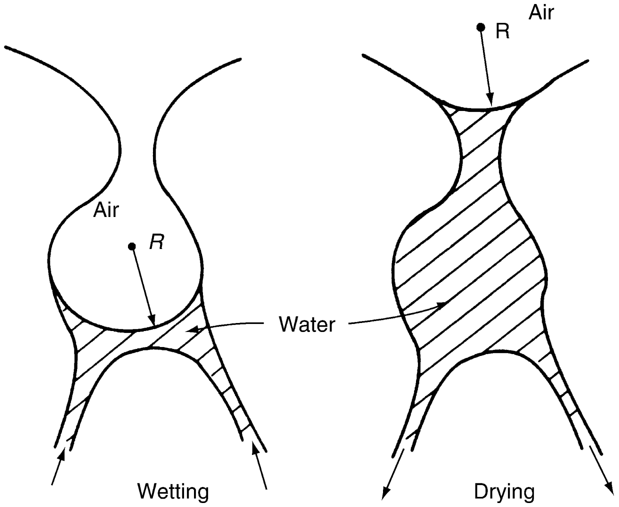


Figure C16 Different degrees of saturation for the same capillary pressure.

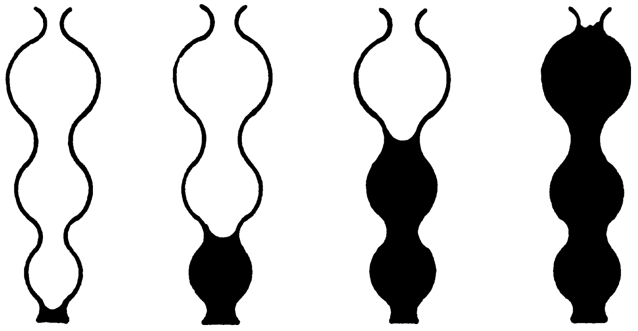


Figure C17 The "ink-bottle" effect.

In general, the wetting angle is not constant. It reaches its maximum value when water (or more general a liquid) moves toward a dry surface and takes it's minimum value when it recedes. This phenomenon can be observed visually in the process of filling and emptying a capillary tube (Figure C18). As a result of this wetting angle hysteresis, a row consisting alternately of air bubbles and of water drops can maintain rest against a significant pressure drop between the two ends of a tube (Figure C19).

Entrapment of air during the imbibition (or wetting) process is another important factor. The appreciable difference between

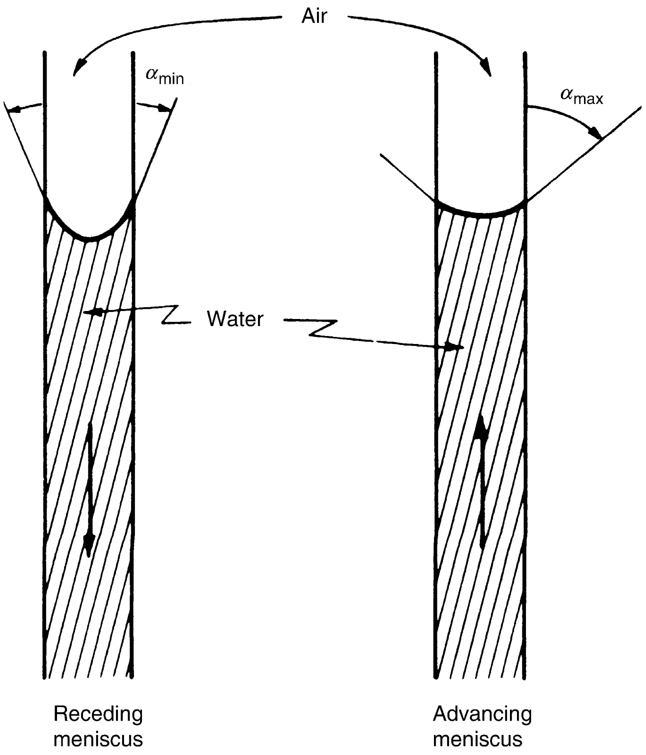


Figure C18 Hysteresis of wetting angle.

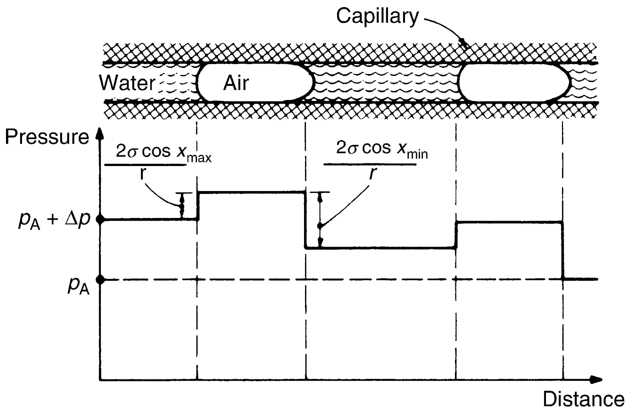


Figure C19 Equilibrium induced by a series of wetting-angle hysteresis.

the first drainage (or drying) curve (abbreviated F.D. curve) and the main drying (M.D.) curve displayed on Figure C15 is the direct result of this air entrapment. This entrapment may be explained in a simple way by the closing of narrow entrances of pores or groups of pores by the wetting fluid in a slow wetting process. The air content in the sample varies with time as air dissolves in water and moves away by diffusion. It is a known fact that if ψ is kept constant for a long time, the water content increases as air disappears from the soil (Bloomsburg and Corey, 1964).

Comparisons of numerical studies of water redistribution in soils, including or excluding the hysteretic effects, have shown that the profiles differ substantially. In the presence of hysteresis higher water contents prevail in the upper part of the soil, and wetting of the lower part is delayed. This delay in the drainage rate enhances the evaporation from the soil surface. For a detailed review and references, see Mualem and Dagan (1972).

Theory of capillary hysteresis

The fundamental theory of hysteresis based on the "independent domains" concept was initiated by Preisach (1935) and Néel (1942–1943) and thoroughly analyzed by Everett and his coworkers (1952–1955) and Enderby (1955). According to this theory a porous medium is viewed as a system consisting of independent elementary pore domains. Each domain is characterized by two length scales, ρ and r, which can be interpreted geometrically as the radius of the pore and the radius of its constricted connection with other pores, respectively. Using the capillary law ($\psi \sim a/R$), the variables ρ and r can be uniquely related to the wetting and drying capillary head ψ_w and ψ_d, respectively. The pore domain has therefore only two stable states, either empty or full (Figure C20). In a wetting process, the pore is empty until ψ reaches the value ψ_w at which time it flips over to a filled state. There is no change in water content of the pore when ψ is increased further. In drainage the pore remains water filled until ψ takes to value of ψ_d. At this point the pore is totally drained. The elementary pore domain displays hysteresis. It is assumed that these properties are independent of the states of the neighboring pores. Denoting ΔV as the pore volume and taking ψ_w and ψ_d as independent variables continuously distributed between ψ_{min} and ψ_{max}, it is possible to define a pore-water density distribution function

$$f(\psi_d, \psi_w) = \frac{\Delta V(\psi_d, \psi_w)}{V} \tag{15}$$

where V is the total volume of the sample. Now $f(\psi_w, \psi_d)\mathrm{d}\psi_w \mathrm{d}\psi_d$ represents the relative pore volume which is filled at ψ_w and drained at ψ_d due to differential changes $\mathrm{d}\psi_w \mathrm{d}\psi_d$. Essentially, $f(\psi_w, \psi_d)$ is positive with $\psi_w \geq \psi_d$. Figure C21b and C21c show the diagram of the filled-pore domains, "Néel diagrams," at a given θ for the main wetting and the main drying processes.

Assuming that the independent-domains theory applies conceptually, it is possible to relate the measurements of ψ and θ to the pore-water density function f. It is customary to operate with finite differences and to define approximately the integral function $F(\psi_{wi}, \psi_{dj}) = f(\psi_{wi}, \psi_{dj})\Delta\psi_w \Delta\psi_d$, which permits calibration of the model on the basis of a family of either primary wetting or primary drying scanning curves.

This model has been experimentally tested for a wide variety of soils and glass-beads samples. While the theory held for some samples, in most cases discrepancies between the measured and the predicted $\theta(\psi)$ curves were observed. Poulovassilis (1962, 1970a) found a good agreement between the predicted and the measured scanning curves for glass beads and sand. Other investigators reported considerable discrepancies between the theory and observations; Topp and Miller (1966), Morrow and Harris (1965), and Bomba and Miller (1967)

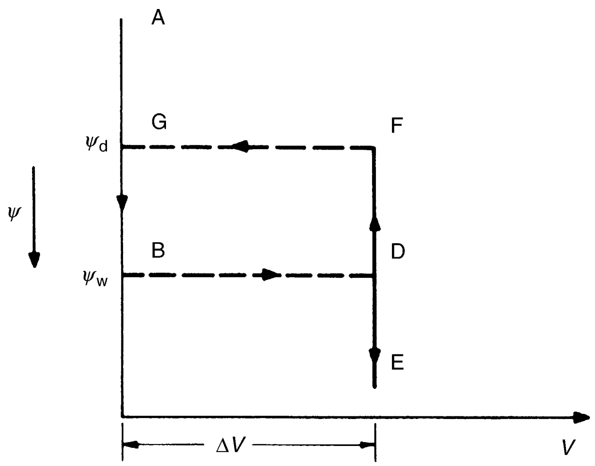


Figure C20 Hysteretical behavior of the isolated pore domain.

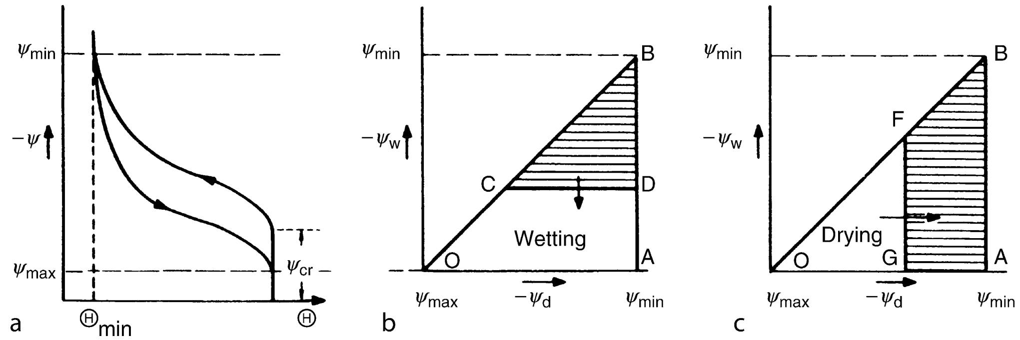


Figure C21 (**a**) Schematic representation of capillary hysteresis. (**b**) Filled-pore diagram (*shadowed region*) for the main wetting process. (**c**) Filled-pore diagram for the main drying process (after Mualem, 1973).

observed discrepancies for glass-beads medium; Vachaud and Thony (1971), Talsma (1970), and Poulovassilis and Childs (1971) observed them for sand; Topp (1969, 1971a) observed them for various loam soils. It seems that the measured discrepancies are due partly to the method of measurement because the poorest agreement between theory and measurements has been observed for unsteady-flow experiments. The main problem, however, stems from the fact that the computed pore-water distribution function derived in this method becomes negative in part of the (ψ_w, ψ_d) domain, in contradiction to its basic definition. As a result, part of the predicted scanning curves are depicted outside the main loop and sometimes indicate a process opposite to the actual one, namely, drainage instead of wetting and vice versa. This phenomenon is intensified when a considerable region of the hysteretical domain is observed within the range (0, ψ_{cr}) and when the sample is dried to a lower water content θ_{min}, close to θ_r.

Mualem (1973), following Philip's (1964) approach, suggested a modified variant of the independent-domain theory. This model used a similarity hypothesis, according to which the pore-water distribution function $f(\psi_w, \psi_d)$ is represented as a product of two independent distribution functions, $h(\psi_w)\ell(\psi_d)$. This hypothesis considerably simplifies the computational procedures. Only the measured boundary curves are required for the calibration of the model, and the scanning curves are expressed analytically. Moreover, the modified model is better adapted to

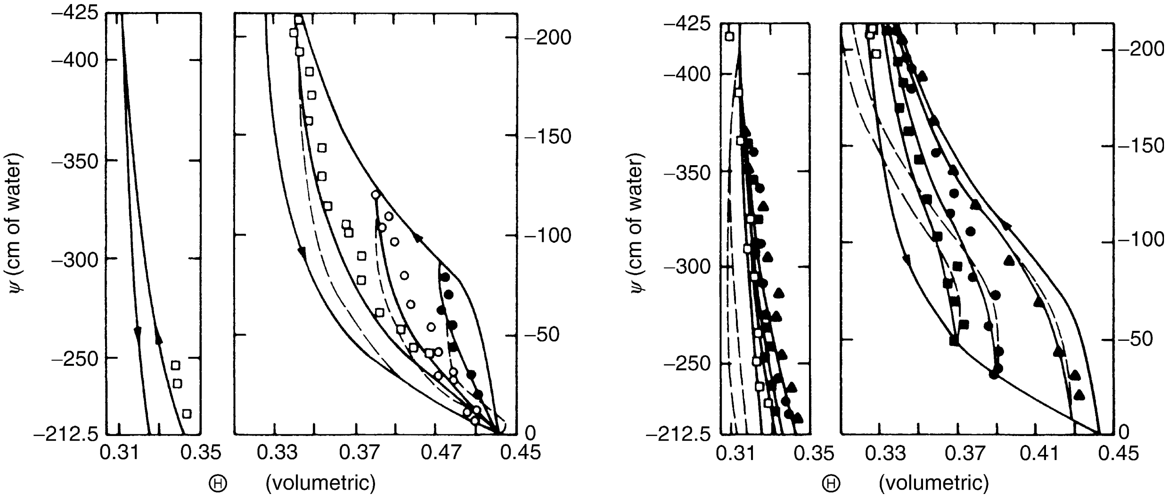


Figure C22 Scanning curves predicted by the usual Néel-Everett model (*dashed line*), by model I (*solid line*), and the measured data for Caribou silt loam (*points*) (after Mualem, 1973).

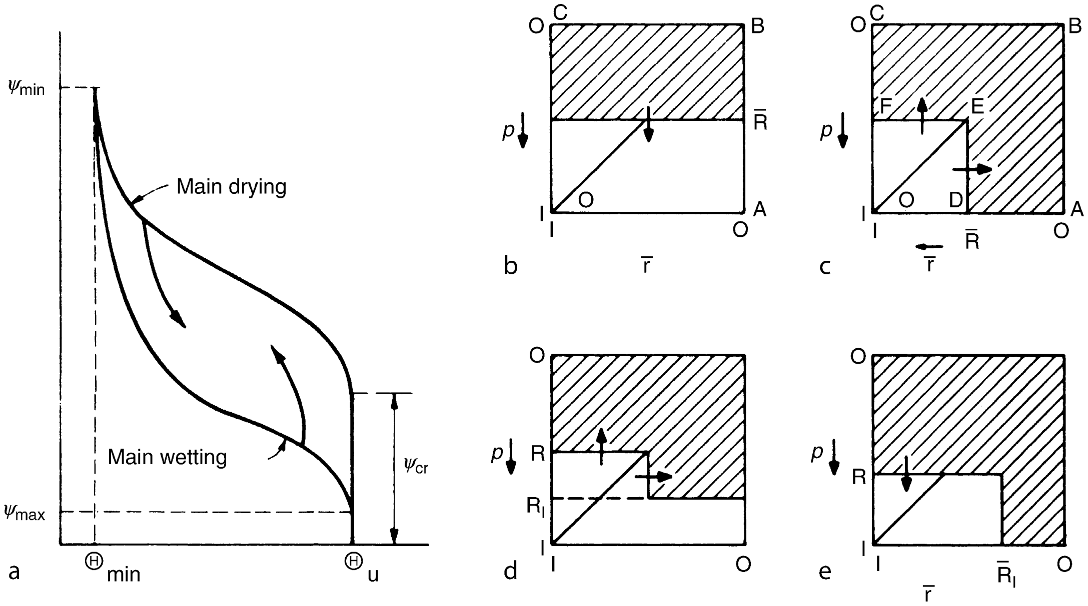


Figure C23 (**a**) Schematic representation of capillary hysteresis and the filled-pore diagrams in the (unknown) $r\rho$ plane (the *shaded domains*) for (**b**) the main wetting process, (**c**) the main drying process, (**d**) the primary drying process, and (**e**) the primary wetting process (after Mualem, 1974).

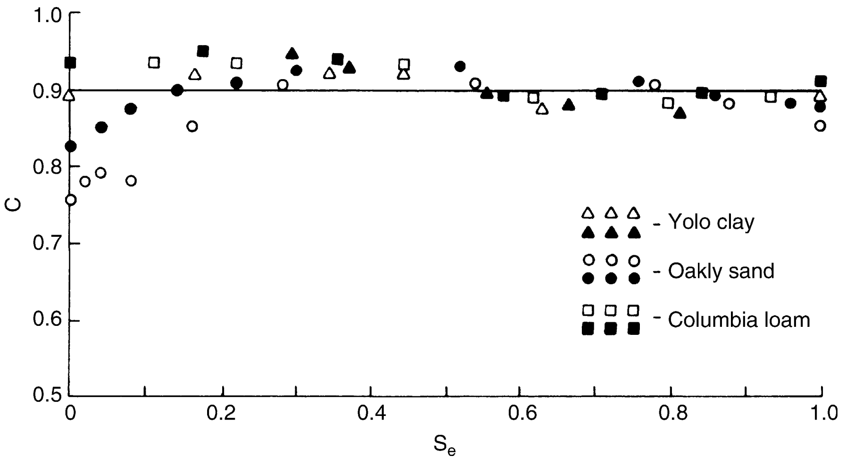


Figure C24 The function $C(S_e)$ for three soils measured after several cycles of imbibition and drying. The *hollow symbols* denote results in the wetting process, and the *solid symbols* denote measurements in the drying process (after Mualem, 1974).

the independent-domain principles (Figure C22) as the computed poredistribution function is always positive. As a result, the predicted $\theta(\psi)$ curves are in better agreement with observations than those derived by using the original Néel-Everett model.

A more flexible independent-domain theory, which accounts also for a reversible contribution of the pore domains to the wetting and drying processes, has been suggested by Mualem (1974). This model is underlain by three basic assumptions:

- The two parameters r and ρ, characterizing a pore volume of the porous medium, vary in the whole range between $R_{\min}$ and $R_{\max}$ (which correspond to $\psi_{\min}$ and $\psi_{\max}$, respectively, by the capillary law $R \sim 1/|\psi|$). After the normalization, that is,

$$\bar{r} = \frac{r - R_{\min}}{R_{\max} - R_{\min}} \qquad \bar{\rho} = \frac{\rho - R_{\min}}{R_{\max} - R_{\min}} \tag{16}$$

  the pore-volume distribution function $f(\bar{r}, \bar{\rho})$ is defined in the square *OABC* of Figure C23.
- In a wetting process under a change from $\psi(\bar{R})$ to $\psi(\bar{R} + d\bar{R})$ pores characterized by $\bar{R} \leq \bar{\rho} \leq \bar{R} + d\bar{R}$ are filled, while in drainage when ψ diminishes from $\psi(\bar{R})$ to $\psi(\bar{R} - d\bar{R})$, only the pores characterized by $\bar{R} - d\bar{R} \leq \bar{\rho} \leq \bar{R}$ and $\bar{R} \leq \bar{r} \leq 1$ are drained. Diagrams of the filled-pore domains in the $\bar{r}, \bar{\rho}$ plane (corresponding to four different processes) are given in Figure C23.
- The simplifying similarity hypothesis

$$f(\bar{r}, \bar{\rho}) = h(\bar{r})\ell(\bar{\rho}) \tag{17}$$

is adopted.

The effective water content θ is subsequently defined as

$$\theta = \Theta - \Theta_{\min} \tag{18}$$

where Θ and $\Theta_{\min}$ are the actual and the residual water content. Two integral distribution functions are defined as

$$L(\bar{R}) = \int_0^{\bar{R}} \ell(\bar{\rho})\mathrm{d}\bar{\rho} \quad H(\bar{R}) = \int_0^{\bar{R}} h(\bar{r})\mathrm{d}\bar{r} \tag{19}$$

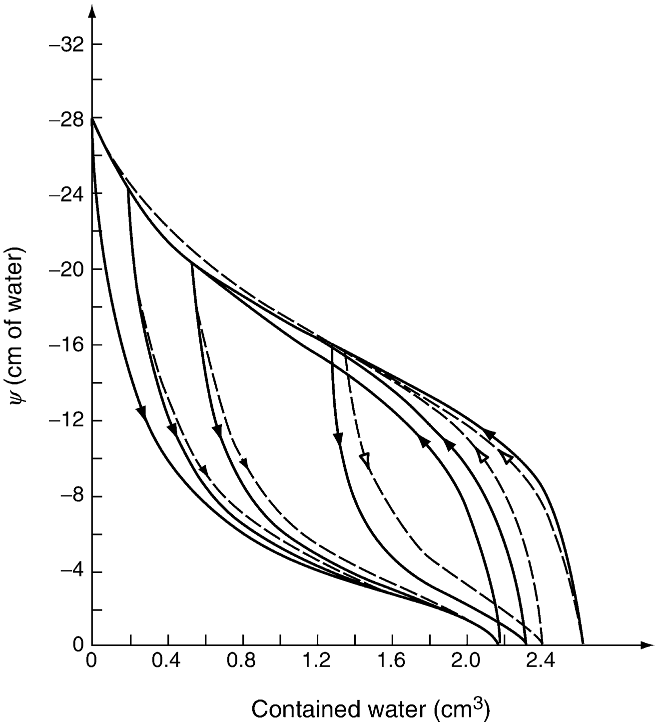


Figure C25 Measured hysteretic curves outside and inside the main loop (*solid lines*) and the predicted curves using model II (*dashed lines*) for glass-beads sample (after Mualem, 1974).

The effective water content in the main wetting process $\theta_w(\bar{R})$ is determined by the integration of $f(\bar{r}, \bar{\rho})$ over the corresponding region of the filled pores (Figure C23b):

$$\theta_w(R) = L(\bar{R})H(1) \tag{20}$$

and similarly, in the main drying process (Figure C23)

$$\theta_d(\bar{R}) = L(\bar{R}) + [L(1) - L(\bar{R})]H(\bar{R}) \tag{21}$$

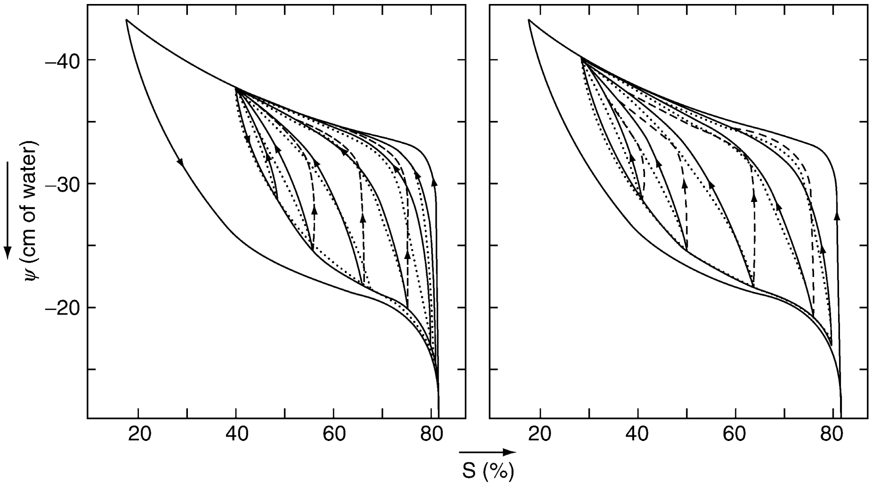


Figure C26 Two families of secondary drying scanning curves predicted with model III (*solid lines*), computed with model II (*dashed lines*), and measured (*dotted lines*) for the glass bead sample (after Mualem and Dagan, 1975).

Choosing $H(1) = 1$ and realizing that there is a unique relationship between $(\bar{R})$ and ψ, we may express H and L as functions depending directly on ψ by

$$L(\psi) = \theta_{\mathrm{w}}(\psi) \tag{22}$$

$$H(\psi) = \frac{\theta_{\mathrm{d}}(\psi) - \theta_{\mathrm{w}}(\psi)}{\theta_{\mathrm{u}} - \theta_{\mathrm{w}}(\psi)} \tag{23}$$

Once $L(\psi)$ and $H(\psi)$ are determined from the two measured boundary curves of a given soil, any hysteretic path is described afterwards in a simple way with the aid of these two basic functions. For instance, the water content along a primary drying scanning curve (obtained by integrating $f(\bar{r}, \bar{\rho})$ over the region of filled pores of Figure C23d is given by

$$\theta\begin{pmatrix} & \psi_1 \\ \psi_{\min} & \psi \end{pmatrix} = \theta_{\mathrm{w}}(\psi) + H(\psi)[L(\psi_1) - L(\psi)] \tag{24}$$

while the primary wetting scanning curve (Figure C23e) is given by

$$\theta\begin{pmatrix} \psi_{\max} & \psi \\ & \psi_1 \end{pmatrix} = \theta_{\mathrm{w}}(\psi) + [\theta_{\mathrm{u}} - L(\psi)]H(\psi_1) \tag{25}$$

This new model considerably facilitates the computational work as $H(\psi)$ and $L(\psi)$ are very simply related to $\theta(\psi)$ on the main boundary curve. Theory has been extended further to account for the entrapment of air. Using Cary's (1967) experiments, it was found that the entrapped air content constitutes a constant fraction of the water content. Figure C24 shows that the factor $c = \theta_{\mathrm{w}}/(\theta_{\mathrm{w}} + \theta_{\mathrm{a}})$, where θ_{a} is entrapped air content, is approximately 0.9. On this basis it was assumed that by rewetting a sample that was previously drained starting from saturation, a well-defined quantity of air is trapped. Moreover, it is assumed that subsequent drying and wetting cycles do not cause additional entrapment. This hypothesis permits predicting the first drying curve and any other scanning curves branching from it (Figure C25). The agreement between the forecast $\theta(\psi)$ relationships and observations is quite satisfactory. It should be noted that this theory permits using the first drying curve and the main wetting curve, solely, for calibration of the model. This way, less experimental work is required while theory applies to the whole hysterectical domain.

In some cases, for soils having a narrow pore size distribution with a major portion of the hysteretic loop in the range of air-entry value or when the soil is drained to a very low water content, the independent-domain models are not really satisfactory. In these cases the pore interaction effects are significant. Everett (1967) and Topp (1971b) suggested a dependent-domain theory, which accounts for pore blockage against air entry near saturation and air blockage against water entry at low water content. While this theory leads to better agreement with observations, Topp's procedure is laborious and requires a large amount of measured data, comprising sets of both drying and wetting families of scanning curves. Poulovassilis and Childs (1971) suggested another dependent-domain model. This model, however, requires even more experimental data.

Mualem (1974, 1976) and Mualem and Dagan (1975) generalized Mualem's model previously discussed to incorporate the fundamental ideas of Everett and Topp. The computational procedure requires one primary drying scanning curve and one primary wetting scanning curve in addition to the boundary loop to determine the two functions corresponding to water and air blockage. They concluded that in most cases pore blockage against air entry is of lesser significance and can be disregarded to simplify computation. The generalized theory, however, significantly improves the prediction when the effect of the pore blockage against air entry is considerable (Figure C26). Thus the new models attain a high degree of generality and capability of representing observed phenomena more accurately.

Hysteretical phenomenon is observed also in the $K(\theta)$ and the $K(\psi)$ relationship. The subject is discussed under the title *Permeability*.

Y. Mualem and H. J. Morel-Seytoux

Bibliography

Bloomsburg, G.L., and Corey, A.T., 1964. Diffusion of entrapped air from porous media. *Hydrology Paper 5.* Fort Collins: Colorado State University.

Bomba, S.J., and Miller, E.E., 1967. Secondary-scan Hysteresis in Glass-bead Media. Preprint for presentation in the discussion section of the 1967 Meeting of the Soil Science Society of America, 62 pp.

Brooks, R.H., and Corey, A.T., 1964. Hydraulic properties of porous media. *Hydrology Paper 3.* Fort Collins: Colorado State University, 27p.

Bruce, R.R., 1972. Hydraulic conductivity evaluation of the soil profile from soil water retensions. *Soil Sci. Soc. Am. Proc.*, **36**: 555–560.

Cary, J.W., 1967. Experimental measurements of soil moisture hysteresis and entrapped air. *Soil Sci.*, **104**: 174–180.

Enderby, J.A., 1955. The domain model of hysteresis. 1. Independent domains. *Faraday Soc. Trans.*, **51**: 835–848.

Everett, D.H., 1954. A General approach to hysteresis. 3. A Formal treatment of the independent domain model of hysteresis. *Faraday Soc. Trans.*, **50**: 1077–1096.

Everett, D.H., 1955. A general approach to hysteresis. 4. An alternative formulation of the domain model. *Faraday Soc. Trans.*, **51**: 1551–1557.

Everett, D.H., 1967. Adsorption hysteresis. In Flood, E.A., ed., *Solid Gas Interface.* New York: Marcel Dekker, 1055–1113.

Everett, D.H., and Smith, F.W., 1954. A general approach to hysteresis, 2. Development of the domain theory. *Faraday Soc. Trans.*, **50**: 187–197.

Everett, D.H., and Whitton, W.I., 1952. A general approach to hysteresis. 1. *Faraday Soc. Trans.*, **48**: 749–752.

Gardner, W.R., 1959. Mathematics of isothermal water conduction in unsaturated soils. *Highway Res. Board, Nat. Res. Council, Rep.*, **40**: 78–82.

van Genuchten, M.Th., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.*, **44**: 892–898.

Haverkamp, R., Reggiani, P., Ross, P.J., and Parlange, J.-Y., 2002. Soil water hysteresis prediction model based on theory and geometric scaling. In Smiles, D., Raats, P., and Warrick, A., eds., *Heat and Mass Transfer in the Natural Environment: A Tribute to J.R. Philip*, Chapter 6.2. Monograph of the American Geophysical Union 129, pp. 213–246.

King, L.G., 1964. Imbibition of fluids by porous solids. Ph.D. Thesis, Fort Collins: Colorado State University, 231 pp.

Kosugi, K., Hopmans, J.W., and Dane, J.H., 2002. Parametric models. In Dane, J.H., and Topp, G.C., eds., *Methods of Soil Analysis, Part 4 Physical Methods.* Soil Science Society of America Book Series Number 5. Madison, WI: Soil Science Society of America, pp. 739–758.

Morel-Seytoux, H.J., 1969. Introduction to flow of immiscible liquids in porous media. In deWiest, R. ed., *Flow Through Porous Media.* New York: Academia, pp. 455–516.

Morrow, N.R., and Harris, C.C., 1965. Capillary equilibrium in porous materials. *Soc. Petrol. Eng. J.*, **5**: 12–14.

Mualem, Y., 1973. Modified approach to capillary hysteresis based on a similarity hypothesis. *Water Resour. Res.*, **9**(5): 1324–1331.

Mualem, Y., 1974. A conceptual model of hysteresis. *Water Resour. Res.*, **10**(3): 514–520.

Mualem, Y., 1976. Hysteretical models for prediction of the hydraulic conductivity of unsaturated porous media. *Water Resour. Res.*, **12**(6): 1248–1254.

Mualem, Y., and Dagan, G., 1972. Hysteresis in Unsaturated Porous Media: a critical review and new simplified approach. Rep. 4, Proj. A10-SWC-177. Haifa: Technion-Israel Institute of Technology, 93 pp.

Mualem, Y., and Dagan, G., 1975. A dependent domain model of capillary hysteresis. *Water Resour. Res.*, **11**(3): 452–460.

Mualem, Y., and Dagan, G., 1976. Methods of predicting the hydraulic conductivity of unsaturated soils. Project 442. Haifa: Technion–Israel Institute of Technology, 78 pp.

Néel, L., 1942. Théories des lois d'aimantation de Lord Rayleigh, 1. *Cahiers Phys.*, **12**: 1–20.

Néel, L., 1943. Théories des lois d'aimantation de Lord Rayleigh, 2. *Cahiers Phys.*, **13**: 19–30.

Philip, J.R., 1964. Similarity hypothesis for capillary hysteresis in porous materials. *J. Geophys. Res.*, **69**(8): 1553–1562.

Poulovassilis, A., 1962. Hysteresis of pore water, an application of the concept of independent domains. *Soil Sci.*, **93**: 405–412.

Poulovassilis, A., 1970a. Hysteresis of pore water in granular porous bodies. *Soil Sci.*, **109**: 5–12.

Poulovassilis, A., 1970b. The effect of the entrapped air on the hysteresis curves of a porous body and its hydraulic conductivity. *Soil Sci.*, **109**: 154–162.

Poulovassilis, A., and Childs, E.E., 1971. The hysteresis of pore water: The nonindependence of domain. *Soil Sci.*, **112**: 301–312.

Preisach, F., 1935. Uber die magnetische Nachwirkung. *Zeitschr. Physik*, **94**: 277–302.

Stallman, R.W., 1969. Multi-phase fluids in porous media – A review of theories pertinent to hydrological studies. *U.S. Geological Survey Prof. Pap.*, **411-E**: 49.

Staple, W.J., 1964. Moisture tension, diffusivity and conductivity of a loam soil during wetting and drying. *Can. J. Soil Sci.*, **45**: 78–86.

Sumner, M.E. 2000. Handbook of Soil Science. Boca Raton, Fla: CRC Press (various pagings).

Talsma, T., 1970. Hysteresis in two sands and the independent domain model. *Water Resour. Res.*, **6**(3): 964–970.

Topp, G.C., 1969. Soil water hysteresis measured in a sandy loam compared with the hysteretic domain model. *Soil Sci. Soc. America Proc.*, **33**: 645–651.

Topp, G.C., 1971a. Soil water hysteresis in silt loam and clay loam soils. *Water Resour. Res.*, **7**(4): 914–920.

Topp, G.C., 1971b. Soil-water hysteresis: the domain model theory extended to pore interaction conditions. *Soil Sci. Soc. Am. Proc.*, **35**: 219–225.

Topp, G.C., and Miller, E.E., 1966. Hysteretic moisture characteristics and hydraulic conductivities for glass-bead media. *Soil Sci. Soc. Am. Proc.*, **30**: 156–162.

Vachaud, G., 1966. Verification de la loi de Darcy generalisee et determination de la conductivite capilaire a partir d'une infiltration horizontal. Wageningen: AIHS-Symposium, 277–292.

Vachaud, G., and Thony, J.L., 1971. Hysteresis during infiltration and redistribution in a soil column at different initial water contents. *Water Resour. Res.*, **7**(1): 111–127.

van Genuchten, M. Th., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Amer. J.*, **44**: 892–898.

Cross-references

Conductivity, Hydraulic
Imbibition
Infiltration
Percolation
Permeability
Soil Pores
Water Budget in Soil
Water Content and Retention
Water Movement
Wetting Front

CARBON CYCLING AND FORMATION OF SOIL ORGANIC MATTER

Carbon (C) can form potentially endless hybridized atomic orbitals resulting in the potential to create a vast array of complex organic compounds. The diversity of C compounds no doubt influenced the evolution of life and the diversity of organisms. Carbon was not found on the primordial earth and only after the continuous bombardment by carbonaceous comets and asteroids did appreciable amounts of C accumulate (Anders, 1989). The extraterrestrial C was complex containing a vast array of hydrocarbons and important biological compounds such as amino acids and carboxylic acids, constituents required to assemble primitive life. Early Earth's atmosphere was thought to contain primarily simple hydrocarbons that were continuously altered through ultraviolet photolysis. In addition, the atmosphere contained appreciable amounts of carbon dioxide (CO_2) as a result of meteor and asteroid impacts and volcanic activity. The CO_2 dissolved in water to form carbonic acid and may have been instrumental in mineral weathering and soil development. The respiratory activities of early microorganisms added to the increasing levels of CO_2 and methane (CH_4) in the atmosphere. Early Earth contained atmospheric CO_2 levels in excess of 100 times of what they are today. The high concentrations of CO_2 lead to the emergence of biological C fixation (photosynthesis), which began to reduce the atmospheric CO_2 level and increase the oxygen level. The evolution of primary producers resulted in the accumulation of complex organic compounds. The production of organic material immobilized essential nutrients, such as nitrogen (N) and phosphorus (P) that had to be recycled by the decomposing activity of heterotrophs to maintain primary production. The biological processes of photosynthesis and decomposition are two fundamental processes that sustain ecosystem productivity and are an integral part of the global C cycle.

The global CO_2 cycle today

Increasing fossil fuel use, forest clearing, and the conversion of land to agriculture have led to a net transfer of terrestrial C to the atmosphere. Today's atmosphere contains approximately 370 ppmV compared to about 260 ppmV CO_2 during the middle of the 19th century. Atmospheric CO_2 continues to increase because of the reliance on fossil fuels and as developing countries embrace a higher standard of living afforded through industrial development. The increasing atmospheric CO_2 level has been partially offset by the net uptake of C into the oceans, which contain the largest reservoir of inorganic C at 38 000 Pg C (Figure C27). In the terrestrial environment, soils contain about 1 500 Pg C. The atmosphere contains approximately 790 Pg C and land vegetation 650 Pg C. Both soils and vegetation have been impacted greatly by anthropogenic activity and thus the C cycle can be considered one of the more sensitive biological cycles subject to human influence. Increased atmospheric CO_2 may lead to higher photosynthetic rates, although elevated CO_2 research has produced little corroborating evidence to suggest plants are C limited. Plant water use efficiency will increase for plant species that rely on the photosynthetic enzyme Ribulose bisphosphate carboxylase to produce a 3C (C_3) sugar during photosynthesis. C_3 plants can loose up to 50% of fixed C to photorespiration and would benefit greatly under higher partial pressures of CO_2 that reduce transpired water loss during photosynthesis. In comparison, plants fixing CO_2 to 4C sugar (C_4) or those using Crassulacean acid metabolism (CAM) are more efficient at fixing CO_2 and show little if any change under elevated CO_2.

The global C cycle is dependent on numerous processes that operate at different spatial or temporal scales. The cycling of the vast majority of C found on Earth is on the order of millions of years as CO_2 from the atmosphere and biological activity is adsorbed by oceans and sequestered into carbonates that eventually form sedimentary rocks such as limestone and dolomite. Over time these rocks release their C back to the atmosphere, either through subduction into the Earth's mantle followed by expulsion of CO_2 through volcanic processes, or as a result of tectonic plate upheaval where they are exposed to weathering processes leading to the release of CO_2 through mineral dissolution and soil development. On a smaller time scale, measured from hours to thousands of years, biological processes dominate the C cycle. The biological cycling of C is dependent on the ability of primary producers such as

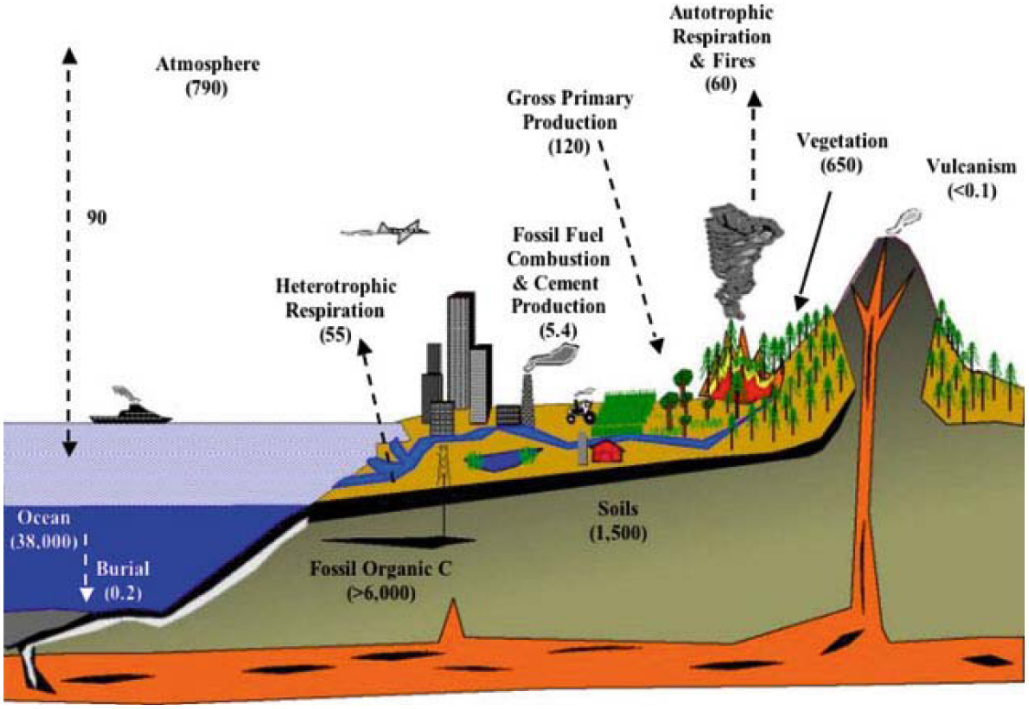


Figure C27 Pool sizes and annual fluxes (Pg C) of major reservoirs (*solid lines*) and fluxes (Pg C/year) (*dashed lines*) in the global C cycle (adapted from Houghton et al., 2001).

plants and cyanobacteria to fix atmospheric CO_2 into organic substances.

The biological fixation of CO_2 or photosynthesis to produce organic compounds is termed gross primary production (GPP). Following losses to respiration, growth and maintenance the newly formed biomass is termed net primary production (NPP). Net secondary production (NSP) occurs when consumers such as herbivores or decomposers of NPP produce new biomass. The decomposition of NPP leads to the selective preservation of some resistant plant constituents, such as lignin. In addition, the turnover of microorganisms produce compounds, which are precursors to soil organic matter (SOM). These precursors or humic substances are resistant to decay and can persist for thousands of years.

Composition and decomposition of soil C inputs

The quantity and quality of NPP and subsequent NSP determines the outcome of decomposition processes and regulates the accumulation of SOM. The various constituents of NPP and NSP consist of a range of materials from simple lipids and organic acids to complex polymers found in plant and microbial cell walls. The constituents of cytoplasm and cell walls require a complex scheme of enzymes to degrade into substrates suitable to be used to produce NSP, indicating that microbial diversity and production are significant controlling factors of decomposition processes. The cell walls of plants and microorganisms are resistant to decomposition and are thought to contribute significantly to the maintenance of SOM. A small yet nutrient rich component of plant litter found within the cytoplasm contains sugars, amino compounds and organic acids and comprises up to 10% of plant residue dry weight (Table C2). The labile cytoplasm components are readily leached from plant residues and provide the initial energy and nutrients to start the decomposition process. The protein content of plant litter and exudates ranges from about 1% in roots to up to 4 or 5% in foliar tissue. Biological N fixers tend to have greater overall tissue N concentrations. The meristimatic regions of plants can have N contents in excess of 20% by weight. The secondary cell walls of higher plants generally have less than 1% N. The majority of secondary cell wall is comprised of hemicellulose and cellulose, comprising up to 70% of total plant residue. Plant lignin ranges from 5 to 30% and is a unique compound of terrestrial plants providing a rigid exoskeleton to counter the effects of gravity and provide a physical defense against pathogens. Extractable phenols and tannins are often a significant component of some plants, especially in forest and shrub systems, and comprise up to 30% of the dry weight.

Table C2 Percentage of cytoplasm and cell wall components in plants. (adapted from Horwath 2002)

Plant component	% of total
Waxes and pigment	1
Amino acids, sugars, nucleotides etc.	5
Starch	2–20
Protein	5–7
Hemicellulose	15–20
Cellulose	4–50
Lignin	8–20
Secondary compounds	2–30

The various components of plant, microbial and faunal soil inputs undergo decomposition at different rates. Ecologists often relate the decomposability or quality of plant litter inputs to C to N ratio, total N or lignin content, which have been shown to influence decomposition and the long-term fate of soil C. Other plant constituents such as polyphenols and tannins (secondary plant metabolites) may impact decomposition through phytotoxic interactions and chemical interactions with both organic and inorganic N sources. The availability of exogenous nutrients is a major determinant of decomposition processes through its regulation of the growth potential of decomposers. Above all, the major factors controlling both NPP and NSP are temperature and moisture. Temperature controls metabolic activity while sufficient moisture is required to maintain metabolic function. Following is a description of plant and microbial components and the factors controlling their fate during decomposition.

Cytoplasm and storage components

Lipids represent a diverse class of compounds ranging from simple fatty acids to complex sterols, phospholipids, chlorophyll, waxes and resins (cutins and suberins). As a class of compounds, the decomposability of lipids depends on their chemical complexity. Long chain aliphatic fatty acids and phospholipids, components of membranes, are degraded relatively quickly depending on the degree of saturation or double bond content. More complex waxes and resins are resistant to decomposition and form some of the most resistant substances in soil. The hydrophobic character of these substances allows them to sorb into hydrophobic domains of SOM, shielding them from enzymatic attack. In addition to plant lipids, the accumulation of polyaromatic hydrocarbons (PAH) from fossil fuel combustion in soils is gaining attention. Enzymes and degradative processes of the more recalcitrant lipid substances and PAH are not well understood.

Starch is a polymer of glucose synthesized and stored in plastids, such as amyloplasts of roots and tubers. Starch consists of two glucose polymers, amylose and amylpectin. Amylose contains long unbranched chains of α(1-4)-glucose units. For most plants, amylose can account for up to 30% of the total starch. Amylopectin has a similar structure linked every 20 to 30 glucose residues by α(1-6)-glucose bonds. A class of enzymes known as amylases readily degrades starch into glucose. Starch represents a significant energy source but requires a supply of exogenous nutrients to complete microbial growth and other NSP.

Hemicelluloses, pectins and cellulose

The majority of plant carbohydrates are found as the polysaccharides, cellulose hemicellulose and pectin in the secondary cell wall. All of the monsaccharides that form cell wall polysaccharides are derived from glucose, which upon alteration form a variety of 5C (pentoses) and 6C (hexoses) sugars. Hemicelluloses contain xylans (xylose polymer), an uronic acids (i.e., sugar acid), and arabinose (another 5C sugar). Pectin is composed of three main polysaccharide types: polygalacturonan (repeating galacturonic acid monosaccharide subunits), rhamnogalacturonan I (alternating rhamnose and galacturonic acid subunits) and rhamnogalacturonan II (highly branched polysaccharide). Hemicellulose/pectin because of their sugar content are a rich energy source, but require an extensive suite of enzymes and exogenous nutrients to complete its decomposition.

Cellulose consists of glucose units linked by β(1-4) bonds to form long glucose chains. The chains are cross-linked by hydrogen bonds to form paracrystalline assemblages called microfibrils. The cellulose microfibrils are cross-linked into a network or scaffold with hemicellulose. Cellulose microfibrils are decomposed by the enzyme system cellulase composed of endoglucanase, exoglucanase and β-glucosidase (also known as cellobiases). Cellulose degradation begins with the disruption of the crystalline structure of the microfibrils followed by the depolymerization into short glucose chains. A wide range of organisms degrade the energy rich cellulose, but only a few have demonstrated the complete depolymerization and hydrolysis of the crystalline microfibril structure in vitro. The conversion of plant polysaccharides into sugars and fuel such as ethanol has received much attention as a source of energy to replace or substitute for fossil fuels.

Lignin

Lignin is a complex and dense amorphous secondary cell wall polymer typically found in the trachea elements and sclerenchyma of terrestrial plants. The dense hydrophobic nature of lignin makes it difficult for enzymes to penetrate. The precursors of lignin come from the shikimic and phenylpropanoid pathway that converts the amino acids phenylalanine and tyrosine to hydroxycinnamyl alcohol and then to monlignols –p-coumaryl, coniferyl and synapyl alcohols. The monolignols are assembled randomly on a protein template. The lignin polymer provides structural rigidity and a mechanical barrier against pest and pathogens.

The decomposition of lignin is primarily attributed to fungi, actinomycetes, and bacteria under aerobic conditions. Fungi are the most efficient lignin degraders in nature and for this reason play a key role in C cycling. Fungal species that degrade lignin are often grouped into soft rot, brown rot and white rot fungi based on the color of the decayed substrate. The majority of wood decay is done by brown and white rot fungi from the Basidiomycetes. White rot fungi are the most active lignin degraders. Several thousand species of white rots are known. White rot fungi are often inhibited by high N levels, suggesting that lignin degradation is a secondary metabolic response. The interaction of cellulose and lignin to form lignocellulose produces a difficult to degrade structure compared to its' individual components. The recalcitrance of the plant cell wall requires that numerous microorganisms and enzyme systems work together to free substrates to complete growth.

Plant secondary compounds

Plants produce an array of secondary compounds or metabolites that are not essential for growth and development. There are three major groups of secondary compounds including terpenoids, alkaloids and phenylpropanoids. Many of these compounds are thought to play a role in defending against herbivory and microbial infection, as attractants for pollinators and seed dispersers and as allelopathic agents. These compounds affect the quality of plant litter residues and exudates by negatively affecting organisms and/or processes controlling decomposition processes. These compounds range in molecular weight from 500 to 3 000 Daltons and commonly precipitate proteins through tannin reactions (Kraus et al., 2003). The tanning of leather is an example where a natural product is protected from microbial attack. The ability to precipitate proteins can have profound effects on N availability and microbial succession during decomposition processes.

Microbial constituents

Microbial biomass represents NSP derived from photosynthetically fixed C. Net secondary production may be recycled to produce more generations of microbial decomposer biomass. The turnover of the soil microbial biomass represents a significant source of labile and resistant C and potential substrate for SOM formation. Bacteria have many C compounds that are similar to plants. Protein makes up 55% of the cell dry weight of common bacteria. Fungi have less protein than bacteria, concentrating their metabolic constituents at the tips of growing hyphae. For this reason, bacteria have narrow C to N ratios that range from 5 to 8 while fungi often have C to N ratios in excess of 8. Differences in C to N ratio and cell wall components are often related to the decomposability of soil organisms, as was mentioned earlier for plant residues.

The complexity of the microbial cell walls makes them resistant to decay, similar to that of plants, but the building blocks are vastly different. Microbial cell walls contain constituents such as amino sugars and the D-form of certain amino acids that are resistant to decay. Most amino sugars in soil are of microbial origin. Bacterial cell walls are composed of a rigid layer of N-acetylglucosamine and N-acetylmuramic acid chains. They are linked into a rigid layer called petidoglycan by peptide bonds. The cross-linked peptidoglycan called murein is composed repeating units of L-alanine, D-alanine, D-glutamic acid, and either lysine or diaminopimelic acid. Bacterial cell walls contain anywhere from 10 to 90% peptidoglycan with gram-positive bacteria containing the most. A major component of the fungal cell wall is chitin, which is composed of repeating units of N-acetylglucosamine. Fungi also contain dark-colored pigments called melanins that are resistant to decay and are thought to contribute directly to SOM formation. The decomposition of plant litter and microbial products normally occurs through a succession of different organisms capable of degrading and utilizing specific chemicals, structures and substrates.

Turnover of soil inputs

The turnover of C inputs to soil is often substrate dependent and therefore follows first order reaction kinetics. Proteins and sugars are degraded rapidly and exhibit high turnover rates. The turnover of polymers such as cellulose, lignin and peptidoglycan that require extensive enzyme suites and microbial succession have longer turnover rates. The rate of turnover of a soil C input or substrate (A) with time (t) is defined as

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -kA \qquad (1)$$

where the product of the decomposition rate constant k and A describes the change in A with time. The time required to transform or turnover substrate A is

$$\text{turnover time} = \frac{1}{k} \qquad (2)$$

The turnover time is often referred to as the mean residence time (MRT). Upon integration Equation (1) becomes

$$A_t = A\,\mathrm{e}^{-kt} \qquad (3)$$

where A_t is the substrate remaining at any time during the decomposition processes. The decomposition rate constant k is expressed as per unit of time (e.g., min^{-1}, h^{-1}, d^{-1}, yr^{-1}, etc.). The time required to turnover one half of substrate A is expressed as the logarithmic function

$$\ln\left[\frac{A\frac{1}{2}}{A}\right] = -k\,t_{1/2} \tag{4}$$

where $t_{1/2}$ is the time required to turn over one half of substrate A (half life). Equation (4) is integrated to

$$t_{1/2} = \frac{0.693}{k} \tag{5}$$

Figure C28 shows both a normal and log plot of a typical turnover response of a substrate that follows first order kinetics. Plotting turnover on a log scale yields a straight line. Table C3 shows typical turnover times of various plant and microbial inputs to soil. The turnover times reflects the decomposability of the soil inputs.

Soil organic matter formation

Soil decomposers act as the "Waste Management" crew of an ecosystem. The decomposition of plant and microbial inputs to soil plays an important role in maintaining the global C budget by cycling most of the CO_2 fixed through NPP back to the atmosphere. The C fixed as NPP and converted to NSP is decomposed at a rate very similar to the amount produced on an annual basis. A small fraction of NPP and NSP is persevered as stable soil C in the form of SOM through a process called humus formation.

Humus formation is an essential process that determines NPP and NSP by controlling the availability of essential nutrients. The most efficient procedure to remove humic substances from soil is an alkali extraction. The extraction yields fulvic and humic acids. Fulvic acids are characterized as having low molecular weight (1 000 to 30 000), soluble in water and are commonly found in soil solution and aquatic environments. Humic acids have higher molecular weight (10 000 to 100 000 and more), are insoluble in water and generally are the larger fraction of the two acids. The higher molecular weight of humic acids is presumably due to the condensation of smaller compounds. The alkali unextractable portion of SOM is termed humin and represents up to 30 to 50% of total SOM. Humin is thought to be strongly attached to soil minerals and according to ^{14}C-dating studies is often 1 000 or more years in age. During the formation of SOM, nutrients such as N, P and S are incorporated into its structure. The structure of SOM consists of approximately 50–55% C, 5% H, 33% O, 4.5% N, and 1% S and P. In addition, other metals and micronutrients, such as Ca, Zn and Cu are present in much smaller amounts. Besides being a reservoir of essential plant nutrients, SOM has qualities that contribute directly to plant and microbial growth through its effect on the physical, chemical, and biological properties of soil. The association of SOM with secondary minerals such as clay and amorphous oxides create soil structure through the formation of aggregates. Aggregate formation enhances soil physical structure by ordering soil mineral grains, promoting aeration and water infiltration and storage.

The formation of humic substances has been studied for more than 200 years because of their influence on soil properties and soil fertility. Since the 17th century, scientists have debated whether plant materials were directly incorporated into these humic substances or altered through microbial activity. Modern analytical techniques have shown that SOM consists of partially decayed plant residues, soil microorganisms, soil fauna, and the byproducts of decomposition. Decomposition of plant and animal residues leads to the formation of byproducts that are highly reactive. The humification process is both biological and nonbiological or abiotic where decomposition byproducts condense randomly to form larger molecules or aggregates of molecules that closely associate with soil minerals. One of the most popular theories of SOM formation is the polyphenol theory. Amino acids are thought to react with a

Table C3 Decomposition rates and turnover of various plant and microbial soil inputs

Soil input	Decomposition rate constant (day^{-1})	Half life (days)	Turnover (days)
Sugar, amino acid	0.2	3.5	5.0
Cellulose	0.08	8.7	12.5
Lignin	0.01	69.0	100.0
Fungal cell wall	0.02	34.7	50.0

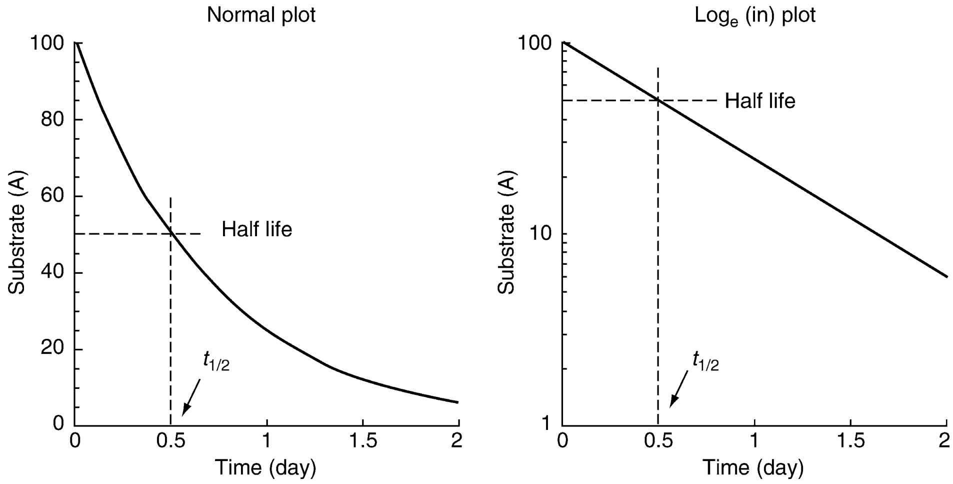


Figure C28 The normal and log plots show the half life ($t_{1/2}$) of substrate A is 0.5 h. Using Equation (5), the decomposition rate constant is ($t_{1/2} = 0.693/k$ or $0.5 = 0.693/k$ or $k = 1.36$) 1.36 units of A per hour. The MRT or turnover is calculated using from Equation (2) ($1/k = 1/1.36 = 0.74$ h).

Table C4 The area, stocks of C, NPP and C turnover of various biomes[a]

Biome	Area (10^9 ha)	Global C stock			NPP (Pg C yr^{-1})	Turnover (years)[b]
		Plant	Soil	Total		
Tropical forests	1.76	340	213	553	17.8	38
Temperate forests	1.04	139	153	292	7.3	29
Boreal forests	1.37	57	338	395	2.9	91
Tropical savannas & grasslands	2.51	79	247	326	16.3	10
Temperate grasslands & shrublands	1.52	23	176	199	6.15	61
Deserts and semi deserts	3.66	10	159	169	2.45	37
Tundra	0.76	2	115	117	0.75	490
Croplands	1.48	4	165	169	5.45	21
Wetlands g	0.35	15	225	240	4.3	520
Total	15.0	669	1791	2460	63.4	

[a] Adapted from Houghton et al. (2001).

[b] Adapted from Raich and Schelsinger (1992) and Paul and Clark (1996).

phenol (catechol) derived either from the alteration of lignin or from microbial products such as pigments (melanins) to produce humic substances. The aminoquinone intermediates condense to form brown, high-molecular-weight nitrogenous humates. Though no two humic substances are presumably alike in structure they behave similarly in function. For example, the sorption of pollutant and pesticides is best explained by total soil C content and generally does not correlate to SOM formed in different ecosystems or environments. Aliphatic long chain C compounds also react with the nitrogenous/aromatic matrix and can comprise the majority of SOM. More details on humification are available in the publications by Aiken et al. (1985), Haider (1992), Stevenson (1994) and Piccolo (1996).

Quantity and distribution of organic matter in soils

The importance of SOM in regulating nutrient cycling and impacting physical properties plays a major role in sustaining ecosystem productivity. The quantity of SOM is dependent on the balance between NPP and the rate of decomposition as previously described. The presence of silt and clay generally preserves more C through organomineral interactions while anaerobic soil (e.g., peat soils) tends to preserve C because of the lack of oxygen to complete decomposition. The highest accumulation of C is found in swamps and marshes (723 t ha^{-1}) (Table C4). Decomposition also is inhibited by cold in tundra soils and C tends to accumulate primarily as partially decomposed litter. Tropical lowland forests and boreal and temperate forests and temperate grasslands all accumulate up to approximately 200 t ha^{-1} with turnover times that range from 29 to 91 years. In contrast to temperate grassland, where C accumulates with an overall turnover time of about 60 years, the low levels of SOM in tropical grassland have turnover rates of about 10 years.

Role of methane in the C cycle

Methane comprises less than 1% of the global C budget. Methane is found as natural gas in fossil fuel deposits, as hydrates or clathrates compounds in ice (e.g., permafrost), deep ocean, and in the atmosphere. Soil microorganisms both produce (methanogens) and consume (methanotrophs) CH_4. Microbial production of methane results from the decomposition of organic materials in the absence of oxygen. Carbon dioxide is used as an electron acceptor and a reduced organic compound as the donor. The reduction of CO_2 will occur in soil under extended reduced conditions such as in flooded environments or where oxygen diffusion is limited such as within soil aggregates. Waterlogged soils such as rice paddies, wetlands, waste disposal sites and the enteric fermentation are typical examples (Table C5). The production and distribution of fossil fuels contributes significantly to CH_4 emissions. Most of the annual flux of methane reacts with atmospheric hydroxyl radicals ($OH^{\bullet}$) to form water and CO_2. Soil organisms consume about 10 to 30 Tg CH_4 yr^{-1}, far below that required to mitigate emissions from anthropogenic sources. The difference between production and consumption of CH_4 results in an increase in atmospheric CH_4 of approximately 28 to 32 Tg CH_4 yr^{-1}. Methane is a more potent greenhouse gas compared to CO_2 and its production and release has garnered much interest from the scientific community.

Table C5 Global sources and sinks for methane

	Tg CH_4 yr^{-1}
Sources	
Wetlands	86–115
Fossil fuel production/distribution	64–101
Enteric fermentation/animal waste	64–94
Rice production	44–60
Biomass burning	30–40
Landfills	30–49
Termites	20–153
Oceans	8–10
Sinks	
Atmospheric removal	308–560
Soil microbial oxidation	10–30
Atmospheric increase	28–32

Adapted from Paul and Clark (1996) and Houghton et al. (2003).

Future considerations

The close link between NPP, NSP, and SOM and their influence on the sources and sinks for greenhouse gases indicates the importance of the global C cycle in regulating ecosystem productivity and climate. The major production and turnover of the components of the C cycle are fairly well characterized at the process level and microscale, for example in a gram of soil. However, on a global scale the interaction of organismal and metabolic diversity, sources and sinks for C, and anthropogenic influences have yet to be fully appreciated. These interactions must be better understood to adequately predict ecosystem response to perturbations such as climate change. Continued research on the biology and physical factors affecting the global C cycle is required to fully comprehend the global C cycle.

William R. Horwath

Bibliography

Aiken, G.R., 1985. Isolation and concentration techniques for aquatic humic substance. In: Aiken, G.R., McKnight, D.M., Wershaw R.L., and McCarthy, P., eds., *Humic Substances in the Soil, sediment and water.* New York: Wiley, pp. 363–385.

Anders, E., 1989. Prebiotic organic matter from comets and asteroids. *Nature*, **342**: 255–257.

Haider, K., 1992. Problems related to the humification processin soils of temperate climates. In Stotsky G., and Bollag, J.-M., eds., *Soil Biochemistry,* Vol.7. New York., Marcel Dekker, pp. 55–94.

Horwath, W.R., 2002. Soil Microbial Biomass. In: *Encyclopedia of Environmental Microbiology.* New York: Academic Press, pp. 663–670.

Houghton, J.T., Ding, Y., Griggs, D.J., Noguer, M., van der Linden, P.J., Dai, X., Maskell, K., and Johnson, C.A., (eds.), 2001. Climate Change 2001: The Scientific Basis. New York: Cambridge University Press. Intergovernmental Panel on Climate Change,

Kraus, T.E.C., Dahlgren, R.A., and Zasoski, R.J., 2003. Tannins in nutrient dynamics of forest ecosystems – a review. *Plant Soil* **25**: 41–66.

Paul, E.A., and Clark, F.E., 1996. Soil microbiology and biochemistry, 2nd edn. New York: Wiley.

Piccolo, A., 1996. Humic Substances in Terrestrial Environments. New York: Elsevier.

Raich, J.W., and Scheslinger, W.H., 1992. The global carbon dioxide in soil respirationand its relationship to vegetation and climate. *Tellus*, **44B**: 81–99.

Stevenson, F.J., 1994. Humus Chemistry: Genesis, Composition, Reactions. New York: Wiley.

Cross-references

Biogeochemical Cycles
Carbon Sequestration in Soil
Earth Cycles
Humic Substances

CARBON SEQUESTRATION IN SOIL

Carbon sequestration is the result of a series of processes through which carbon dioxide in the atmosphere is removed from biogeochemical circulation and accumulated in soil and biomass. The present article emphasizes the soil-dependent factors that have bearing on the effectiveness of C sequestration regardless of the general climatic constraints.

In a first stage, atmospheric carbon is incorporated by photosynthetic plants, which synthesize complex biomacromolecules. When organic remains in addition to microbial bodies decay in soil, a portion of the C stabilizes into the soil (soil C sequestration or humification), the remainder being released mainly as CO_2 and H_2O (mineralization). In environmental situations where the above balance shifts to humification, a progressive increase in soil C concentration will be produced through time. This contributes to alleviating the greenhouse effect, global warming and hence climatic change (Batjes, 1998).

Rough estimations point to the fact that the principal C reservoir in the Earth's surface is not terrestrial or marine biomass, but soil organic matter, the latter amounting about 1 500 to 2 000 Pg (1 Pg = petagram = 1 billion t) soil organic C (Batjes, 1996; Post et al., 1982). Assuming that soil organic matter pool represents more than twice the C in living vegetation (around 560 Pg) or in the atmosphere (750 Pg), it is clear that changes in soil C sequestration rates in local sinks could have a noticeable bearing on the global C balance (Buringh, 1984; Eswaran et al., 1995).

Despite their importance on a global scale, the major formation mechanisms of biodegradation-resistant humic substances are understood only in very broad terms. It is clear that the effectiveness of the whole C sequestration process varies from one soil type to another, as well as in the different ecosystem compartments. It is more intense when several abiotic (climatic, geologic and so on) and biotic (vegetation type, microbial community) factors work together to strengthen the effect. For this reason, studies of the potential of the soil as a reservoir of C, as reported for different bioclimatic regions and in soils developed on different geological substrates, provide a wide range of results so that the topic remains controversial.

Side-effects of soil C sequestration

The sequestration of C in soils has both positive and negative side-effects. Apart from alleviating the greenhouse effect, soil C sequestration leads to additional benefits regarding soil quality defined in terms of sustainable productivity. These indirect benefits are mostly reflected in the improvement of soil structural stability, water holding capacity, continuous release of available nutrients, biological activity, and others. In addition, the stabilized organo-mineral matrix also enhances the potential of the soil to act as an environmental filter regulating leachability and bioavailability of organic and mineral pollutants in the soil solution such could be some agrochemicals and heavy metals (Almendros, 1995; Wershaw, 1977).

On the negative side, the stabilization and sequestration of atmospheric C into soil is connected with the fact that, in addition to C, other bioelements such as N, P and S, are also sequestered in slowly bioavailable forms. Therefore (and this is mainly in forest ecosystems) effective plant and soil C sequestration may often be associated with the accumulation of raw humus types (*moder*, *mor*), low-performance biogeochemical cycles, limited primary productivity and (though this is not necessarily causally related) a low biodiversity. In such soil systems the organic matter is weakly associated to the mineral fraction compared to systems with active (*mull*) humus, and most of the pedogenic processes do not end in the formation of stable organo-mineral complexes. This causes the vertical redistribution of the organic matter down the soil profile on a macroscopic scale. It is also connected with the generation of leachates and the exportation of plant nutrients out of the soil. In some cases, this may have undesirable effects on water quality.

In other words, in a global soil management policy, it will perhaps be more important to monitor the *quality* rather than the *total quantity* of the organic matter sequestered in the soil. Certain forest or brushwood sites in the semi-arid Mediterranean region provide an illustration. Here, deeply transformed soil organic matter is commonly in low concentration (e.g., less than 20 g kg^{-1}). However, it is of high resilience as regards any possible future climatic change. This is in marked contrast with soil formations in the boreal forest for example, where there are greater amounts of slightly transformed organic matter. With the possible rise in ambient temperature occasioned by future global warming, these areas could turn into active CO_2 sources, because the thick layers of organic matter they contain, are of a low degree of humification with a weak association between the organic and mineral fraction. Peat and bog soils in temperate zones (often

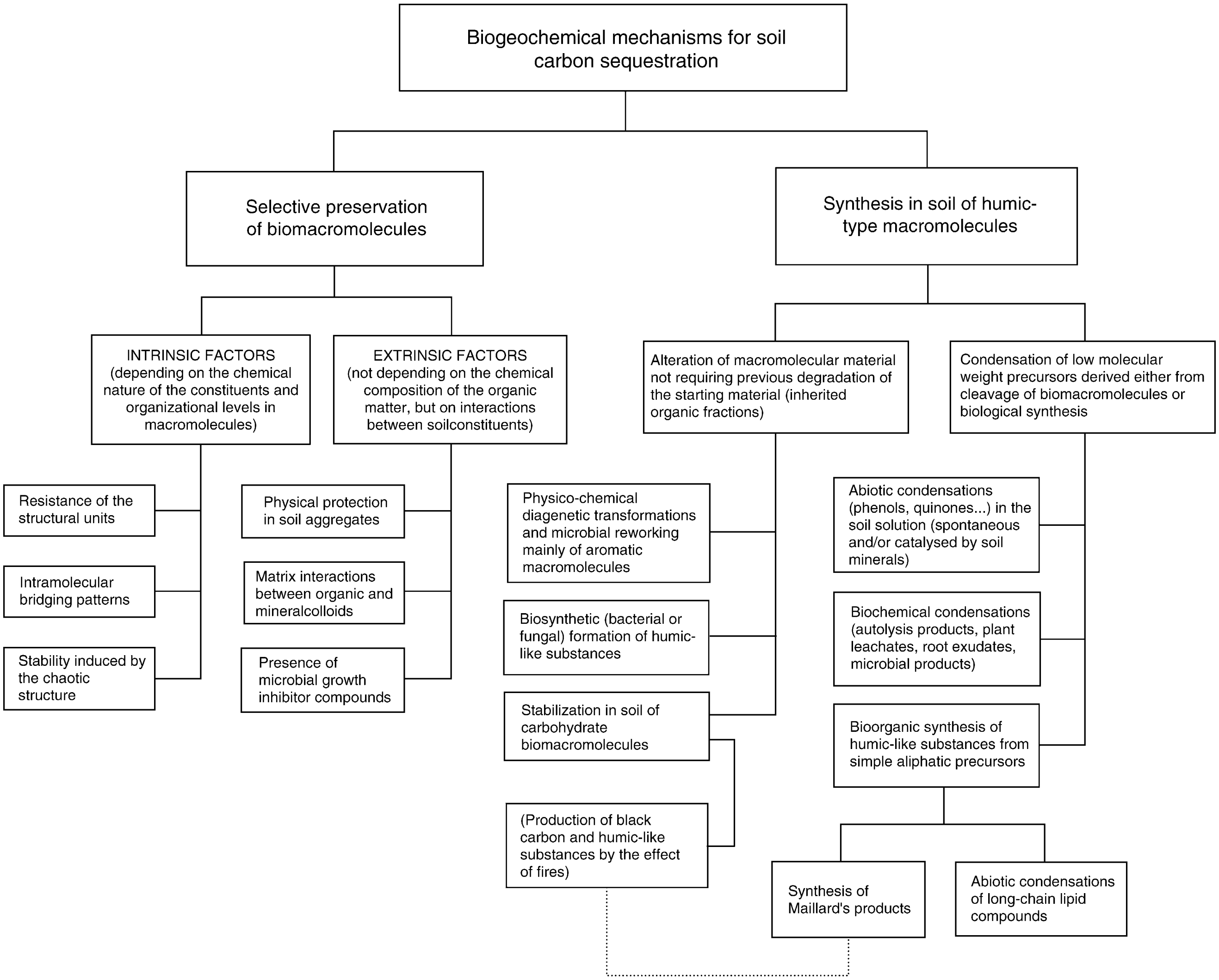


Figure C29 Hypothetical soil-dependent processes responsible for the formation of humic substances and soil C sequestration.

sapric in type, with low C/N ratio) are also at risk. Global temperature rise would likely have a drying effect, and it is well known that a drop in the phreatic level of a few centimeters is enough to turn these local C sinks into self-burning sources of CO_2 after an intense episode of microbial thermophilic activity.

Basic research on soil C sequestration – Experimental approaches to monitor soil C stabilization mechanisms

The scientific reappraisal of humification mechanisms has acquired renewed interest in the light of the global change scenario. Progress over the last few years has taken advantage from the development of new analytical and instrumental tools.

Clearly, different processes are involved in soil C sequestration (Figure C29): such as selective preservation of biomass, diagenetic alteration of biomacromolecules and humification by neoformation *sensu stricto* (microbial, enzymatic or abiotic). All these mechanisms occur simultaneously and are closely interrelated. In the most favorable cases, the assessment of their variable extent, in space and time, can be carried out by using specific techniques of isolation and analysis of free biomarker – or signature – compounds occurring in the lipid fractions. This is often complemented by the molecular characterization of humic substances by chemical and thermal degradation followed by mass spectrometry. Alternatively, non-destructive methods such as visible, infrared or nuclear magnetic resonance spectroscopies are available. In some cases, there is no valid experimental approach to identify the substances formed by each of the above processes. Commonly, different humification pathways lead to substances with common structures and properties.

These and future techniques will be necessary to quantify the processes involved in soil C sequestration, and will enable a better assessment than was formerly possible of the potential of soil as a repository of C in ameliorating the effects of a global increase in temperature.

G. Almendros

Bibliography

Almendros, G., 1995. Sorptive interactions of pesticides in soils treated with modified humic acids. *Eur. J. Soil Sci.* **46**: 287–301.

Batjes, N.H., 1996. Total carbon and nitrogen in the soils of the world. *Eur. J. Soil Sci.*, **47**: 151–163.

Batjes, N.H., 1998. Mitigation of atmospheric CO_2 concentrations by increased carbon sequestration in the soil. *Biol. Fertil. Soils*, **27**: 230–235.

Buringh, P., 1984. Organic carbon in soils of the world. In Woodwell, G.M., (ed.), *The Role of Terrestrial Vegetation in the Global Carbon Cycle. Measurement by Remote Sensing*. SCOPE 23, New York: Wiley, pp. 91–109.

Eswaran, H., Berg, Van den P., Reich, P., Kimble, J., 1995. Global soil carbon resources. In Lal, R., Kimble, J.M., Levine, E., and Stewart, B.A., eds., *Soils and Global Change.* Boca Raton, FL: CRC/Lewis Publishers, pp. 25–43.

Post, W.M., Enmanuel, W.R., Zinke, P.J., and Stangenberger, A.G., 1982. Soil carbon pools and world life zones. *Nature*, **289**: 156–159.

Wershaw, R.L., Pinckney, D.J., and Booker, S.E., 1977. Chemical structure of humic acids– Part 1. A generalized structural model. *J. Res. U.S. Geol. Survey*, **5**: 565–569.

Cross-references

Carbon Cycling
Histosols
Humic Substances
Peat

CARBONATES

The essential structural unit of the carbonates is the $(CO_3)^{2-}$ group. Deer et al. (1992) state that there are about 60 known carbonates in nature though only one, calcite, commonly forms in soil. Dolomite is the second most common in soils, though it is always inherited rather than neoformed. The only other carbonate likely to be encountered in the soil environment is siderite, which forms in hydromorphic environments. Basic properties of these three carbonates are shown in Table C6. All three carbonates have high birefringence, and show the phenomenon of twinkling in thin section. This is strongest in the case of calcite.

Calcite

$CaCO_3$ exists in several polymorphous forms. Calcite is the only common one in soil, with aragonite occurring in high-pressure metamorphic rocks, or in a low-pressure modification in the tests of some invertebrate organisms. The structure of calcite is analogous to a distorted halite, in which Ca and $(CO)_3$ ions replace Na and Cl ions respectively in the structure. The cube of the halite structure is imagined as being compressed along one of its axes of three-fold symmetry to produce a face-centered rhomb. The distortion makes it possible to accommodate the large planar (CO_3) groups into the structure. Most calcites in nature are close to the ideal composition, though substitution of Mg, Fe and other metal-cations for Ca occurs. For calcites formed in low temperature environments, the substitutions are negligible.

In calcareous soils calcite is invariably accompanied by silicates, and in humid climates is the most reactive common mineral there. Consequently, if calcite is present in a soil, it has the effect of generating an alkaline pH (usually between 7 and 8). The relevant reactions may be considered within the framework of the system $CaO–H_2O–CO_2$.

The system $CaO–H_2O–CO_2$

An isobaric, isothermal cross section of this system is shown schematically in Figure C30. There are two stable two-phase assemblages and two stable three-phase assemblages. The two-phase assemblages are:

a. calcite + aqueous solution (at higher partial pressures of CO_2).
b. portlandite + aqueous solution (at lower partial pressures of CO_2).

The three phase assemblages are:

a. calcite + aqueous solution + CO_2
b. calcite + portlandite + aqueous solution
c. calcite + portlandite + lime (in the absence of aqueous solution).

Clearly, lime will not be stable in soil since the partial pressure of water is never going to be close enough to zero. Neither will portlandite be stable, since the partial pressure of CO_2 for the three-phase assemblage c, is approximately 10^{-13} atmospheres (point x in Figure C30). Calcite will be stable as the three phase assemblage c with point y lying between P_{CO2} values of $10^{-3.5}$ atmospheres (the average value in the Earth's

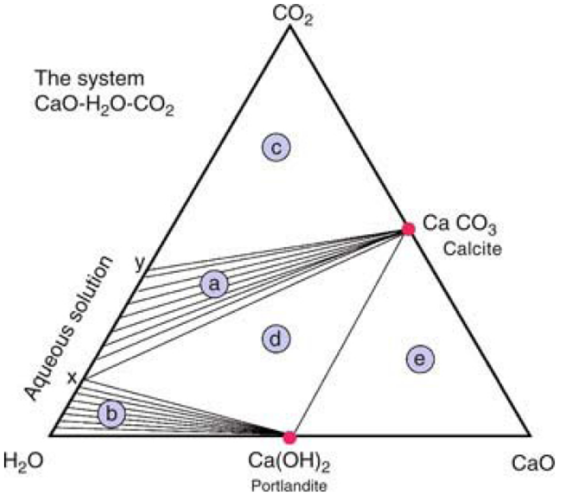


Figure C30 The system $CaO–H_2O–CO_2$ at 1 atmosphere (100 kPa) total pressure and 25 °C (see text for explanation). The positions of x and y are schematic in the interests of clarity. All natural conditions in terrestrial soils will be on the CO_2 side of the Calcite-x tie line.

Table C6 The commonest carbonates in soil

Name	Formula	Crystal system	Effervescence with dilute HCl	Stain color
Calcite	$CaCO_3$	Trigonal	Vigorous	Pink to red-brown with Alizarin Red S
Dolomite	$CaMg(CO_3)_2$	Trigonal	Slow in the cold	Very pale blue with K ferricyanide
Siderite	$FeCO_3$	Trigonal	Unreactive in the cold	Deep blue with K ferricyanide

atmosphere) to $10^{-1.5}$ atmospheres (the possible maximum in the solum – this being due to the respiration of roots, and the microbial breakdown of organic matter).

Figure C30 does not give the complete picture since it contains no direct information on the conditions of pH under which calcite is stable at the surface of the Earth.

Table C7 presents the data for answering this question.

The calculation is in three steps:

$$[H_2CO_3^*] = KH\,P_{CO2} = 10^{-5} \tag{1}$$

$$[HCO_3^-] = ([H_2CO_3^*]/[H^+])K_a = 10^{-11.35}/[H^+] \tag{2}$$

$$\begin{aligned}[Ca^{2+}] &= ([H^+]K_S)/[HCO_3^-]\\ &= ([H^+]/10^{1.91})/(10^{-11.35}/[H^+])\\ &= [H^+]^2 \times 10^{13.26}\end{aligned} \tag{3}$$

The last relationship can be written in the form:

$$\log[Ca^{2+}] = 2\log[H^+] + 13.26$$

or

$$-\log[Ca^{2+}] = -2\log[H^+] - 13.26$$

or

$$pC_{Ca2+} = 2\,pH - 13.26$$

This is plotted as a pC-pH diagram for the system H_2O–CO_2 (Figure C31). The point of charge balance in the presence of calcite is achieved where the concentration of HCO_3^- is twice the concentration of Ca^{2+}. The point of charge balance is calculated in the following way:

$$[Ca^{2+}] = [HCO_3^-]/2 \tag{4}$$

which is substituted into Equation (3) to give

$$[HCO_3^-]^2 = 2[H^+]K_S \tag{5}$$

which is substituted into Equation (2) to give

$$[HCO_3^-]^2 = 10^{-22.7}/[H^+]^2 \tag{6}$$

Equating (5) and (6):

$$2[H^+]K_S = 10^{-22.7}/[H^+]^2 \tag{7}$$

$$\begin{aligned}[H^+]^3 &= 10^{-22.7}/2 \times 10^{1.91}\\ &= 10^{-24.61}/2\end{aligned}$$

$$[H^+] = 0.5 \times 10^{-8.2} = 10^{-8.5}$$

In other words at the partial pressure of CO_2 ($10^{-3.5}$ atmospheres) in the atmosphere, at 25 °C, and 100 kPa (1 atmosphere) total pressure, calcite becomes stable at pH 8.5. This means that rainwater falling on a limestone-dominated landscape would rise in pH from 5.7 to 8.5. For this reason limestone terrain is almost always considered to be at low risk from acid rain. Under a humid climate this high value is not likely to be reached in a calcite-bearing soil, since P_{CO2} may be as high as $10^{-1.5}$ atmospheres. In the latter case a pH of 7.6 will prevail in the presence of calcite and provided there is a continuous supply of rain, this will be the pH (water) of the soil. In semi-arid or arid climates however, where atmospheric precipitations are infrequent, the pH may rise to higher values because there is no tendency for calcite to dissolve to give the isobaric, isothermal value of the equilibrium pH.

Table C7 Values for the partial pressure of CO_2 and for equilibrium constants of significant reactions, used in the calculations. It is difficult to distinguish H_2CO_3 and CO_2 in solution. $H_2CO_3^*$ is a hypothetical species that represents them both

P_{CO_2}	$10^{-3.5}$ atmospheres
$H_2O + CO_2 = H_2CO_3^*$	$K_H = 10^{-1.47}$
$H_2CO_3^* = H^+ + HCO_3^-$	$K_a = 10^{-6.35}$
$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$	$K_S = 10^{1.91}$

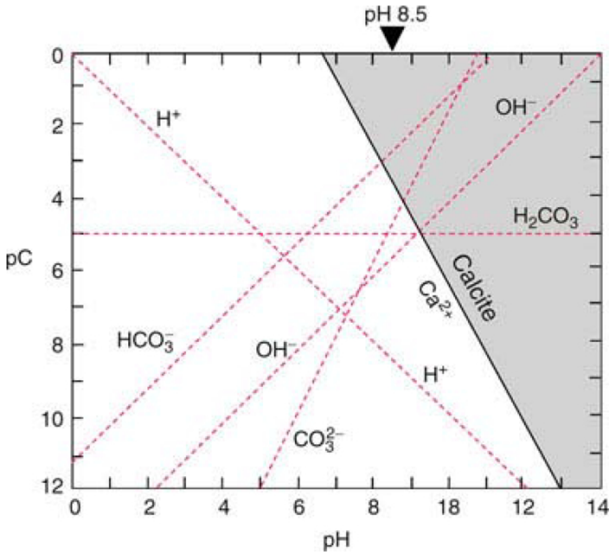


Figure C31 pC–pH diagram for the system CaO–H_2O–CO_2 for $[H_2CO_3^*] = 10^{-5}$. Temperature is 25 °C and pressure 100 kPa. The point of charge balance (and pH of the system) is 8.5.

Dolomite

The structure of dolomite is similar to that of calcite and can be thought of as comprising alternating layers of calcite with magnesite ($MgCO_3$). In the field it is distinguishable from calcite in only reacting notably with dilute HCl, when the acid is heated. In thin section it takes on a pale blue tinge with potassium ferricyanide, which is also true for a low Fe ferroan calcite. However, unlike the latter, it does not react with the stain alizarin red S.

Dolomite does not appear to form in weathering systems but is inherited from soil parent materials. It weathers more slowly than calcite in humid climatic zones, though in a mature soil will eventually be removed from the solum, as will calcite. Calcite may reprecipitate in the C horizon (of a Luvisol, for example), whereas dolomite will not. A small fraction of the released Mg however may be incorporated into the secondary calcite.

The system MgO–CaO–H_2O–CO_2

Dolomite is common in calcareous soils derived from dolomitic limestones or from sediments such as tills derived from rocks of this kind. It is invariably accompanied by calcite and the two carbonates together determine the pH of soils in which they both occur. This is supported by the measurements of soil water composition in the C horizons of Luvisols in the Blue Springs watershed in Southern Ontario, about 100 km west of Toronto (Figure C32; Shulman and Chesworth, 1985).

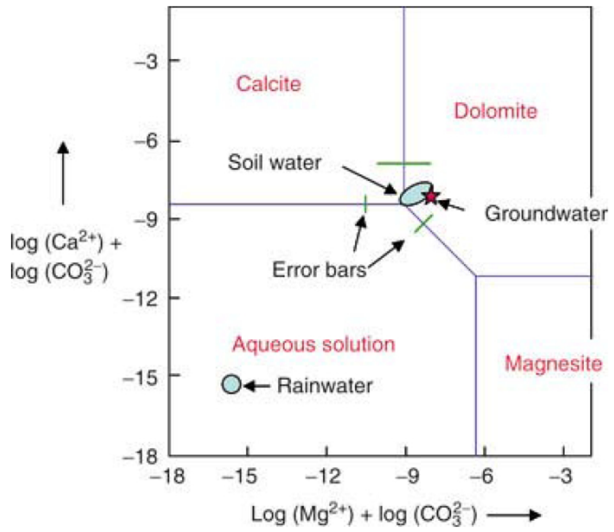


Figure C32 The system $MgO–CaO–H_2O–CO_2$ at 1 atmosphere (100 Pa) total pressure and 25 °C. Water compositions were monitored in the Blue Springs watershed of Southern Ontario. The soil water and groundwater compositions fall within the uncertainty zone for the three-phase equilibrium calcite + dolomite + aqueous solution. This is consistent with the soil water and groundwater having compositions in part controlled by this equilibrium (Shulman and Chesworth, 1985).

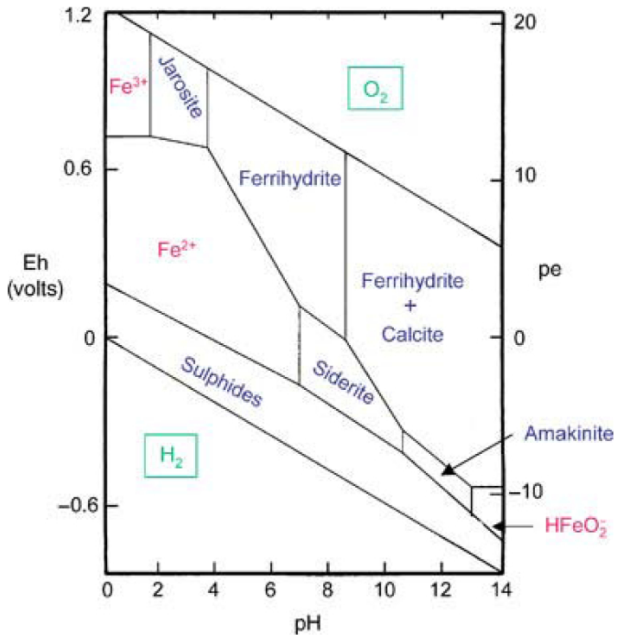


Figure C33 Redox-pH relationships among minerals and an aqueous phase for the system Fe–Ca–K–S–C–H–O. Conditions: 1 atmosphere total pressure, 25 °C, $P_{CO2} = 10^{-3.5}$ atmospheres, activities of Fe and Ca = 10^{-5}, S activity unspecified, the sulfide field is shown at its maximum possible extent.

Siderite

In structure siderite is similar to calcite, though unlike calcite, the composition may depart substantially from the ideal formula of Table C7, with Mg and Mn as common substitutes for Fe. Iron is present in ferrous form, so that siderite is a product only of reducing environments. Its usual occurrence in soils is in CO_2-rich hydromorphic environments such as peatlands.

Redox-pH conditions for siderite

Figure C33 shows the predominance field for siderite in terms of Eh (pe) and pH. Clearly the conditions required are highly reducing and might be expected to prevail in a hydric environment. In the absence of substantial concentrations of HS^- in solution, so that pyrite does not form, siderite will be produced provided that the requisite partial pressure of CO_2 develops. In a peatland this may come about from the respiration or decay of water plants such as sphagnum species.

Ward Chesworth

Bibliography

Brookings, D.G., 1988. *Eh–pH Diagrams for Geochemistry.* New York: Springer.

Deer, W.A., Howie, R.A., and Zussman, J., 1992. *An introduction to the Rock Forming Minerals.* Harlow, UK: Longmans. 696 pp.

Shulman, D., and Chesworth, W., 1985. Calcium carbonate solubility in the C horizon of a Southern Ontario, Canada, luvisol. *Chem. Geol.*, **51**: 115–122.

Cross-references

Acidity
Biomes and their Soils
Bog
Calcareous Soils
Calcisols
Duricrusts and Induration
Hydric Soils
Luvisols
Micromorphology
Mire
Peat

CATCHMENT

Term applied to a natural drainage area or basin, wherein the rainfall is caught and collected to supply the local rivers, streams, lakes and subsurface waters. Also catchment basin.

CATENA

A chain, string, or connected series of soils, related by their sequence in a landscape. Synonymous in part with toposequence chronosequence. The variability of soils in a topographic sequence is a function of gradient and position on the slope (Birkeland, 1999, p 235).

Bibliography

Birkeland, P.W., 1999. Soils and Geomorphology, 3rd edn. New York: Oxford University Press, 430 pp.

CATION EXCHANGE

Ion exchange involving cations. In soils the exchange takes place on the surfaces of clay minerals, amorphous inorganic phases and organic matter. The cation exchange capacity (CEC) is the quantity of cations reversibly adsorbed per unit weight of the solid (McBride, 1994, chapter 3). The conventional unit for CEC is cmoles/kg.

Bibliography

McBride, M.B., 1994. *Environmental Chemistry of Soils.* New York: Oxford University Press, 406 pp.

Cross-reference

Sorption Phenomena

CEMENT

Any substance, which binds together the discrete particles in a soil or sediment. See Consistence and *Pan*.

CHELUVIATION

The downward movement of chemical species in a soil in chelated form. A combination of chelation and eluviation. Organic constituents are integral to the process in providing acid to attack the mineralogical components of a soil, and complexants capable of holding released elements such as Al in solution, in which form they are capable of being transported downwards in the profile. See Table 1 in van Ranst and de Coninck (2002).

Bibliography

Van Ranst, E., and De Coninck, F., 2002. Evaluation of ferrolysis in soil formation. *Eur. J. Soil Sci.*, **53**(4): 513–520.

CHEMICAL ANALYSES

Introduction

Chemical analyses of soils are important in assessing the nutrient status of soils for agricultural production, and in determining the environmental hazards imposed on soils by industrial, municipal, and agricultural wastes. Traditionally, the emphasis of soil chemical analyses has been on evaluating soils in regard to their agricultural productivity. Specifically, to measure plant nutrient levels and other chemical factors (pH, organic matter content, cation exchange capacity, etc.) which determine a soil's suitability as a plant growth medium. More recently, the scope of soil chemical analyses has expanded to evaluation of a soil in regard to environmental quality. Worldwide, concerns have been expressed about numerous soil and water contaminants. These include nitrates and phosphates, metalloids and metals such as arsenic, cadmium, chromium, copper, lead, mercury, and nickel; radionuclides, pesticides, and contaminants from municipal and animal wastes.

Soil chemical analyses range from simple routine tests that can be conducted with hand kits in the field or in soil testing laboratories, to costly sophisticated analyses involving state-of-the-art equipment. Chemicals, both inorganic and organic, undergo sorption reactions in soil systems that often render them insoluble. It is therefore necessary to use appropriate reagent solutions to extract chemicals of interest prior to conducting the actual analysis. After the pertinent extraction is complete, chemical analysis is generally accomplished using either spectroscopic, chromatographic, potentiometric, gravimetric, or titrimetric techniques. These techniques utilize instruments such as: colorimeters, atomic absorption and inductively coupled plasma spectrometers and gas, high-performance liquid, and ion chromatographs. A routine chemical characterization of a soil should include a determination of pH, organic matter content, cation exchange capacity, and extractable bases such as Ca, Mg, K, and Na. These measurements provide general information concerning the chemical nature of a soil.

Soil chemical extractions

Chemical components (defined as any of the minimum number of substances required to completely specify the composition of all phases of a chemical system) can precipitate from the soil solution, and can be electrostatically or chemically adsorbed to the surfaces of soil minerals. Furthermore, the soil organic fraction can bind inorganic and organic ions, as well as partition non-polar organic molecules. These retention processes render chemical components insoluble; therefore, it is often necessary to treat the soil with reagent solutions to extract the particular chemical component of interest (Peck and Soltanpour, 1990). However, prior to conducting any chemical analysis, soils are usually air-dried, pulverized, sieved (generally through a 2 mm sieve), and mixed to obtain a homogeneous composite sample.

Several extracting solutions, along with their functions, are listed in Table C8. Each of these extractants was designed to remove a distinct category of chemical constituent from a soil. For example, the total sorbed metals procedure used by the U.S. Environmental Protection Agency would be the recommended extractant to evaluate heavy metals in soils. This extractant is comprised of concentrated HNO_3 and HCl acids, and hydrogen peroxide (30%). It provides a measure of total metal concentrations that are exchangeable or adsorbed by soil components (Risser and Baker, 1990). To determine plant available micronutrients, an extractant containing the chelate diethylenetriaminepentaacetic acid (0.005 M DTPA) along with 0.01 M $CaCl_2$ and 0.1 M triethanolamine (TEA) may be employed. This extractant, developed by Lindsay and Norvell (1978), removes labile pools of metals that correlate well with plant nutrient concentrations. Other trace metal extractants that are in common use globally include 1 M or 0.1 M HCl or HNO_3, 0.5 M CH_3COOH, 1 M CH_3COONH_4, 0.05 M Na_2-EDTA or (NH_4)-EDTA, 0.01 M $CaCl_2$, and boiling water (Hamilton, 1980).

Extraction schemes have also been developed that fractionate a soil element into different pools. Kuo (1996) cites a fractionation method for inorganic P pools, which are based on the ability of specific extractants to solubilize P present in

Table C8 Common soil chemical extractants

Extractants	Elements
2 M KCl	Exchangeable NH_4^+, NO_2^-, NO_3^-, and Al^{3+}
Bray-1 (0.03 M NH4F, 0.025 M HCl)	Plant available P
Olsen-P (0.5 M $NaHCO_3$, pH 8.5)	" " "
1M Ammonium Acetate (pH 7.0)	Exchangeable K, Ca, Mg, Na
DTPA (0.005 M DTPA, 0.01 M $CaCl_2$, 0.1 M triethanolamine (TEA), pH 7.3)	Plant available Zn, Fe, Mn, and Cu
USEPA 3050 (conc. HNO_3, conc. HCl, 30% H_2O_2)	Total sorbed metals
*Mehlich 3 (0.2 M CH_3COOH, 0.25 M NH_4NO_3, 0.15 M NH_4F, 0.13 M HNO_3, 0.001 M EDTA)	Plant available P, K, Na, Ca, Mg, Mn, Zn, and Cu
AB-DTPA (1 M NH_4HCO_3, 0.005 M DTPA, pH 7.6)	Plant available P, NO_3^-, K, Zn, Fe, Cu, and Mn

* Mehlich, A. 1984.
References for all other extractants are given in the texts: Page et al. (1982) and Westerman (1990).

Al-, Fe- and Ca phosphates, and accounts for P that is occluded and nonoccluded within Fe- and Al oxides. The procedure consists of the following extractions: *(i)* 0.1 M NaOH to remove nonoccluded Al- and Fe- bound P, *(ii)* 1 M NaCl and citrate-bicarbonate (CB) to remove P sorbed by carbonates during the preceding NaOH extraction, *(iii)* citrate-dithionite-bicarbonate (CDB) to remove P occluded within Fe- and hydrous oxides, and *(iv)* 1 M HCl to remove Ca- bound P. Similar extraction schemes are also used for fractionation of heavy metals in soils, such as nickel, cadmium and lead (Amacher, 1996) and organic S (Tabatabai, 1996).

Solutions used to extract a particular element may vary regionally due to inherent differences in the chemical, physical, and biological properties of soils. For example, an extractant comprised of dilute acid (0.025 M HCl) and dilute ammonium fluoride (0.03 M NH_4F) is frequently used as an index of available P in the Eastern and Midwestern states of the USA. This extractant is appropriate for slightly acid to neutral soils. The NH_4F complexes with Fe and Al in the acidic solution, hence, dissolving Fe- and Al-phosphates (Kuo, 1996). In contrast, a solution consisting of 0.5 M $NaHCO_3$ at pH 8.5 is more regularly used to extract available P from soils in the Western region of the USA that are often alkaline and calcareous and contain Ca-phosphates. This extractant prompts precipitation of Ca as $CaCO_3$, decreasing the Ca concentration and consequently, increasing the P concentration in the soil solution (Olsen and Sommers, 1982).

Many laboratories have adopted the use of "universal extractants" that can extract several elements simultaneously. Two of these are the Mehlich-III (0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.15 M NH_4F + 0.013 M HNO_3 + 0.001 M EDTA, adjusted to pH 2.5) developed to extract plant available P, K, Na, Ca, Mg, Mn, Zn and Cu (Mehlich, 1984) and the ammonium bicarbonate (AB)-DTPA extractant (AB-DTPA: 1 M NH_4HCO_3 + 0.005 M DTPA, adjusted to pH 7.6), which removes available P, NO_3, K, Zn, Fe, Cu, and Mn (Soltanpour and Schwab, 1977; Kuo, 1996). The versatility of these "universal" extractants can be illustrated using the AB-DTPA mixture as an example. The DTPA is used to chelate micronutrients, the NH_4^+ extracts K, and the HCO_3^- extracts P (Kuo, 1996). The use of the universal extracts also varies regionally. For instance, the Mehlich-III extractant is generally preferred in the Eastern region of the U.S., while the AB-DTPA extractant is favored in the Western states.

Soil chemists, pedologists, as well as soil microbiologists are often interested in determining the total elemental composition of soils and/or soil constituents. A total elemental analysis of soils and rocks, however, initially requires that these materials be solubilized by acid digestion or fusion with various fluxes. The usual dissolution procedure for total elemental analysis is the use of hydrofluoric acid (HF) with perchloric acid ($HClO_4$) for decomposition of both the inorganic and organic soil fraction. Hydrofluoric acid dissolves silicates by the reaction of F with Si to form SiF, which is volatile when heated with strong acids. Perchloric acid becomes a strong oxidizer of organic matter when heated and also effectively removes excess HF from the sample. Variations of the HF digestion technique are reported in Hossner (1996).

The sodium carbonate fusion technique is used for determination of total soil Si, Al, Fe, Ti, Ca, Mg, Mn, and trace metals and was originally designed for elemental analysis of silicate rocks and minerals. Fusion of silicates with sodium carbonate renders them soluble in hydrochloric acid. However, the presence of Fe- and Mn-oxides should be considered because they form alloys with the platinum crucibles during fusion, which can damage them. Therefore, it is recommended that samples containing >40% Fe and >1% Mn oxides be pretreated with aqua regia to dissolve the majority of oxides.

In summary, extracting solutions are used to solubilize chemical components that are "fixed" or rendered insoluble by soil systems. They are designed to extract a particular soil fraction, for example, the plant available fraction or perhaps all sorbed species (electrostatically and chemically adsorbed species). The type of extractant used depends upon the inherent nature of a soil and therefore, extracting solutions used for a specific element may vary regionally. Many laboratories are employing "universal" extractants that can simultaneously remove several elements, and efforts are now being made to standardize procedures. To determine the total elemental composition of soils, HF acid digests as well as fusion techniques are employed which decompose the soil matrix, solubilizing soil chemical elements.

Soil chemical characterization

There are a number of routine soil chemical analyses that provide the investigator with general information regarding the chemical nature of a soil (Table C9). Examples of these include: soil pH, organic matter content, and cation exchange capacity. A brief discussion of these three important analyses will be given.

Soil pH

Soil pH is one of the most common soil chemical measurements. It provides the investigator with information about the solubility of various soil compounds, the adsorption behavior of ions to soil surfaces, and the microbial activity of soil systems. Most soil

Table C9 Routine soil chemical analyses[a]

pH
Lime requirement
Total alkalinity
Organic matter content
Cation exchange capacity (CEC)
Exchangeable cations
Soluble salts
Sodium adsorption ratio
Exchangeable sodium percentage
Calcite equivalent

[a] References for these analyses are given in the texts: Page et al. (1982) and Westerman (1990).

laboratories measure soil pH using a combination glass indicator electrode coupled with a calomel reference electrode connected to a pH meter. A potentiometrically measured soil pH is essentially an index of the H^+ ion activity in a solution that is in equilibrium with soil particles (van Lierop, 1990).

Detailed reviews on soil pH are provided by McLean (1982) and Thomas (1996). Both suggest using a soil to solution ratio (weight of air- or oven-dried soil: volume of water) of 1 : 1 when water is used as the suspension medium. However, factors such as salt or electrolyte content and liquid junction potential can influence soil pH measurements. Cations of salts (e.g., K^+ in KCl) can displace H^+ and Al^{3+} ions, decreasing soil solution pH. Furthermore, a liquid junction potential can arise at the interface where two dissimilar electrolyte concentrations are in contact (e.g., soil suspensions) and is a basic limitation in accurately making direct potentiometric measurements (Harris, 2002). When a pH electrode is placed in a soil suspension, the mobilities of K^+ and Cl^- ions from the salt bridge are no longer similar, as they would be in aqueous solution, and a liquid junction potential develops. The differential mobilities are a result of the attraction of K^+ ions to negatively charged soil particles. Therefore, soil pH is often measured in a 0.01 M $CaCl_2$ solution (soil : solution ratio equal to 1 : 2) to mask the influence of variable salt content and minimize the liquid junction potential (McLean, 1982; Thomas, 1996). Junction potential can also be minimized by placing the KCl salt bridge in the clear supernatant and the glass indicator electrode in the settled soil suspension.

Soil organic matter

Soil organic matter is defined by Brady and Weil (2004) as the organic fraction of the soil that includes plant and animal residues at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by the soil population. The active colloidal behavior of the organic fraction has a significant influence on the chemical and physical properties of soils. It can account for one third or more of the cation exchange capacity (CEC) of surface soils and is the most significant factor responsible for the stability of soil aggregates.

Soil organic matter (SOM) is usually measured by determining the organic C content of a soil, and multiplying this value by a constant based on the percentage of organic C (48 to 58% by weight) in organic matter – published values for this constant range from 1.7 to 2 (Nelson and Sommers, 1996). Nelson and Sommers (1996) provide a detailed review of procedures and instrumentation used for SOM determination. They recommend that the actual organic C content be reported rather than the percent organic matter due to the difficulties in accurately determining SOM.

Soil organic carbon (SOC) content is measured using dry or wet combustion techniques. Dry combustion utilizes either medium-temperature resistance or high-temperature induction furnaces that provide the heat necessary for the combustion of organic C to CO_2. The CO_2 liberated is then quantified using gravimetric, titrimetric, volumetric, infrared, or thermal conductimetric methods. Resistance furnaces heat samples by radiation, conduction, and convection in a sample holder surrounded by high-resistance materials. Accelerators such as CuO are often mixed with a soil sample to promote the combustion of SOC. Induction furnaces use high frequency electromagnetic radiation as the heat source. Since soils cannot be heated by induction, it is necessary to add susceptors (Fe or Sn) that indirectly heat the sample by radiation, conduction, and convection.

Wet combustion usually involves digesting a sample with a 60 : 40 $H_2SO_4 : H_3PO_4$ mixture containing $K_2Cr_2O_7$ and boiling the sample at 210 °C. The SOC content is determined from the CO_2 evolved, which is adsorbed by a suitable adsorbent and weighed, or it is absorbed by a standard base and titrated. Since dry and wet combustion techniques are a measure of total soil C content (organic plus inorganic C), it is necessary to correct for the inorganic C contribution. This is accomplished by predigesting the sample to remove inorganic C present as carbonates, or measuring inorganic C and subtracting it from the total C content.

Alternately, soil organic matter content is frequently determined using the Walkley-Black method, described in detail by Allison (1965). This method, which involves oxidation of soil organic C by $Cr_2O_7^{2-}$, can be described by the following reaction:

$$2Cr_2O_7^{2-} + 3C + 16H^+ = 4Cr^{3+} + 3CO_2 + 8H_2O \qquad (1)$$

where organic C is assumed to have an average valence of zero. The excess dichromate is then titrimetrically measured with a standard $FeSO_4$ solution and the amount of organic C oxidized is calculated from the amount of dichromate reduced. A colorimetric determination of the amount of Cr^{3+} produced can also be used to quantify organic C.

Cation exchange capacity

The cation exchange capacity (CEC) of a soil is defined as the sum total of exchangeable cations that a soil can adsorb, expressed in moles of positive charge adsorbed per unit mass ($cmol_c\ kg^{-1}$) (Brady and Weil, 2004). It is the quantity of readily exchangeable cations required to neutralize negative charge in soils (Sumner and Miller, 1996). The negative charge of soil colloids is derived from isomorphous substitution within the structure of layer silicate minerals, broken bonds at mineral edges and external surfaces, dissociation of organic acid functional groups, and preferential adsorption of specific ions on particle surfaces. Thus, CEC is a soil property that is often dependent upon the conditions under which it is measured. For instance, in soils containing variable charge minerals such as kaolinite, metal oxides, and OM, CEC increases with an increase in pH.

There are numerous methods used for CEC analyses that can be categorized as: summation, direct displacement, displacement after washing, and radioactive tracer methods (Rhoades, 1982; Sumner and Miller, 1996). The *summation* method involves displacing the exchangeable cations on a soil with a saturating salt solution such as ammonium acetate. The CEC is equivalent to the sum of exchangeable cations present in the leachate. The *direct displacement* method consists of saturating the exchange sites with an index cation. Then the adsorbed index cation, and the small amount of entrained solution left in the soil after centrifugation, is directly displaced with another salt solution. The saturating index cation and anion concentrations are measured and the CEC is calculated from these values. In the *displacement after washing* method, exchange sites are saturated with an index cation. The soil is then washed free of excess saturating salt; the index cation is displaced and then quantitatively measured. The *radioactive tracer* method involves using a radioactive isotope of the saturating cation. The CEC is then calculated by measuring the distribution of the tracer between the soil and soil solution.

Ammonium acetate (pH 7.0) and sodium acetate (pH 8.2) are traditionally used as saturating solutions for CEC determinations in neutral and alkaline soils. However, with these solutions one must be concerned with dissolution of compounds such as $CaCO_3$ and $CaSO_4$, and the interaction of NH_4^+ and Na^+ with layer silicates (Chapman, 1965; Rhoades, 1982; Sumner and Miller, 1996). Modified procedures for CEC determination of arid and acid soils are presented by Rhoades (1982). With arid soils, a saturating solution of a 0.4 M sodium acetate/0.1 M NaCl in 60% ethanol, pH 8.2 mixture is used, while 0.1 M barium chloride dihydrate is recommended as the saturating solution with acid soils.

Summary

Soil pH, organic matter content, and cation exchange capacity provide a general description of the chemical character of a soil. These determinations, along with physical and clay mineralogical data, provide the analyst with the necessary information to assess the general usefulness of a soil as a medium for plant growth or as a waste disposal site.

Analytical techniques

Most quantitative soil chemical analyses are conducted using spectroscopic techniques. These primarily include molecular (ultraviolet (UV) – visible) absorption, atomic absorption, and inductively coupled plasma (ICP) spectrometry. Chromatographic techniques, which include gas, high-performance liquid, and ion chromatography, are also frequently utilized for the analyses of organic compounds and ions. Other important techniques that deserve mention include X-ray fluorescence spectrometry (Karathanasis and Hajek, 1996) and neutron activation (Helmke, 1996) for sensitive elemental analysis of soils, and the use of ion selective electrodes for potentiometric determination of ion activities (i.e., K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, NO_3^-, Cl^-, Br^-, and F^-) in soil solutions (Talibudeen, 1991).

Molecular absorption spectrometry

This technique utilizes a spectrophotometer (colorimeter) for the quantitative determination of compounds that absorb light. The spectrophotometer measures the transmission of light at a specific wavelength through a solution of a colored species that absorbs strongly at that wavelength (Smith and Scott, 1983). The basic components of a spectrophotometer are the radiation source, a monochromator, a sample cell, and a detector. Absorption of light is commonly measured by absorbance (A) or transmittance (T), which are defined as $A = \log(I_o/I)$ and $T = I/I_o$, where I_o is the intensity of the incident light beam and I is the intensity of the transmitted light beam. The most common analytical application of spectrophotometry utilizes the relationship between absorbance and concentration. This relationship is described by Beer's law: $A = abc$, where absorbance (A) is proportional to the concentration (c) of the absorbing species, b is the pathlength of the light through the solution, and a is the absorptivity, a proportionality coefficient. Beer's law works best for dilute solutions (<0.01 M) of a light absorbing species. At higher concentrations, deviations from Beer's law occur that result in changes in the absorbing species or in the properties of the bulk solution (Harris, 2002).

A typical measurement using molecular absorption spectrometry would involve measuring the proportionality between the concentration and absorbance of a set of standards. Subsequently, an unknown quantity of the same species can be determined by directly comparing its absorbance to the standards. Orthophosphate concentrations in soil and aqueous solutions, for example, are commonly measured using colorimetry. Phosphate reacts with an acid molybdate solution to form a phosphomolybdate complex (Harwood et al., 1969; Kuo, 1996). This complex turns blue upon chemical reduction and the darkness of the color is an indicator of phosphate concentration.

Atomic absorption and emission spectrometry

Atomic absorption and emission spectrometry have become two of the principle analytical techniques for elemental analysis in agricultural and environmental laboratories. They are relatively easy to use and have detection limits sufficient for most elemental analyses. They routinely measure concentrations in the parts per million range, and in many cases concentrations in the parts per billion range. Atomic spectrometric methods require that a sample be atomized at high temperatures. The concentration of chosen atoms is then determined by measuring absorption or emission at characteristic wavelengths. The spectra of atoms consist of very sharp lines and are a result of transitions between electronic states of an atom. Because each element has its own distinct atomic spectrum, there is little overlap between spectra of elements in the same sample. For these techniques, standard curves are used to establish the relation between signal and concentration. For more detailed information readers are referred to Ure (1991) and Sharp (1991), Wright and Stuczynski (1996), Soltanpour et al. (1996).

The basic components of an atomic absorption (AA) spectrometer are a hollow cathode discharge lamp, a burner/nebulizer, a monochromator, a photomultiplier detector and an output device (Ure, 1991). The hollow cathode lamp is made from the element being analyzed and emits a spectrum characteristic of that element. The light generated by the hollow cathode lamp passes through the flame atomizer. A typical AA spectrometer uses a flame with a temperature of about 2 400–2 700 K produced from a fuel-oxidizer combination consisting of acetylene and air, respectively. The sample analyte is sprayed as a fine mist into the flame by a pneumatic nebulizer. Thermal processes in the flame atomize the spray mist and the analyte atoms absorb light from the hollow cathode lamp at the wavelength of the absorbing analyte line.

For greater sensitivity and smaller sample size, an atomic absorption spectrometer with an electrothermal furnace for sample atomization is used. Usually 1 to 2 ml of sample solution are consumed during flame analysis, however, only 1 µl is sufficient for use in a graphite furnace. Furthermore, since the graphite furnace temperature is 3 000 °C and the entire sample is confined in the light path for a few seconds, atomization is more complete and the analytical sensitivity much higher. Instrument operation, however, requires greater skill. The light passing through the flame or furnace is received by a monochromator, which isolates the absorbing resonance line from other nonabsorbing lines. The photomultiplier detector produces an output current proportional to the incident light emitted by the monochromator. This current signal is amplified, electronically processed and finally exhibited by a readout device (printout or digital display).

With AA spectrometry one must be aware of spectral, chemical and ionization interferences. For example, spectral interferences are unwanted signals that overlap the analyte signal, while chemical interferences result from chemical reactions that decrease the concentration of the analyte atoms (formation of oxides as they rise through the outer core of the flame). Ionization interferences are caused by the ionization of analyte atoms decreasing the concentration of neutral analyte atoms in the flame.

Inductively Coupled Plasma (ICP) Atomic Emission spectrometry is a widely used technique for chemical analyses of soils. ICP utilizes a high temperature plasma resulting in more complete sample atomization and consequently, elimination of many interferences and sources of error encountered with conventional flames. It also offers the sensitivity and precision of an AA spectrometer and has simultaneous multielement capability. The plasma is generated in a quartz torch apparatus that is surrounded by a radio frequency induction coil. High purity argon gas is fed into the torch inlet and is ionized by a spark from a tesla coil. The Ar^+ ions are immediately accelerated by the radio-frequency field oscillating around the load coil. The accelerated ions transfer energy to the entire gas by collisions between atoms. The temperature is maintained at 6 000 to 10 000 K in the flame and the quartz burner is protected from the high temperatures by argon coolant gas. Analyte is introduced into the plasma using a conventional nebulizer. The ICP requires no light source; atoms in the plasma are promoted to excited electronic states by collisions with other atoms. The excited atoms emit their characteristic radiation as they return to their ground state. A grating monochromator selects and isolates the specific wavelength of the analyte element. The emission intensity at a characteristic wavelength of an element is generally proportional to the concentration of the element in the sample being measured. A photomultiplier detector collects the emission light from an element, and converts it to an electric current signal. This signal is amplified, electronically processed, and displayed on a readout device. The coupling of ICP with mass spectrometry (ICP-MS) enables isotopic analyses to be made (e.g., Tyler and Olsson, 2001). An accessible description of the technique is given in Soltanpour et al. (1996) and Kennett et al. (2001).

Chromatographic methods

Chromatography is a technique where molecules in a mobile phase are separated because of their different affinities for a stationary phase. The greater the affinity for the stationary phase, the longer the molecule is retained by that phase. The chromatographic methods most commonly used by soil science researchers are gas (GC), high performance liquid (HPLC), and ion chromatography (IC). Detailed reviews on chromatography are provided by Skoog (1985), Harris (2002), Smith and Arah (1991), Eagle et al. (1991), and Tabatabai and Frankenbuger (1996).

In gas chromatography a volatile liquid or gaseous solute is carried by a gaseous mobile phase over a stationary liquid that is coated on a solid support. A compound is then identified by its retention time on different columns. Gas chromatography is used by soil scientists to measure gaseous constituents (permanent gases and volatile compounds) in soil atmospheres. The important features of gas chromatographs are: (1) a carrier gas system, (2) an apparatus that introduces the sample into the carrier gas stream, (3) a column that separates the components of the sample (commonly used adsorbents are synthetic zeolites, porous polymer beds, alumina, silica gel, activated charcoal, and graphitized carbon black materials), (4) a detector (usually measuring either thermal conductivity or flame ionization of sample analyte) signals the elution of each constituent and provides a quantitative measure of each component, and (5) a recording system (Smith and Arah, 1991).

High Performance Liquid Chromatography (HPLC) is similar to GC except that the solvent is a liquid, which is forced through a column using a high-pressure pump (Harris, 2002). It can separate and identify an extensive variety of volatile and nonvolatile organic compounds. The most common stationary phase usually contains nonpolar groups, which are covalently bound to 5 to 10 μm silica particles. High performance liquid chromatography employs isocratic elution (separation using a single solvent of constant composition) or separation efficiency can be enhanced using gradient elution (separation using two or more solvents that differ in polarity). Generally, HPLC detectors measure ultraviolet absorbance, refractive index, or polargraphic current of elution bands (Harris, 2002).

Ion chromatography is very similar to HPLC, and the columns are comprised of ion exchange resins (Harris, 2002). An IC contains a combination of separator and suppressor columns. The former separates the analyte ions and the latter replaces the ionic eluent with a nonionic species. Thus, it is possible to measure analyte ions using a conductivity detector. Ion chromatography is especially useful for measuring the soil solution concentration of anionic species, such as nitrate, chloride, sulfate, phosphate, and bromine.

State-of-the-art research techniques

Many soil and environmental chemists are utilizing sophisticated spectroscopic and microscopic techniques to obtain information about interactions between soil surfaces and inorganic and organic molecules. Some of these techniques include Fourier transform infrared (FTIR), electron paramagnetic resonance (EPR), X-ray photoelectron (XPS), and X-ray absorption fine structure (XAFS) spectroscopies (Fendorf and Sparks, 1996; Johnston and Aochi, 1996; Senesi, 1996; and Vempati et al., 1996) along with scanning electron (SEM), transmission electron (TEM), and atomic force (AFM) microscopies.

For example, FTIR is often used to characterize the solid/liquid interface at oxide and clay mineral surfaces, and can provide information regarding sorbed inorganic and organic pollutants at these inferfaces. XPS is another surface sensitive technique that has been used to provide information on the adsorption of species on mineral surfaces, leaching and weathering of mineral surfaces, atomic structure of minerals and glass, and the oxidation state of near surface atoms. Recently, there has been considerable interest in XAFS, a technique used for *in-situ* determination of the local chemical environment around a specific X-ray absorbing element (Fendorf and Sparks, 1996; Brown et al., 1999). It can probe most elements at structural sites within crystals and glasses, as well as at mineral/water interfaces. XAFS has provided valuable information about the structural characteristics of heavy metals sorbed to the surfaces of iron and aluminum oxides.

Soil biochemists also routinely use spectroscopic techniques such as FTIR and ^{13}C-nuclear magnetic resonance (NMR) to characterize humic substances (Mao et al., 2000). Specifically, these methods are used to identify and to a certain extent quantify functional groups present in humic and fulvic acids. These structures include aliphatic and aromatic C and also phenolic, carboxyl, methoxy, and amino groups.

Summary

Chemical analyses of soil systems are necessary to understand their highly variable and complex nature. Prior to conducting any chemical determination, soils are treated with solution reagents to extract the particular chemical component of interest. Extracts are designed to draw from a specific soil fraction. For example, some extracts will remove elements associated with the plant available fraction, while others will remove all elements sorbed to soil particles. After extraction, soil extracts are usually chemically analyzed (quantitatively) using colorimetric, atomic spectrometric, and chromatographic techniques. A routine chemical characterization of a soil should include determination of soil pH, soil organic matter, and cation exchange capacity.

Paul R. Grossl and Donald L. Sparks

Bibliography

Allison, L.E., 1965. Organic Carbon. In Black C.A., et al., eds., *Methods of Soil Analysis: Part 2 – Chemical and Microbiological Properties.* Madison, WI: American Society of Agronomy, pp. 1367–1378.

Amacher, M.C., 1996. Nickel, cadmium, and lead. In Sparks D.L, et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties,* 3rd edn. Madison, WI: American Society of Agronomy, pp. 739–768.

Brady, N.C., and Weil, R.R., 2004. *Elements of The Nature and Properties of Soils,* 2nd edn. Upper Saddle, NJ: Prentice-Hall.

Brown, G.E., Foster, A.L., and Ostergren, J.D., 1999. Mineral surfaces and bioavailability of heavy metals: a molecular scale perspective. *Proc. Natl. Acad. Sci.*, **96**: 3388–3395.

Chapman, H.D., 1965. Cation-Exchange Capacity. In Black C.A., et al., eds., *Methods of Soil Analysis: Part 2 – Chemical and Microbiological Properties.* Madison, WI: American Society of Agronomy, pp. 891–901.

Eagle, D. J., Jones, J.L.O., Jewell, E.J., and Paxton, R.P., 1991. Determination of Pesticides by Gas Chromatography and High-Pressure Liquid Chromatography. In Smith, K.A., ed. *Soil Analysis: Modern Instrumental Techniques,* 2nd edn., New York: Marcel Dekker, pp. 547–600.

Fendorf, S., and Sparks. D.L., 1996. X-Ray Absorption Fine Structure Spectroscopy. In Sparks D.L., et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 377–416.

Hamilton, E.I., 1980. Analysis for Trace Elements I: Sample Treatment and Laboratory Quality Control, Chapter 2. In Davies, B.E., ed., *Applied Soil Trace Elements.* New York: Wiley, pp. 21–68.

Harris, D.C., 2002. Quantitative Chemical Analysis. 6th edn. New York: W.H. Freeman and Company.

Harwood, J.E., Steenderen, R.A., and Kuhn, A.L., 1969. A Rapid Method for Orthophosphate Analysis at High Concentrations in Water. *Water Res.*, **3**: 417–423.

Helmke, P.A., 1996. Neutron Activation Analysis. In Sparks, D.L., et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, Inc. pp. 141–160.

Hossner, L.R., 1996. Dissolution for Total Elemental Analysis. In Sparks, D.L., et al., eds., *In Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 49–64.

Johnston, C.T., and Aochi, Y.O., 1996. Fourier Transform Infrared and Raman Spectroscopy. In Sparks, D.L., et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 161–224.

Karathanasis, A.D., and Hajek, B.F., 1996. Elemental Analysis by X-ray Fluorescence Spectroscopy. In Sparks, D.L, et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties,* 3rd edn. Madison, WI: American Society of Agronomy, pp. 161–224.

Kennett, D.J., Neff, H., Glascock, M.D., and Mason, A.Z., 2001. A geochemical revolution: inductively coupled plasma mass spectrometry. *The Archaeological Record*, **1**: 22–26.

Kuo, S., 1996. Phosphorus. In Sparks, D.L, et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 869–919.

van Lierop, W., 1990. Soil pH and Lime Requirement Determination. In Westerman, R.L., ed., *Soil Testing and Plant Analysis,* 3rd edn. Madison, WI: Soil Science Society of America, pp. 73–126.

Lindsay, W.L., and Norvell, W.A., 1978. Development of a DTPA Soil Test for Zinc, Iron, Manganese, and Copper. *Soil Sci. Soc. Am. J.* **42**: 421–428.

Mao, J.-D., Hu, W.-G., Schmidt-Rohr, K., Davies, G., Ghabbour, E.A., and Xing, B., 2000. Quantitative Characterization of Humic Substances by Solid-State Carbon-13 Nuclear Magnetic Resonance. *Soil Sci. Soc. Am. J.* **64**: 873–884.

McLean, E.O., 1982. Soil pH and Lime Requirement. In Page, A.L., Miller, R.H., and Keeney, D.R., eds., *Methods of Soil Analysis: Part 2 – Chemical and Microbiological Properties*, 3rd edn., Madison, WI: American Society of Agronomy, pp. 199–224.

Mehlich, A., 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.*, **15**(12): 1409–1416.

Nelson, D.W., and Sommers. L.E., 1996. Total Carbon, Organic Carbon, and Organic Matter. In Sparks, D.L, et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 961–1010.

Olsen, S.R., and Sommers, L.E., 1982. Phosphorus. In Page, A.L., Miller, R.H., and Keeney, D.R., eds., *Methods of Soil Analysis: Part 2 – Chemical and Microbiological Properties*, 2nd edn. Madison, WI: American Society of Agronomy, pp 403–430.

Peck, T.R., and Soltanpour, P.N., 1990. The Principles of Soil Testing. In Westerman, R.L., ed., *In Soil Testing and Plant Analysis*, 3rd edn. Madison, WI: Soil Science Society of America, pp. 1–10.

Rhoades, J.D., 1982. Cation Exchange Capacity. In Page, A.L., Miller, R.H., and Keeney, D.R., eds., *Methods of Soil Analysis: Part 2 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, 149–158.

Risser, J.A., and Baker, D.E., 1990. Testing Soils for Toxic Metals. In Westerman, R.L., ed., *In Soil Testing and Plant Analysis*, 3rd edn. Madison, WI: Soil Science Society of America, 275–298.

Senesi, N., 1996. Electron spin (or paramagnetic) resonance spectroscopy. In Sparks, D.L., et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 323–356.

Sharp, B.L., 1991. Inductively coupled plasma spectrometry. In Smith, K.A., ed. *Soil Analysis: Modern Instrumental Techniques*, 2nd edn. New York: Marcel Dekker, pp. 63–110.

Skoog, D.A., 1985. *Principles of Instrumental Analysis*, 3rd edn. Phildelphia: Saunders.

Smith, K.A., and Arah, J.R.M., 1991. Gas chromatographic analysis of the soil atmosphere. In Smith, K.A., ed., *Soil Analysis: Modern Instrumental Techniques*, 2nd edn. New York: Marcel Dekker, pp. 505–546.

Smith, K.A., and Scott, A., 1991. Continuous-flow, flow-injection, and discrete analysis. In Smith, K.A., ed., *Soil Analysis: Modern Instrumental Techniques*, 2nd edn. New York: Marcel Dekker, pp. 183–228.

Soltanpour, P.N. and Schwab, A.P., 1977. A new soil test for simultaneous extraction of macro- and micronutrients in alkaline soils. *Commun. Soil Sci. Plant Anal.*, **8**: 195–207.

Soltanpour, P.N., Johnson, G.W., Workman, S.M., Benton Jones, J., Jr., and Miller, R.O., 1996. Inductively coupled plasma-mass spectroscopy. In Sparks, D.L, et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 91–140.

Sparks, D.L. (ed.), 1996. *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy.

Sumner, M.E., and Miller., W.P., 1996. Cation exchange capacity and exchange coefficients. In Sparks, D.L., et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 1201–1230.

Tabatabai, M.A., 1996. Sulfur. In Sparks, D.L., et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 501–538.

Tabatabai, M.A., and Frankenburger, W.T., Jr., 1996. Liquid Chromatography. In Sparks, D.L., et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 225–246.

Talibudeen, O., 1991. Ion-selective electrodes. In Smith, K.A., ed., *Soil Analysis: Modern Instrumental Techniques*, 2nd edn. New York: Marcel Dekker, pp. 111–182.

Thomas, G.W., 1996. Soil pH and soil acidity. In Sparks, D.L., et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 475–490.

Tyler, G., and Olsson, T., 2001. Concentrations of 60 elements in the soil solution as related to the soil acidity. *Eur. J. Soil Sci.*, **52**: 151–165.

Ure, A.M., 1991. Atomic absorption and flame emission spectrometry. In Smith, K.A., eds., *Soil Analysis: Modern Instrumental Techniques*, 2nd edn. New York: Marcel Dekker, pp. 1–62.

Vempati, R.K., Hess, T.R., and Cocke, D.L., 1996. X-ray photoelectron spectroscopy. In Sparks, D.L., et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 357–376.

Westerman, R.L. (ed.), 1990. *Soil Testing and Plant Analysis*, 3rd edn. Madison, WI: Soil Science Society of America.

Wright, R.J., and Stuczynski, T.I., 1996. Atomic anbsorption and flame emission spectrometry. In Sparks, D.L., et al., eds., *Methods of Soil Analysis: Part 3 – Chemical and Microbiological Properties*, 3rd edn. Madison, WI: American Society of Agronomy, pp. 65–90.

Cross-references

Acidity
Acids, Alkalis, Bases and pH
Base Saturation
Carbonates
Humic Substances
Soil Mineralogy
Sorption Phenomena

CHEMICAL COMPOSITION

See *Chemical Analyses*.

CHEMISORPTION

Adsorption, usually irreversible, involving chemical action. Adsorbed ions or molecules are held to a surface by a strong chemical bond. The heat of adsorption is >20kcal/mole, as opposed to physical adsorption: <10kcal/mole (McBride, 1994, p 344).

Bibliography

McBride, M.B., 1994. *Environmental Chemistry of Soils*. New York: Oxford University Press, 406 pp.

Cross-reference

Sorption Phenomena

CHERNOZEMS

Chernozems are soils with a thick black, organic-rich, surface layer. The name was coined by Dokuchaev in 1883 for the typical soils of the tall grass steppes in continental Russia. This article is based on FAO (2001).

Connotation. Black soils rich in organic matter; from R. *chern*, black, and *zemlja*, earth or land.

Synonyms. Equivalent to the chernozemic Soils in Canada, and to several sub-orders of the mollisols (Soil Taxonomy). Black Soils is a common term used internationally.

Definition. Defined in FAO (2001) as soils having

1. a *mollic* horizon with a moist chroma of 2 or less if the texture is finer than sandy loam, *or* less than 3.5 if the texture is sandy loam or coarser, both to a depth of at least 20 cm, *or* having these chromas directly below any plow layer; and
2. concentrations of *secondary carbonates* starting within 200 cm from the soil surface; and
3. no *petrocalcic* horizon between 25 and 100 cm from the soil surface; and
4. no secondary gypsum; and
5. no uncoated silt and sand grains on structural ped faces.

Parent material. Mostly aeolian and aeolian sediments reworked by water (loess).

Environment. Regions with a continental climate with cold winters and hot summers; in flat to undulating plains with tall-grass vegetation (forest in the northern transitional zone) (see Figure C34).

Profile development. AhBC profiles with a dark brown to black *mollic* surface horizon over a *cambic* or *argic* subsurface horizon, commonly with redistribution of calcium carbonate to a *calcic* horizon or pockets of *secondary carbonates* in the subsurface soil.

Origin. The combination of inherently very fertile loess, and a sub-humid climate produces the typical flourishing grasslands (prairie, steppe, pampas) under which Chernozems develop. The important formative processes are the accumulation of humus, bioturbation and translocation of calcite. In tall grass prairie, the above ground biomass may be 1 to 1.5 t of dry matter per hectare, with 4 to 6 t ha^{-1} of corresponding root mass below ground. The formation and accumulation of humus occurs principally in the upper 60 cm of soil where plant roots are mainly concentrated. An active mixing is generally brought about by earthworms, which produce the Vermic Chernozem. Larger, animals excavate burrows and may help to homogenize the soil by bioturbation. Calcite (ubiquitous in loess) tend to

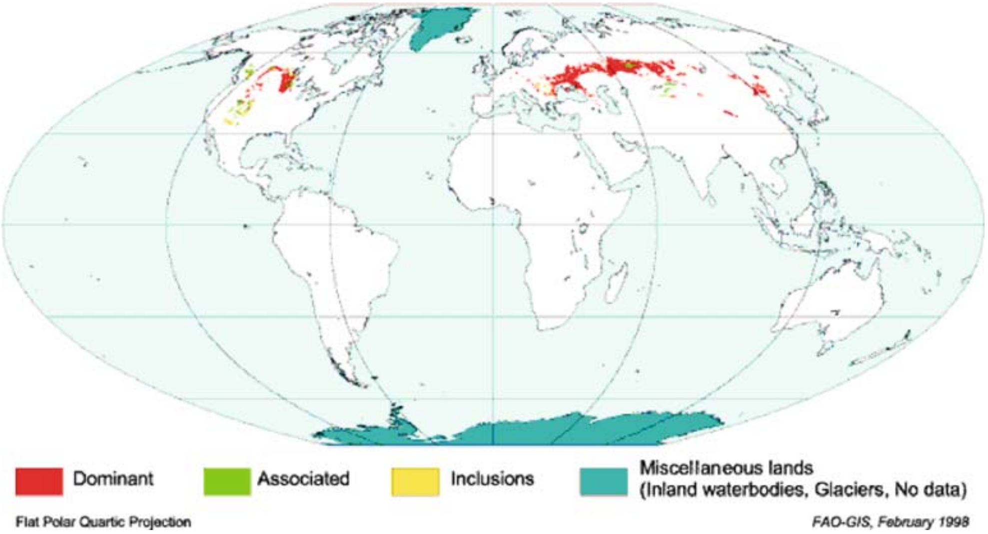


Figure C34 Distribution of Chernozems.

be dissolved in the upper part of the profile in wet periods, to be precipitated at depth, while drier periods encourage the capillary uprise of soil solutions rich in Ca^{2+} and cause calcite to form higher in the profile.

Use. The high natural fertility of Chernozems and their favorable topography permit a wide range of agricultural uses including arable cropping (with supplemental irrigation in dry summers) and cattle ranging.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Biomes and their Soils
Calcareous Soils
Classification of Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles

CHRONOLOGY OF SOILS

A timetable for an evolving soil on a geologic time scale, apart from recent anthropic (man-made) modification, depends on:

a. *Parent material* (which may be the geological bed-rock, or wind-blown cover such as loess or sand dunes, or littoral accumulations such as beachridges, or alluvial deposits associated with flood plains).
b. *Zonal climate* (which may be roughly stated as "latitude", but more precisely modified by oceanicity, or maritimicity, continentality, altitude and aspect, i.e., exposure to insolation, fetch, and prevailing wind).
c. *Geomorphic history* (which generally spans the period of time since the latest ice ages, thus in North America and Europe since about 12 000 years ago, but in South America, South Africa, India and Australia, about 265 Myr. ago. Even more for North Africa and much of Arabia, where it is 445 Myr).

Study of these three variables is integral to what constitutes "Soil Stratigraphy", a science that for understandable reasons found its birthplace in Australia, a continent relatively unscathed by the giant ice sheets that affected North America and northern Europe. A given paleosol in Australia can often be tracked down to a specific date in the stratigraphic timetable. Its basic composition may be cemented in place by the widespread silicification that commonly affects that continent's 15 to 35° S latitudes (see *Duricrusts and induration*). Because of these silicified paleosols, some quite remarkable examples of ancient soil stratigraphy are preserved, such as the "Kirup Conglomerate" found by Finkl on some hilltops in southwestern Australia. The paleosol in question contained glacially faceted boulders of the Permian glaciation and occupied former stream channels that must date from about 250 Myr (Fairbridge and Finkl, 1978).

This sort of history is not unusual for the former soils associated with the landscapes of the ancient continent of Gondwanaland. For much of that history the landscapes in question were associated with the global distribution of the dinosaurs which required (in the case of the herbivores) a fertile soil and nearly universal spread of vegetation.

The plate-tectonic break-up of Gondwanaland was a progressive phenomenon, with one segment after another (Fairbridge, 1982). With each new rupture the isostatic response of the crust led to rapidly rising shoulders and a topography that changed from a flat plateau to a steep-sided escarpment such as marks the present-day Red Sea and typically developed in Yemen or northern Ethiopia.

With each fracture zone initiation ("taphrogenic triggering") with its Red-Sea-type sea-floor spreading, a new geomorphic cycle and soil-forming cycle is set in motion. The time clock is re-set. Lester King, in his magisterial "*Morphology of the Earth*" (1962), summarized cycles of this sort very well for Gondwanaland. For Eurasia and North America the problem was (and remains) a much more challenging one, because of Cenozoic glaciation and complex tectonics. The Gondwana cycles began soon after the end of the Permo–Carboniferous ice ages and could be followed across the southern continents in a succession of uplifted erosion surfaces mostly preserved today as "etchplains".

Each planation cycle corresponds to what Erhart (1956) called the "biostatic phase" in his "Theory of Biorhexistasy". And each taphrogenic break-up triggered his brief but violent "rhexistatic phase". The first, the biostatic condition, was one of adjustment of river networks to the new general base level and climatic stability. Fairbridge and Finkl (1980) called this a "cratonic regime", that is, corresponding to the continental interior plateaus, and in contrast to the continental margins (both cliffed and with coastal plains), which are subject to the new tectonic activity, maritime climates and multiple eustatic fluctuations.

Each of these rhexistatic cycles (e.g., mid-Mesozoic, terminal Cretaceous, mid-Cenozoic, etc.) is typically represented by paleosols with massive duricrusts (usually lateritized or silicified). In places these have often been buried by younger sedimentary strata, but may be re-exhumed, to be preserved today as monadnocks or plateaus. In the case of the Appalachian Mountains in the non-glaciated part of North America, the late Mesozoic was a biostatic phase that was progressively brought to an end by the plate-tectonic opening of the North Atlantic and catastrophically punctuated by the K/T asteroid event with its major drop in sea level. During the biostatic phase the porous sandstones of Paleozoic age became deeply silicified (10–20 m or more), but during the early Tertiary rhexistasy there was deep incision of major river valleys and progressive uplift, while progressive, differential erosion occurred in the soft-shale and calcareous sediments, leaving the silicified ridges behind. "Water gaps" mark the successful drainage systems. During the glacial advances, the entire region was subjected to periglacial erosion, still preserved today by patterned ground and boulder streams. The forest cover appears to be anchored in the "skeletal" or "fragmental" soils that survived the periglacial erosion (largely aeolian), but were supplemented by the small contributions from the wind-borne loess storms that swept across the Midwest.

Techniques for working out a soil chronology in a given region must vary with the materials available. Isotopic dating methods have some usefulness where a given horizon has been exposed to insolation or geochemical crusting. The role of dew may be significant when dust is trapped and forms a thin veneer or "desert varnish" over an exposed surface such as a pebble, boulder or rocky outcrop. Less precise, but nevertheless often very useful, are the stratigraphic "sandwich" methods, for example, an exhumed paleosol surface at some point is often found to plunge beneath a stratigraphic horizon that is datable from its fossils or isotopic aspects. This date then constitutes an upper limit of the paleosol. The archaeologists call this an "*ante quem*" date. Then a "*post quem*" date is one where a paleosol is found truncating that stratigraphic formation; the paleosol is then younger.

In the use of a sequence of paleosols, one over another, this is what Fairbridge and Finkl (1980) refer to as "stacked veneers". These are often to be found near the margins of cratonic units, where repeated uplift and successive climate changes can vary the characteristics of the individual veneers.

Climatic proxies can often serve as accurate pointers to the former climate associated with a given paleosol. Different types of duricrust reviewed in Fairbridge (1968), and include: ferricrete, or lateritic duricrust, i.e., generally silicified latosols; or calcrete, i.e., calcified duricrust, "hardpan" or "caliche"; or silicrete, i.e., a silicified concretionary hardpan. They are all characteristic of different parent materials but have a commonality in the form of a semi-arid and strongly seasonal climate. Each is a distinctive indication of a specific climatic type: *(a)* the latosol speaks only of the tropical monsoon climate; *(b)* the calcrete is derived from a coastal belt fed by wave and wind action on comminuted shells and carbonate foraminifera, the carbonate dust being blown inland, but exceptionally the parent material consists of pre-existing limestones; *(c)* the silcrete is formed in swamps (with a distinctive pH range) which dry out seasonally.

"Stone lines" are a diagnostic feature of certain soils. They are most typical of tropical soils, in the rhexistatic belts. Clearly, they are relics of a colluvial nature, i.e., slope deposits, stone pavements or lag gravels. The stratification and transport may be the result of slope wash or even a mudflow, which can be tropical or even periglacial ("solifluction"), but certainly limited to heavy precipitation events or brief melt-seasons. The stones are angular to rounded, of resistant nature such as quartzite, granite and even fragments of termitaria (termite mounds). The pebbles may be concentrated by aeolian winnowing (a selection of photographs is provided in Fairbridge and Finkl, 1984).

Another aspect of paleoclimate indicators is the widespread development of white, podzolized sand plains and sandy deserts in the low latitudes (Paton et al., 1995). They are known as "siliciclastic", being dominated by quartz and other minerals of low solubility. It appears that they are the end products of either *(a)* tropical weathering, typically of granite or granitoid crystalline parent material under hydrologic processes, where the feldspars and micas revert to clays easily removed by running water. Or *(b)* recycled from glacial outwash where the sands have been mechanically generated and feldspatic components are well preserved; but when exposed to post-glacial humid weathering the insoluble components are eventually released.

The origin of the celebrated sands of the Sahara has long been debated. Three prominent source areas contribute: *(a)* Outwash from the Atlas Mts, Hoggar and other uplifts; *(b)* Recycled Ordovician glacial outwash in the western and central Sahara; *(c)* Recycled Nubian Sandstone in the east (a Cretaceous to Cenozoic product of former tropical rivers emanating from Central Africa. Eolian systems have changed throughout the Quaternary, so that the present dunes are representing a "well-stirred pot", predominantly quartz today, but Pleistocene dunes are often reddish in color, from the ferromagnesian minerals mobilized into solution during the long interglacial and monsoon-dominated intervals.

Podzolization and laterization

These are two distinctive processes in the chronology of the paleosols. Both are essentially "end-members" in evolving histories.

According to Duchaufour (1978), *podzolized soils* are "characterized by the biochemical weathering of silicates by soluble and acid organic matter, with formation of more or less mobile organomineral complexes which accumulate in one or two 'spodic' type horizons rich in amorphous material (dark B_h horizon enriched with humic acids, and ocherous B_o horizon enriched with hydroxides)." The name "pod" comes from the Russian word for "ash", i.e., silica-enriched, with iron and aluminum complexes leached out. In temperate latitudes podzolization is only scattered but widespread in the boreal forests of northern Canada and Siberia. In the hydromorphic (acid) conditions of tropical coastal belts it is widespread, being derived from the polymictous beach and dune sands after extensive leaching of their carbonate content. From the paleoclimatic point of view they reflect extended intervals of intense pluviosity, which has led to their present status as "leached residuals" (Fairbridge and Finkl, 1984).

The other "end-member" state is here referred to as "laterization", a process recognized by geologists, but in the U.S. Soil Taxonomy represented by the OXISOLS, on the FAO-UNESCO World Map Legend as FERRALSOLS, or in Bridge's review (1978) as "ferrallitic soils". One of the problems associated with the varied terminologies is that the classic "laterite" is not found in North America or Europe. It stems from India, where it was described by Buchanan in a paper nearly two centuries ago. There the soft hydrous ferrallitic clay is commercially formed into brick-like shapes and laid out in the sun to dehydrate, the hydrous gel breaks down and the process is irreversible, so that an all-weather building material is created. The term *latericius* is Latin for "brick". The same process occurs in an environmentally catastrophic way when tropical rainforest is cleared as in the Amazon basin. Unless it is immediately replanted the soil becomes rock-hard and resistant to further tillage.

Both the economically sound and the disastrous activities serve to illustrate the term "laterization" (the *Glossary of Geology* places "lateritization" in synonymy). In the U.S. Soil Taxonomy it is called "plinthite", a product of ferrallitic desiccation, leading to a hardpan, durable crust or "carapace". It is a typical feature of the cratonic landscapes of India, Australia, Africa and Brazil. These landscapes have been repeatedly subjected to an alternation of intense rainfall and deforestation associated with ice-age desiccation that can be dated over about the last three million years. Isotopic dating of certain laterites in Australia disclose a Miocene date for their beginning. Others have been dated by igneous dikes of known age or overlapped by fossiliferous sedimentary formations.

In short, the process of "laterization" can hardly be regarded as a normal contemporary soil-forming process, but it should be borne in mind as a potential hazard in environmental review.

Rhodes W. Fairbridge

Bibliography

Bridges, E.M., 1978. *World Soils*, 2nd edn. Cambridge: Cambridge University Press, 128 pp.

Duchaufour, P., 1978. *Ecological Atlas of Soils of the World.* New York: Masson, 178 pp.

Erhart, H., 1956. *La Genese des Sols. Esquisse d'une Théorie Géoligique: Biostasie et Rhexistasie.* Paris: Masson, 90 pp.

Fairbridge, R.W., 1968. *The Encyclopedia of Geomorphology.* New York: Van Nostrand Reinhold, 1295 pp.

Fairbridge, R.W., and Finkl, C.W., Jr., 1978. Geomorphic analysis of the rifted cratonic margins of Western Australia. *Zeitschr. f. Geomorph., N.F.*, **22**(4): 369–389.

King, L.D., 1967. *The Morphology of the Earth,* 2nd edn. Edinburgh: Oliver & Boyd.

Cross-references

Classification of Soils
Crusts, Crusting
Duricrusts and Induration
Ferralsols
Ice Erosion
Iron Oxides
Podzols
Profile
Weathering Systems in Soil Science

CHRONOSEQUENCE

A sequence of soils in which the dominant variable accounting for any physical, chemical and biological differences has been the duration in time over which the sequence has developed. (Birkeland, 1999, p 178).

Bibliography

Birkeland, Peter W., 1999. Soils and geomorphology. 3rd ed. New York: Oxford University Press. 430 pp.

CLASSIFICATION OF SOILS: FAO

The FAO soil classification system is based on the Legend for the Soil Map of the world (FAO/UNESCO, 1974).

The FAO legend was largely based on the diagnostic horizon approach developed under Soil Taxonomy (Soil Survey Staff, 1960) by the USDA during the 1950s and 1960s. Similar horizons were defined, and where definitions of the diagnostic horizons were slightly simplified, different names were used for comparable horizons such as the ferralic horizon equivalent to the oxic horizon, or the argic horizon equivalent to the argillic horizon in Soil Taxonomy. The grouping is based on measurable as well as observable soil properties.

Certain historical soil names were retained to accommodate some national sensitivities. Examples of these at the highest level were rendzinas, Solonetzes, Solonchaks, and Chernozems. Some of the names had a dubious scientific connotation (such as the podzoluvisols in which no podzolization takes place), while others were nearly identical to those developed in Soil Taxonomy, such as the Vertisols (Nachtergaele, 2003).

In contrast with Soil Taxonomy, climatic characteristics were not retained in the FAO Legend, although the xerosols and yermosols largely coincided with soils developed under an aridic moisture regime.

The FAO Legend of 1974 recognized 26 Great Soil Groups (world classes) subdivided in 106 Soil Units (world subclasses), which were the lowest category recognized on the world soil map. The units are designed primarily for the legends of the Soil Map of the World and do not correspond exactly to categories in other systems but they are generally comparable at the "Great Group" level. These map units are sufficiently broad to contain sufficient elements to reflect as precisely as possible the soil pattern of a large region.

In addition to the Great Soil Groups and Soil Units, twelve soil phases were recognized: This subdivision is based on characteristics, which are significant to use, or management. They are:

- *stony phase*: mechanized agricultural equipment impracticable.
- *lithic phase*: hard rock within 50 cm of surface.
- *petric phase*: a layer with >40% oxidic concretions >25 cm thick, the upper part occurring within 100 cm of the surface.
- *petrocalcic phase*: petrocalcic horizon within 100 cm of the surface.
- *petrogypsic phase*: petrogypsic horizon within 100 cm of the surface.
- *petroferric phase*: petroferric horizon within 100 cm of the surface.
- *phraetic phase:* ground-water table between 3 and 5 m from the surface.
- *fragipan phase:* fragipan within 100 cm of the surface.
- *duripan phase:* duripan within 100 cm of the surface.
- *saline phase:* electrical conductivity of >4 mmho cm^{-1} within 100 cm of the surface.
- *sodic phase:* more than 6% exchangeable sodium saturation within 100 cm of the surface.
- *cerado phase:* areas with tall grass and low contorted trees.

Three general texture classes:

- *coarse textured*: sands, loamy sands and sandy loams with less than 18% clay and more than 65% sand.
- *medium textured*: sandy loams, loams, sandy clay loams, silt loams, silt, silty clay loams and clay loams with less than 35% clay and less than 65% sand; the sand fraction may be as high as 82% if a minimum of 18% clay is present.
- *fine textured:* clays, silty clays, sandy clays, clay loams and silty clay loams with more than 35% clay.

Three general slope classes:

- *level to gently undulating*: dominant slopes ranging between 0 and 8%.
- *rolling and hilly*: dominant slope ranging between 8 and 30%.
- *steeply dissected to mountainous*: dominant slopes are over 30%.

Most soil mapping units were in fact soil associations, the composition of which was indicated at the back of each paper map sheet (Nachtergaele, 2003). The dominant soil unit gave its name (and appropriate color) to the mapping unit, followed by a number unique to the associated soils and inclusions. Texture (1, 2, and 3) and slope symbols (a, b, and c) were included in the mapping unit symbol.

Although initially developed as a Legend for a specific map, not a soil classification system, the FAO Legend found quick acceptance as an international soil correlation system, and was used for several national soil classifications, as well as for soil inventories as in the soil map of the European Union. With the application as a soil classification, numerous comments and suggestions were received to improve the coherence of the system. The revision effort undertaken in the 1980s finally resulted in the publication of the Revised Legend of the FAO/UNESCO Soil Map of the World (FAO/UNESCO/ISRIC, 1988) (see Table C10). This revised legend was applied to the World Soil Resources Map at 1 : 25 000 000 scale, accompanied by a report (FAO, 1993) and presented at the Kyoto ISSS Congress.

Table C10 The revised FAO World Classes (Great Soil Groups) of soils and their equivalents at the order, suborder and great group levels in the USDA Soil Classification System (adapted after Fitzpatrick, 1980, FAO, 1993)

	FAO	USDA
1	Acrisols	Ultisols (all suborders)
2	Andosols	Andepts
3	Arenosols	Psamments
4	Cambisols	Ochrepts, tropepts, umbrepts
5	Chernozems	Borolls
6	Ferralsols	Oxisols (all suborders)
7	Fluvisols	Fluvents
8	Gleysols	Aquents, aquepts, aquolls
9	Lixisols	Oxic Alfisols
10	Alisols	Vertisols with high activity clays
11	Greyzems	Borolls, aquolls
12	Histosols	Histosols (all suborders)
13	Kastanozems	Ustolls, borolls
14	Luvisols	Udalfs, xeralfs, ustalfs, aqualfs, boralfs
15	Nitosols	Udalfs, ustalfs, udults, ustults, xerults, humults
16	Phaeozems	Udolls, aquolls
17	Planosols	Aqualfs, xeralfs, argids, ustalfs, aquults, albolls, borolls
18	Solonchaks	Orthids, ustolls
19	Solonetz	Ustalfs, xeralfs, argids
20	Podzols	Orthods, ferrods, humods, aquods
21	Podzoluvisols	Udalfs, boralfs, aqualfs
22	Leptosols	Lithosols, lithic subgroups
23	Regosols	Orthents, psamments
24	Vertisols	Uderts, usterts, xererts, torrerts
25	Calcisols	Calcic Aridisols
26	Gypsisols	Aridisols
27	Lithosols	
28	Anthrosols	Various orders

In the revised legend, the number of Great Soil Groups increased from 26 to 28: the rankers and rendzinas were grouped with the Leptosols, the "aridic" yermosols and xerosols disappeared, and new Great Soil groups of Calcisols and Gypsisols were created. The Luvisols (alfisols)–Acrisols (ultisols) division was further divided according to the activity of the clay fraction, resulting in four symmetric groups (Luvisols, high base saturation, high-activity clays; Acrisols, low base saturation, low-activity clays; Lixisols, high base saturation, low-activity clays; and Alisols with low base saturation and high-activity clays). The revised legend also created at the highest level the Anthrosols, grouping soils strongly influenced by human activities. The number of Soil Units increased from 106 to 152. Texture and slope classes remained unchanged, but were not represented on the map produced. A third hierarchical level of "Soil Subunits" was introduced to support soil inventory on larger scales. Soil subunits were not defined as such but guidelines for their identification and naming were given. This converted the map legend, with a finite number of entries, into an open-ended, globally applicable FAO-UNESCO Soil Classification System.

In a parallel development, a working group of the ISSS had been active in the development of an internationally acceptable soil classification system (first meeting in Sofia, 1982). In 1992, at a meeting of the Working Group RB (Reference Base), the strong recommendation was made that rather than developing a new soil classification system, the Working Group should consider the FAO Revised Legend as a base and give it more scientific depth and coherence. This principle was accepted, and the first draft of the World Reference Base (WRB) appeared in 1994 (ISSS/ISRIC/FAO, 1994), still showing large similarities with the FAO revised legend.

In 1998, the International Union of Soil Sciences (IUSS) officially adopted the World Reference Base for Soil Resources (WRB) as the Union's system for soil correlation. The structure, concepts and definitions of the WRB are strongly influenced by the FAO-Unesco Soil Classification System. At the time of its inception, the WRB proposed 30 "Soil Reference Groups" accommodating more than 200 ("second level") Soil Units (FAO, 2001, World Soil Resources Reports, 94). Two new reference groups have since been added (FAO, 2006).

Arieh Singer

References

FAO, 1993. World Soil Resources. An explanatory note on the FAO World Soil Resources Map at 1:25.000.000 scale, 1991. Rev. 1993. World Soil Resources Reports #66. Rome: FAO.

FAO, 2001. Lecture notes on the major soils of the world. In Driessen, P., Deckers, J., Nachtergaele, F., eds., World Soil Resources Reports #94, Rome: FAO.

FAO. 2006. World reference base for soil resources, 2006: a framework for international classification, correlation, and communication. Rome: Food and Agriculture Organization of the United Nations. 128 pp.

FAO/UNESCO, 1974. FAO–UNESCO Soil Map of the World. Vol. 1. Legend. Paris: UNESCO.

FAO/UNESCO/ISRIC, 1988. FAO–UNESCO Soil Map of the World. Revised Legend. World Soil Resources Report #60, Rome: FAO.

Fitzpatrick, E.A., 1980. *Soils – Their Formation, Classification and Distribution.* London: Longman, 353 pp.

ISSS/ISRIC/FAO, 1994. World Reference Base for Soil Resources. Draft. O. Spaargaren. Ed. Wageningen/Rome.

Nachtergaele, F., 2003. The future of the FAO Legend and the FAO/UNESCO soil map of the world. In Eswaran, H., Rice, T., Ahrens, R., Stewart, B., eds., *Soil Classification.* Washington, DC: CRC Press, pp. 147–156.

Soil Survey Staff, 1960. Soil classification, A comprehensive system. Seventh Approximation, SCS, USDA. Washington, DC: U.S. Government Printing Office.

Cross-references

Classification of Soils: Soil Taxonomy
Classification of Soils: World Reference Base (WRB) for Soil Resources
Horizon Designations in the WRB

CLASSIFICATION OF SOILS: SOIL TAXONOMY

Introduction

Most countries of the world have some kind of soil survey program. Some programs assess soil resources at the farm level, while others are designed for county, state, or national levels. The United States began soil resource assessment around 1899, but it began an institutionalized, systematic detailed soil survey only in the nineteen thirties. By the end of the nineteen forties, about fifty million acres of land per year were being surveyed and more than one thousand soil scientists from the Soil Conservation Service (now called the Natural Resources Conservation Service – NRCS) and U.S. universities were involved. The then existing classification system did not serve the purpose of standardization, quality control, and communication between soil scientists. It was recognized that the national soil survey program needed a system of soil classification that could be applied uniformly by soil scientists, could be the basis of the soil survey program, serve the purpose of technical communication between soil scientists, and have the capability to predict the consequence of alternative uses. Soil surveys are useful because they have a scientific basis (which ensures their reproducibility) and because they can be employed for practical land use purposes. The role of soil classification is to act as a bridge to synthesize soil survey information and provide pragmatic groupings for the needed precise predictions. These were some of the motivating reasons for creating Soil Taxonomy, which was published in 1975 (Soil Survey Staff. 1975) for the purpose of making and interpreting soil surveys. Several modifications have been made since its publication and in 1999 the second edition of the manual was published (Soil Survey Staff. 1999) to commemorate the 100th anniversary of the national soil survey program.

The system of soil classification was developed over a period of 25 years, commencing in 1951, with Dr. Guy D. Smith coordinating the effort (Smith, 1983). By 1960, a working draft was already available and was tested in the field over the next decade. Publication of the system took place in 1975. The system was developed by U.S. soil scientists with the collaboration of scientists from around the world. Major contributors to the nomenclature, for example, were Professors Rene Tavernier and Jacque Leeman of the University of Gent, Belgium. The system of soil classification was influenced by similar developments in other national classification systems, specifically those in Europe, Australia, and New Zealand and the FAO-UNESCO legend of the Soil Map of the World (FAO-UNESCO, 1971–1981). Many of these national systems have undergone modifications since their inception and a recent review (Eswaran et al., 2003) gives information on the current structures.

Principles of the soil classification system

Classification of discrete objects such as plants or animals is in many ways easier than a continuum with no distinct boundaries such as soils. Every classification system attempts to group similar things together. Though this can be achieved by an analysis of soil properties, the additional dimension in soil classification is that 'similar soils' must have similar performance in most uses. In addition, because the system is designed to support a soil survey program, it must be able to differentiate between all soils on a landscape and the goal was also that every soil in the world would find a place in the system. Existing systems in the nineteen fifties were genetic in concept and based on soil processes, actual or perceived. To meet new requirements, a major shift in approach was necessary. This proved to be a major challenge and some compromises had to be made.

The guiding principles of Soil Taxonomy are enunciated by Cline (1949), Smith (1963), and Arnold and Eswaran (2003). The major principle stresses that the classification is of soils and not of soil-forming processes or factors. This is a major distinction from the Russian school of classification. Soil genesis is employed to guide our thinking about soils but is not used as the basis for classification because if the genesis of a soil is not known the soil cannot be classified. Other principles employed to develop the system are as follows:

- Definitions are based on soil properties so that users can apply them systematically;
- The system is multi-categorical with the information content increasing in the lower categories; this enables ease of use of the system and the selection of categories based on the detail required by the purpose;

- The defined units must be of real bodies that are known to occur in the world;
- Although properties are precisely defined, to facilitate the field soil scientist an initial assessment could also be made in the field either through simple field tests or interpretation from landscape, vegetation, and/or geology;
- The system must be modular so that with new knowledge, changes may be made without disrupting the whole system;
- Properties selected are not markedly affected by normal management, so that the classification is not changed by plowing or fertilizing or other farming techniques;
- Finally the system should differentiate all soils in a landscape and provide a place for all known soils.

Diagnostic horizons and features

The use of diagnostic horizons and features probably distinguishes Soil Taxonomy from most other classification systems. Diagnostic horizons and features are the building blocks of the system and serve to define the different categories of the system. The significance of each horizon or feature is a function of the soil. Some diagnostic horizons or features are used to define the Order category, such as the mollic epipedon of mollisols. Within the mollisols, a diagnostic feature such as an ustic soil moisture regime (SMR) defines the Suborder, a diagnostic subsurface horizon defines the great group (argillic horizon for the argiustoll), and another diagnostic feature such as an aquic soil water regime is used for the subgroup (aquic argiustoll). The relative importance of the diagnostic horizons and features differs with soils, and selection is made based on the principles enunciated before.

Categories and nomenclature

The six categories in the classification system are Order, Suborder, Great Group, Subgroup, Family, and Series. There are twelve Orders, which are differentiated by the presence or absence of diagnostic features, or horizons which indicate differences in the intensity and kind of dominant soil forming processes, or their absence. These are:

- histosols – organic soils resulting from accumulation of organic matter (histic materials) under very wet or cold environments;
- gelisols – are soils that freeze sometime during the year and have a layer of frozen soils called permafrost at shallow depths;
- spodosols – soils that have a spodic horizon that formed by the translocation and accumulation of iron, aluminum, and/or organic carbon;
- andisols – soils that formed in volcanic materials (andic materials) in which weathering results in dominance of amorphous colloids;
- oxisols – soils that have an oxic horizon characterized by low activity clays;
- vertisols – soils that have vertic properties resulting from high amounts of clays such as montmorillionite that shrink when dry and swell when wet;
- aridisols – soils that have an aridic soil moisture regime that can have in horizons of accumulated carbonates, gypsum, and soluble salts;
- ultisols – soils that have an argillic horizon and low base saturation (low pH or acid) because of leaching;
- mollisols – soils that have a mollic epipedon characterized by black colors and relatively high organic carbon content;
- alfisols – soils that have an argillic horizon and high base saturation or high pH;
- inceptisols – soils that have a cambic horizon or are at a youthful stage in soil formation;
- entisols – soils that have no diagnostic horizon (except for an ochric epipedon) and formed in recent materials.

Each Order has four to six suborders defined on the basis of properties that are major controls of soil formation or absence of such controls. Soil moisture and temperature regimes are considered as the controls and are employed at this level. The Great Groups are defined by the arrangement of diagnostic horizons in the soil and/or subordinate controls of soil-forming processes. The Subgroups are designed to show linkages to other categories in the system (intergrades) or to some special properties or even non-soil features (extra grades) such as a rock contact at shallow depth. Within each Subgroup, the Family is defined on similar physical and chemical properties that affect their response to management and manipulation for use. The lowest category, the Series, is defined almost essentially on field observable properties that are within the range of the Family. This is partly because; the Series category is used for detailed maps and for most farm level interpretations and recommendations. The definitions and functions of these categories are provided in Soil Taxonomy (Soil Survey Staff. 1975, 1999). Periodic refinements are made to the classification system and these are published in the monograph called "Keys to Soil Taxonomy"; the most recent is published by Soil Survey Staff (2003).

A number of classification systems already existed at the time of development of the U.S. system. In addition, many terms, such as laterite, have popular meanings, the original scientific definition being lost through popular use. A concerted effort was made to create new terms with each name being short, easy to pronounce, distinctive in meaning, and connotative. The name was also required to indicate the categorical level and thereby its position in the classification.

The names of the categories are recognized as follows:

- Order – each Order name ends in '*sol*': andisols, histosols;
- Suborder – names are two syllables with the second syllable carrying the formative name of the Order: udox (oxisols), aquult (ultisols), orthent (entisols);
- Great group – carries the suborder name and a prefix: *haplu*dox, *kandi*aquult, and *torri*orthent.
- Subgroup – carries the great group name and an adjective: *typic* hapludox, *aeric* kandiaquult, *vertic* Torriorthent.
- Family – names are polynomial and carry the subgroup name and adjectives that indicate one or more significant features (usually particle size class, mineralogy, and soil temperature regime): clayey, kaolinitic, isohyperthermic, typic hapludox.
- Series – names are abstract and usually taken from place names where the soil was first recognized: Kluang series (a soil in Malaysia) is a member of the clayey, kaolinitic, isohyperthermic Family of typic hapludoxs.

Determining the taxonomic class of a soil

The taxonomic class of a soil is determined by using the keys and definitions to the various categories in Soil Taxonomy. Prior to attempting to classify the soil, it is necessary to determine if the soil has diagnostic horizons and/or diagnostic features. The profile description, which is the field assessment of the soil, provides clues to possible diagnostic features. These are confirmed by testing the required criteria for the horizons. An estimate of the soil moisture regime (SMR) and soil temperature (STR) is also made from climatic records of the closest meteorological station if actual measurements at the site are not available.

Armed with this information of the soil, the Order placement is determined by using the ‘Keys to Soil Orders’ in the book (Soil Survey Staff. 2003). The Keys are structured to systematically and sequentially test a class. If a soil does not meet criteria of the eleven Orders, it is placed in the last class, entisols. A soil must meet the class definition to qualify for the class. A page number directs the user to the appropriate Suborder key. This process of searching and elimination or fitness is done for each category until the Family category. For example, a soil in Malaysia (Kluang Series) has a SMR of udic and STR of isohyperthermic (continuously wet and continuously hot), an ochric epipedon (surface horizon) and an oxic subsurface horizon. It does not have any other features. In the “Keys to Soil Orders”, the soil does not meet the definition of a gelisol, histosol, andisol, or spodosol, but meets the requirements of an oxisol. The soil is thus an oxisol. Following a similar procedure of testing of class membership, the soil is placed in the Suborder udox. The “Keys” for each category can then be followed systematically without short cuts, and the soil is finally determined to belong to the clayey, kaolinitic, isohyperthermic Family of the typic hapludoxs.

Evaluating soil properties from soil name

Apart from being mnemonic, soil names also are designed to provide information about the soils themselves. The Kluang Series described previously is used as an example.

- Oxisol – the soil has low nutrient holding capacity; it has few weatherable minerals and thus has low potential to provide nutrient elements through weathering; it generally has a low water holding capacity; it has few rock fragments and thus has few restrictions to root growth.
- Udox – the soil experiences little or no moisture stress.
- Hapludox – the soil does not have high base saturation nor is it acid; it has no plinthite and has very little organic matter.
- Typic hapludox – the soil is well drained and has few physical root-restricting layers.
- Clayey, kaolinitic, isohyperthermic typic hapludox – soil temperature is not a constraint; nutrient fixation is not high though leaching losses may be high; tillage is easy.
- Kluang Series – the soil has all the above properties. It is an ideal soil for growing rubber (*Hevea braziliensis*) and less suitable for oil-palm (*Elais guinensis*). Annual crops require good fertilizer management.

Global distribution of soils

Many countries have classified their soils according to Soil Taxonomy, and it is possible to translate other classification systems to Soil Taxonomy. However, estimates of the distribution of the soils globally, are still not possible because many countries have yet to make detailed inventories. Table C11 provides some preliminary estimates made by the World Soil Resources section of the Natural Resources Conservation Service, U.S. Department of Agriculture and Figure C35 is a map showing the distribution.

In Table C11, the estimates of the soil Orders and Suborders occurring in the different climatic or major eco-regions are provided in addition to the global distribution; examples of each Order is shown in Figure C36. Only the suborders that are extensive enough to be shown on the world map are listed. Soil patterns are distinct and show the role of soil moisture and temperature regimes interacting with parent materials. In Europe, the soil moisture regimes show a north-south trend and the consequent effect on soil formation is illustrated by horizontal patterns of the soils. In North America and particularly in the United States, the soil moisture regimes show an east-west trend and the soil patterns reflect this trend. On the eastern seaboard, the soils are ultisols, and as one proceeds westward, they give way to mollisols, alfisols, and aridisols. Finally, in the Rocky Mountains, the soils are inceptisols and some andisols. Farther north in North America, the soils are dominantly inceptisols and spodosols, which give way to histosols and gelisols in the northern tundra zone.

Gelisols, the most recent soil order introduced into the system of Soil Taxonomy, occupy about 9.1% of the ice-free land surface. Few detailed soil maps depict these soils, as previous classification systems did not differentiate the soils based on permafrost. The lower geographic limit of gelisols for this map is defined by a mean annual soil temperature of less than 0 °C and by a mean summer soil temperature of less than 10 °C. The northern part of the gelisol zone grades to ice. Areas of soils are indicated as a percent of the ice-free land surface.

Organic soils, or histosols, occupy about 1.2% of the land surface. This percentage does not include the 0.8% of histels, which are present in the gelisol region and which form the largest contiguous extent of organic soils. The next largest area of organic soils is adjacent to the tundra soils in the boreal belt. These organic soils are the “cryo” great groups of fibrists, hemists, and saprists. Tropical histosols are dominantly in Southeast Asia, mainly in Sumatra and Kalimantan. Many of the tropical histosols are on coastal plains and have very low pH because of the presence of acid sulfate materials. Unlike the temperate and boreal histosols, which formed in areas of moss and grassy vegetation, tropical histosols are woody and frequently contain large trunks of undecomposed trees. These woody materials make cultivation of such soils difficult.

Spodosols are dominantly in the colder regions of the world where STR is mesic or colder and SMR is udic or perudic. These boreal spodosols occupy about 2.2% of the land surface. Podzolization results from release of large quantities of organic acids in the organic-rich surface soil horizons. Characteristically, these soils form in sandy materials or in materials with only small amounts of weatherable minerals that have the potential to alter and release bases. In the Tropics, soils with similar morphology are in areas of coastal beach deposits. The largest contiguous extent of such soils is on the coastal plains of the Amazon Basin. The soils are described and classified as spodosols but frequently are not the result of the podzolization process that operates in the temperate or boreal climates. The sandy levee deposits or stranded beach deposits occur in association with aquepts and saprists. The dissolved organic colloids seep up the sands (capillary effect) and precipitate at the capillary fringe of the ground water table. The resulting morphology is that of a spodic horizon.

Andisols dominate the circum-Pacific belt, or the Ring of Fire. They are frequently associated with current or former volcanic activity. Depending on the intensity and periodicity of the volcanic activity, deposits of several ages may characterize a soil. In the colder and moister parts of the world, andisols are characterized by dark mollic-like or umbric-like epipedon. Buried horizons with similar organic-rich horizons may be typical. In the Tropics, organic accumulation is not so rapid. In addition, weathering and mineral alteration lead to the formation of a clay fraction dominated by halloysite and kaolinite. A normal toposequence in the Tropics is andisols on the upper slopes, in association with inceptisols, which give way to ultisols and oxisols on the gentler topography. In some andisols in which

Table C11 Preliminary estimates about the global distribution of soils made by the World Soil Resources section of the Natural Resources Conservation Service, U.S. Department of Agriculture (see also Figure C33)

Soil order	Sub-order	Area (x1 000)																	
		Ice-free land		Tropical		Temperate		Boreal		Tundra		Aridic		Xeric		Ustic		Udic	
		Sq. km.	Percent	Sq. km.	Percent	Sq. km.	Percent	Sq. km.	Percent	Sq. km.	Percent	Sq. km.	Percent	Sq. km.	Percent	Sq. km.	Percent	Sq. km.	Percent
	Histels	1 013.358	0.77		–		–		–	1 011.295	0.77		–		–		–		–
	Turbels	5 138.116	3.93		–		–		–	5 130.754	3.92		–		–		–		–
	Orthels	5 717.831	4.37		–		–		–	5 707.147	4.36		–		–		–		–
Gelisols		11 869.31	9.07		–		–		–	11 849.2	9.06		–		–		–		–
	Folists		0		–		–		–		–		–		–		–		–
	Fibrists	197.387	0.15		–		–	194.056	0.15		–	11.674	0.01		–	42.689	0.03	139.694	0.11
	Hemists	988.264	0.76		–	99.508	0.08	884.897	0.68		–	103.452	0.08	8.551	0.01	268.205	0.21	604.197	0.46
	Saprists	340.781	0.26	317.753	0.24	22.201	0.02		–		–		–		–	40.54	0.03	299.415	0.23
Histosols		1 526.432	1.17	317.753	0.24	121.709	0.09	1 078.953	0.82		–	115.126	0.09	8.551	0.01	351.434	0.27	1 043.306	0.8
	Aquods	169.124	0.13	13.364	0.01	55.748	0.04	99.631	0.08		–		–		–		–	168.743	0.13
	Cryods	2 588.482	1.98		–		–	2 584.417	1.98		–		–	6.278	0	226.372	0.17	2 324.054	1.78
	Humods	57.87	0.04	29.242	0.02	28.476	0.02	0.078	0		–		–	6.546	0.01	10.081	0.01	41.091	0.03
	Orthods	666.784	0.51	18.103	0.01	508.527	0.39	138.221	0.11		–		–	32.739	0.03	95.15	0.07	536.962	0.41
	Gelods	1 113.368	0.85		–		–		–	1 112.453	0.85		–		–		–		–
Spodosols		4 595.628	3.51	60.709	0.05	592.751	0.45	2 822.347	2.16	1 112.453	0.85		–	45.563	0.03	331.603	0.25	3 070.85	2.35
	Cryands	255.195	0.2		–		–	254.426	0.19		–	13.99	0.01		–	47.144	0.04	193.292	0.15
	Torrands	1.598	0	1.598	0		–		–		–	1.598	0		–		–		–
	Xerands	32.128	0.02		–	32.118	0.02		–		–		–	32.118	0.02		–		–
	Vitrands	281.07	0.21	202.457	0.15	77.443	0.06	0.605	0		–	26.158	0.02		–	161.689	0.12	92.658	0.07
	Ustands	62.822	0.05	58.857	0.04	3.69	0		–		–		–		–	62.547	0.05		–
	Udands	279.427	0.21	185.821	0.14	89.49	0.07	1.765	0		–		–		–		–	277.076	0.21
	Gelands	62.27	0.05		–		–		–	62.201	0.05		–		–		–		–
Andisols		974.51	0.75	448.733	0.34	202.741	0.16	256.796	0.2	62.201	0.05	41.746	0.03	32.118	0.02	271.38	0.21	563.026	0.43
	Aquox	320.065	0.24	320.065	0.24		–		–		–		–		–	300.272	0.23	19.792	0.02
	Torrox	31.233	0.02	27.118	0.02	4.115	0		–		–	31.233	0.02		–		–		–
	Ustox	3 096.452	2.37	3 086.719	2.36	9.465	0.01		–		–		–		–	3 096.185	2.37		–
	Perox	1 161.98	0.89	1 010.135	0.77	151.49	0.12		–		–		–		–		–	1 161.626	0.89
	Udox	5 201.102	3.98	5 166.551	3.95	32.506	0.02		–		–		–		–		–	5 199.065	3.97
Oxisols		9 810.832	7.5	9 610.588	7.35	197.576	0.15		–		–	31.233	0.02		–	3 396.457	2.6	6 380.483	4.88
	Aquerts	5.484	0	0.763	0	4.721	0		–		–		–		–		–	5.484	0
	Cryerts	17.22	0.01		–		–	17.2	0.01		–	0.034	0	0.113	0	2.288	0	14.764	0.01
	Xererts	98.718	0.08		–	98.577	0.08		–		–		–	98.577	0.08		–		–
	Torrerts	889.353	0.68	238.41	0.18	647.662	0.5		–		–	886.072	0.68		–		–		–
	Usterts	1 765.352	1.35	1 169.403	0.89	594.367	0.45		–		–		–		–	1 763.77	1.35		–
	Uderts	384.358	0.29	86.105	0.07	297.273	0.23		–		–		–		–		–	383.378	0.29
Vertisols		3 160.485	2.42	1 494.681	1.14	1 642.6	1.26	17.2	0.01		–	886.106	0.68	98.69	0.08	1 766.058	1.35	403.626	0.31
	Cryids	1 051.381	0.8		–		–	1 047.373	0.8		–	902.071	0.69	20.339	0.02	55.348	0.04	69.615	0.05
	Salids	773.271	0.59	52.91	0.04	632.946	0.48	80.734	0.06	0.691	0	728.108	0.56	17.32	0.01	13.883	0.01	7.279	0.01
	Gypsids	682.963	0.52	228.484	0.17	429.405	0.33	24.126	0.02		–	601.964	0.46	22.692	0.02	57.359	0.04		–
	Argids	5 333.753	4.08	573.248	0.44	4 035.105	3.09	708.965	0.54		–	4 942.508	3.78	93.618	0.07	268.535	0.21	12.656	0.01
	Calcids	4 872.554	3.73	451.161	0.34	4 400.123	3.36	13.823	0.01		–	4 728.72	3.62	71.574	0.05	61.18	0.05	3.637	0
	Cambids	2 915.533	2.23	561.394	0.43	2 063.362	1.58	286.395	0.22		–	2 911.136	2.23		–		–		–
Aridisols		15 629.46	11.95	1 867.197	1	11 560.94	9	2 161.416	2	0.691	0	14 814.51	11.33	225.543	0.17	456.305	0.35	93.187	0.07
	Aquults	1 280.989	0.98	1 042.999	0.8	235.985	0.18	0.058	0		–		–	1.337	0	729.665	0.56	548.038	0.42
	Humults	343.518	0.26	277.802	0.21	61.013	0.05	4.691	0		–		–	18.159	0.01	38.007	0.03	287.339	0.22
	Udults	5 539.906	4.24	2 654.476	2.03	2 872.711	2.2	9.523	0.01		–		–		–		–	5 536.706	4.23
	Ustults	3 869.722	2.96	3 630.467	2.78	234.877	0.18	1.471	0		–		–		–	3 866.828	2.96		–
	Xerults	18.815	0.01		–	0.94	0	17.875	0.01		–		–	18.815	0.01		–		–
Ultisols		11 052.95	8.45	7 605.744	6	3 405.526	3	33.618	0		–		–	38.311	0.03	4 634.5	3.54	6 372.083	4.87
	Albolls	6.674	0.01		–	1.372	0	5.301	0		–		–		–	0.018	0	6.656	0.01
	Aquolls	118.072	0.09	1.156	0	84.787	0.06	31.974	0.02		–		–	0.009	0	18.191	0.01	99.717	0.08
	Rendolls	265.827	0.2	120.959	0.09	103.513	0.08	40.986	0.03		–		–	0.408	0	15.371	0.01	249.68	0.19
	Xerolls	924.394	0.71		–	873.511	0.67	50.365	0.04		–		–	923.876	0.71	0	–		–
	Cryolls	2 464.951	1.88		–		–	2 458.523	1.88		–	1 298.062	0.99	271.415	0.21	588.171	0.45	300.877	0.23
	Ustolls	3 964.441	3.03	184.731	0.14	2 370.624	1.81	1 405.342	1.07		–	2 110.438	1.61		–	1 850.262	1.41		–
	Udolls	1 261.051	0.96	54.22	0.04	1 058.004	0.81	146.619	0.11		–		–		–		–	1 258.841	0.96

Continued

Table C11 Continued

Soil order	Sub-order	Area (x1 000)																	
		Ice-free land		Tropical		Temperate		Boreal		Tundra		Aridic		Xeric		Ustic		Udic	
		Sq. Km.	Percent	Sq. Km.	Percent	Sq. Km.	Percent	Sq. Km.	Percent	Sq. Km.	Percent	Sq. Km.	Percent	Sq. Km.	Percent	Sq. Km.	Percent	Sq. Km.	Percent
	Gelolls	155.677	0.12		–		–		–	154.819	0.12				–		–		–
Mollisols		9 161.087	7	361.066	0	4 491.811	3	4 139.11	3	154.819	0.12	3 408.5	2.61	1 195.708	0.91	2 472.013	1.89	1 915.771	1.46
	Aqualfs	836.077	0.64	407.123	0.31	373.655	0.29	54.76	0.04		–		–	9.925	0.01	548.919	0.42	276.695	0.21
	Cryalfs	2 535.02	1.94		–		–	2 526.763	1.93		–		–	80.551	0.06	815.271	0.62	1 630.933	1.25
	Ustalfs	5 663.56	4.33	3 773.322	2.88	1 719.484	1.31	164.715	0.13		–		–		–	5 657.528	4.33	0	–
	Xeralfs	894.247	0.68		–	848.514	0.65	43.479	0.03		–		–	891.994	0.68		–	0	–
	Udalfs	2 691.995	2.06	616.696	0.47	1 926.532	1.47	143.891	0.11		–		–		–		–	2 687.113	2.05
Alfisols		12 620.9	9.65	4 797.141	3.67	4 868.185	3.72	2 933.608	2.24		–		–	982.47	0.75	7 021.718	5.37	4 594.741	3.51
	Aquepts	4 126.442	3.15	1 498.377	1.15	1 183.134	0.9	502.454	0.38	925.838	0.71		–	7.5	0.01	1 050.621	0.8	2 125.835	1.63
	Anthrepts		0		–		–		–		–		–		–		–		–
	Cryepts	2 619.576	2		–		–	2 612.743	2		–		–	79.516	0.06	129.194	0.1	2 404.048	1.84
	Ustepts	4 184.127	3.2	2 804.601	2.14	1 372.212	1.05	3.392	0		–		–		–	4 180.206	3.2		–
	Xerepts	685.336	0.52		–	674.694	0.52	9.76	0.01		–		–	684.454	0.52		–		–
	Udepts	4 123.193	3.15	1 755.023	1.34	2 153.364	1.65	209.803	0.16		–		–		–		–	4 118.182	3.15
	Gelepts	6 066.738	4.64		–		–	242.429	0.19	5 811.383	4.44		–		–		–	242.429	0.19
Inceptisols		21 805.41	16.67	6 058.001	4.63	5 383.404	4.12	3 580.581	2.74	6 737.221	5.15		–	771.47	0.59	5 360.021	4.1	8 890.494	6.8
	Aquents	116.087	0.09	105.614	0.08	10.222	0.01		–		–	3.589	0		–	83.087	0.06	29.16	0.02
	Psamments	4 428.052	3.39	2 799.768	2.14	1 625.304	1.24	1.333	0		–	1 466.816	1.12	56.315	0.04	2 324.022	1.78	579.248	0.44
	Fluvents	3 066.413	2.34	1 017.875	0.78	1 455.341	1.11	368.407	0.28	198.323	0.15	830.887	0.64	174.24	0.13	967.198	0.74	869.295	0.66
	Orthents	13 856.55	10.59	2 095.961	1.6	11 264.33	8.61	413.154	0.32	73.454	0.06	10 432.87	7.98	620.154	0.47	1 188.609	0.91	1 531.763	1.17
Entisols		21 467.11	16.41	6 019.218	4.6	14 355.2	10.98	782.894	0.6	271.777	0.21	12 734.17	9.74	850.709	0.65	4 562.916	3.49	3 009.466	2.3
	Shifting sands	5 321.875	4.07	545.835	0.42	4 680.128	3.58	92.912	0.07		–	5 279.51	4.04	7.255	0.01	27.137	0.02	4.972	0
	Rock	1 800.586	1.38	7.055	0.01	363.324	0.28	1 428.075	1.09		–	1139	0.87	151.764	0.12	507.688	0.39		–
	Ice	14 640.1		0		0		0		0		0		0		0		0	
Miscellaneous		0		552.89	0.42	5 043.452	3.86	1 520.987	1.16		–	6 418.51	4.91	159.019	0.12	534.825	0.41	4.972	0
Total		130 796.6	100	39 193.72	29.97	51 865.89	39.65	19 327.51	14.78	20 188.36	15.43	38 449.89	29.4	4 408.152	3.37	31 159.23	23.82	36 342.01	27.79

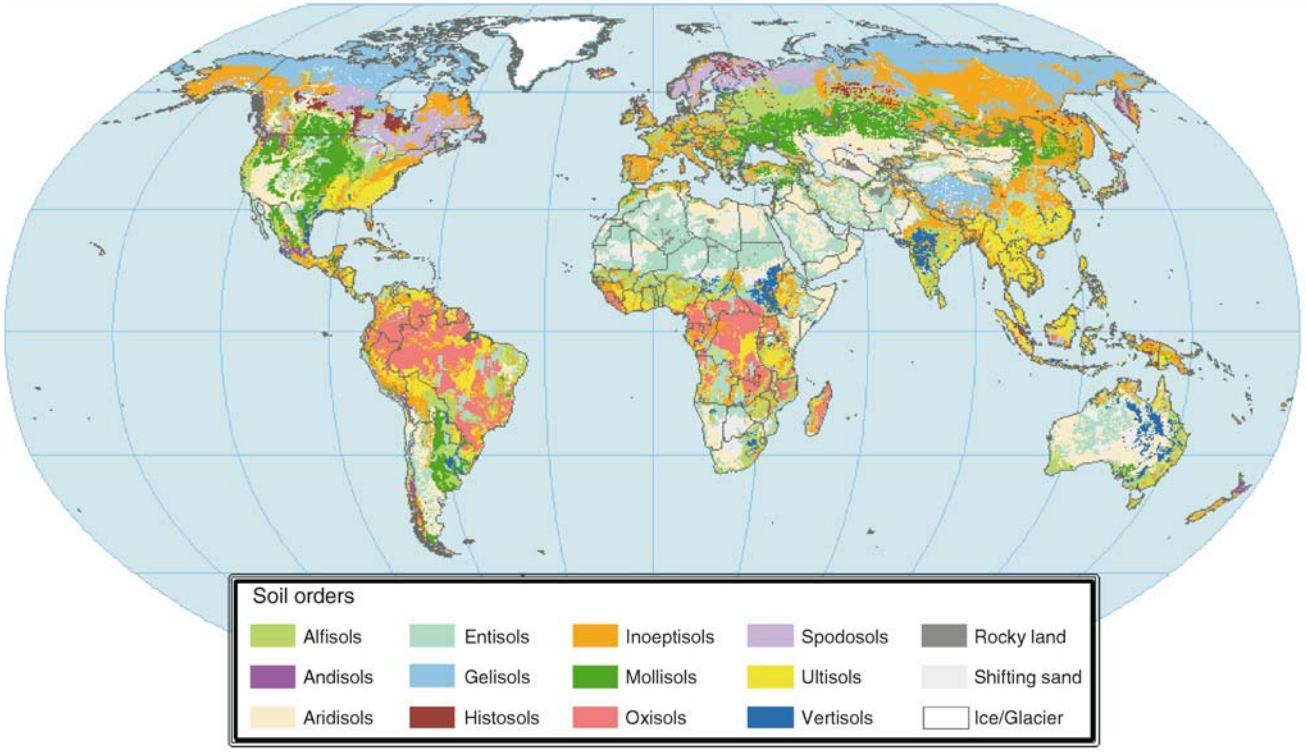


Figure C35 A generalized soil map of the world.

the content of organic matter is low and short-range-order minerals dominate the colloids, the soils may have a net positive charge. These andisols are counterparts of the suborder Anionic acrudox in terms of mineral-chemical composition.

Oxisols are confined to the intertropical regions, which by definition have an *iso* STR. Most of the oxisols occur between the Tropics of Cancer and Capricorn. The largest extent is in Brazil, followed by the Congo Basin in Central Africa. Characteristically, oxisols formed in pre-weathered and transported deposits. Weathering may continue in the post-depositional phase. Other pedogenic processes are slow unless there is a fluctuating water table. On the volcanic islands of the Pacific and in Southeast Asia, basic or ultrabasic rocks may weather to form oxisols. Although there is always the possibility of admixture with alluvial or colluvial products, these soils are generally thought to have formed directly on the rocks, unlike the oxisols of the Amazon or Congo Basins.

Vertisols occupy about 2.4% of the land surface and are about equally distributed in tropical and temperate areas. They are among the soils in which soil properties are a function of the mineralogical composition of the clay fraction. For the smectites to form and persist in the soils, one of the requirements is that the soil solution has a high pH, which results in high amounts of bases and soluble silica. Thus, most of the vertisols occur in semiarid or arid environments. The countries with large areas of vertisols are Sudan, India, Australia, and the United States. In semiarid southern Africa, large contiguous areas of vertisols are in Zambia, Zimbabwe, and South Africa. In other areas vertisols occur sporadically in basins adjoining andisols.

Although about a third of the landmass of the world is arid, aridisols occupy only about 12% of the land surface. By definition, aridisols must have a diagnostic horizon; the remaining soils in arid regions are entisols with associated unstabilized dunes and rocky land. About 75% of the aridisols are in the temperate parts of the world. The rest have tropical and boreal climates. Argids are the most extensive aridisols and are frequently in areas where the aridic SMR borders on the ustic or xeric SMR. Calcids, which occupy about 3.7% of the land area, are associated with the argids. Translocation and subsurface accumulation of carbonates, gypsum, and salts require some moisture. Formation of the horizons diagnostic for these suborders may be a current process or may have taken place in historic or geologic periods. Because of the current aridity of the sites where these soils occur, it is generally assumed that many of the diagnostic features may have a “paleo” origin.

Ultisols and alfisols occupy 8.5 and 9.7% of the land surface, respectively. Ultisols are more common in the intertropical areas, while alfisols are in the temperate areas. Also, there is greater proportion of alfisols than of ultisols in the semiarid parts of the world. The dominant feature of both ultisols and alfisols is the presence of an argillic horizon. Other diagnostic horizons or properties define the subclasses. A lighter textured surface soil, which makes tillage easy, and a heavier textured underlying argillic horizon, which enables greater storage of water and nutrients, favors crop production. Many of these soils occur on flat to gently undulating landscapes and have been used by farmers since the beginning of civilization.

Mollisols, which have a thick, organic-rich surface horizon, are among the most productive soils in the world. Some of the world’s record yields have been obtained on these soils. Mollisols occupy about 7% of the land mass and are concentrated in the temperate and boreal regions of the world. They are important soils in the semiarid parts of the world, particularly in the

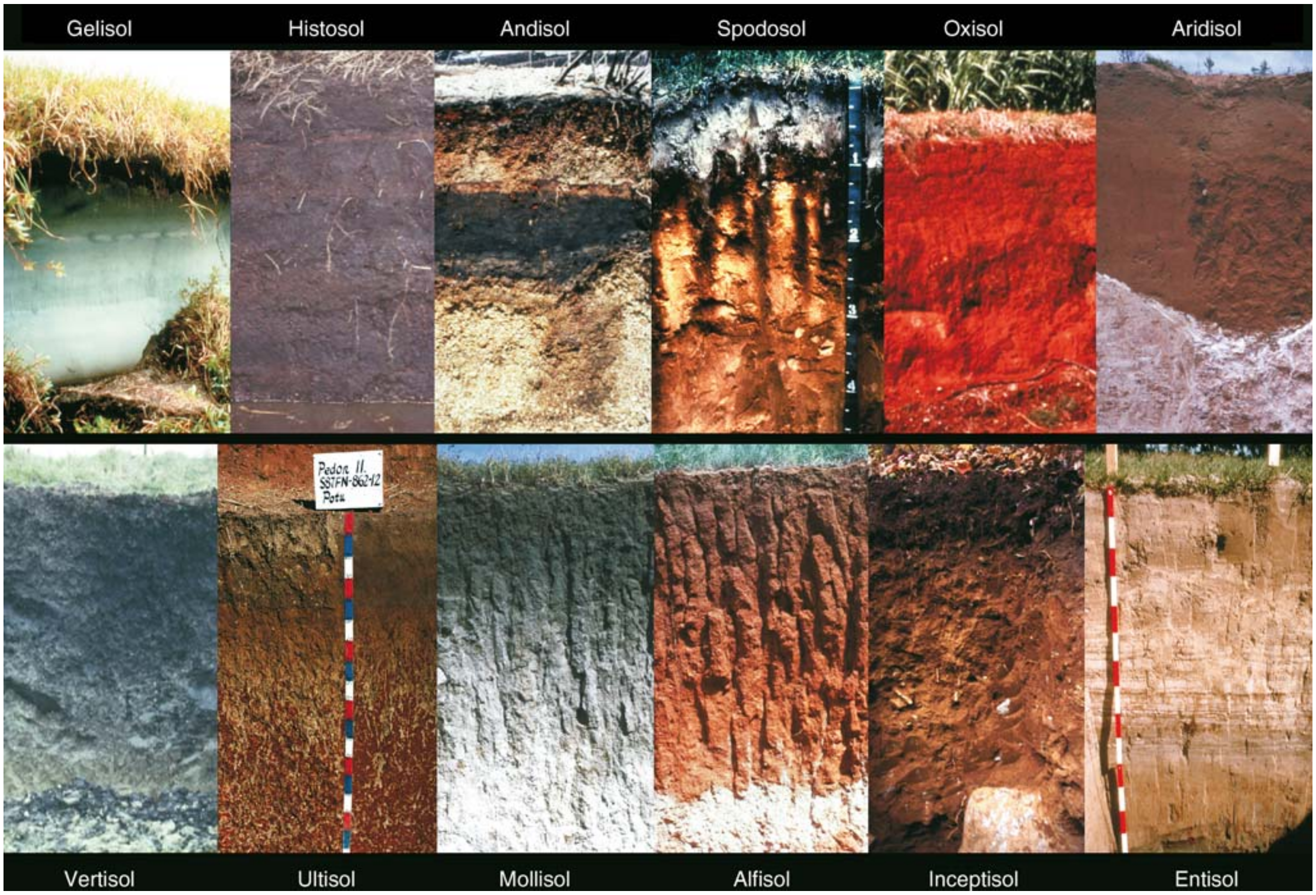


Figure C36 Examples of the major soil orders.

regions with a Mediterranean climate. The cool climate permits a slow accumulation of the humified organic matter. Because of the excellent quality of the soils and the very favorable climate, these soils are very productive and make up the breadbasket of modern times. Large areas of such soils characterize the Midwest in the United States, the steppes of the former Soviet Union, the northern part of Argentina, and part of Uruguay.

Inceptisols and entisols together occupy about 33% of the land surface. Generally on young surfaces, they occur in association with rock outcrops and sand dunes. These soils formed in recent coastal and riverine deposits. They formed in marine alluvium under brackish water conditions. Entisols are potential acid sulfate soils, and inceptisols are actual acid sulfate soils. When drained, potential acid sulfate soils (sulfaquents) are converted to actual acid sulfate soils (sulfaquepts). The process results in release of a considerable amount of sulfuric acid, making these soils and the soils adjacent to them extremely acid.

Concluding remarks

In the annals of Soil Science, Soil Taxonomy will remain as not only a major scientific and conceptual innovation but also the fact that it has withstood the test of time. In the last five decades it has demonstrated its value specifically in the United States; around the world, its technical merit has resulted in it being adopted for national use or major aspects being incorporated in the advancement of local systems. With the advent of advances in information technology, the future of Soil Taxonomy or any soil classification systems will be debated. With the ability to process large quantities of data and to generate any kind of use-related information from this data, soil classification systems must undergo marked modifications or remain as historical benchmarks.

Hari Eswaran

Bibliography

Arnold, R.W., and Eswaran. H., 2003. Conceptual basis for soil classification: lessons learnt from the past. In Eswaran, H., Rice, T., Ahrens, R., and Stewart, B., eds., *Soil Classification: A Global Desk Reference.* New York: CRC Press, pp. 27–42.

Cline, M.G., 1949. Basic principles of soil classification. *Soil Sci.*, **67**: 81–91.

Eswaran, H., Rice, T., Ahrens, R., and Stewart, B. (eds.), 2003. Soil Classification: A Global Desk Reference. New York: CRC Press, 263 pp.

FAO-UNESCO, 1971–1981. FAO/UNESCO Soil Map of the World, 1:5 million. Vols. 1–10. Rome, Italy: FAO/UNESCO.

Smith, G.D., 1963. Objectives and basic assumptions of the new classification system. *Soil Sci.*, **96**: 6–16.

Smith, G.D., 1983. Historical developments of soil taxonomy: background. In Wilding, L.P., Smeck, N.E., and Hall, G.F., eds., *Pedogenesis and Soil Taxonomy. I. Concepts and Interactions.* New York: Elsevier, pp. 23–49.

Soil Survey Staff, 1975. Soil taxonomy: a basic system of soil classification for making and interpreting soil surveys, *U.S. Dept. Agric. Handbook 436*. Govt. Printing Office, 754 pp.

Soil Survey Staff, 1999. Soil taxonomy: a basic system of soil classification for making and interpreting soil surveys. *U.S. Dept. Agric. Handbook 436*, 2nd edn. Govt. Printing Office. 869 pp.

Soil Survey Staff, 2003. *Keys to Soil Taxonomy*, 9th edn. U.S. Department of Agriculture, Natural Resources Conservation Service. Washington D.C. 332 pp.

Cross-references

Acid Soils
Alkaline Soils
Calcareous Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Horizon
Hydric Soils
Near-Neutral Soils
Soil

CLASSIFICATION OF SOILS: WORLD REFERENCE BASE (WRB) FOR SOIL RESOURCES

In 1998, the International Union of Soil Sciences (IUSS) adopted the *World Reference Base for Soil Resources* (WRB) as the official system for international correlation of soils. In addition, the WRB is the accepted common scheme of soil databases and maps of the European Union (see Figure C37).

The structure, concepts and definitions of the WRB are strongly influenced by the revised legend of the FAO/UNESCO Soil Map of the World (FAO/UNESCO-ISRIC, 1988), which in turn borrowed the diagnostic horizons and properties approach from USDA Soil Taxonomy.

The taxonomic units of the WRB are defined in terms of measurable and observable '*diagnostic horizons*', the basic identifiers in soil classification. Diagnostic horizons are defined by (combinations of) characteristic '*soil properties*' and/or '*soil materials*'.

WRB comprises two levels:

1. the "Reference Base", which is limited to the first level only having 30 reference soil groups; and
2. the second level consists of combinations of qualifiers added to the reference soil groups providing more specific characterization and classification of soils.

Short summary of the reference groups

Organic soils, such as peat, are brought together in one reference soil group called *Histosols* while all *man-made soils*, which vary widely in properties and appearance but have in common that their properties are strongly affected by human intervention are aggregated to the *Anthrosols* reference soil group. In some man altered environments non-natural materials, called 'technic materials' dominate the unit, therefore Technosols have now been added as a new Reference Group of the WRB.

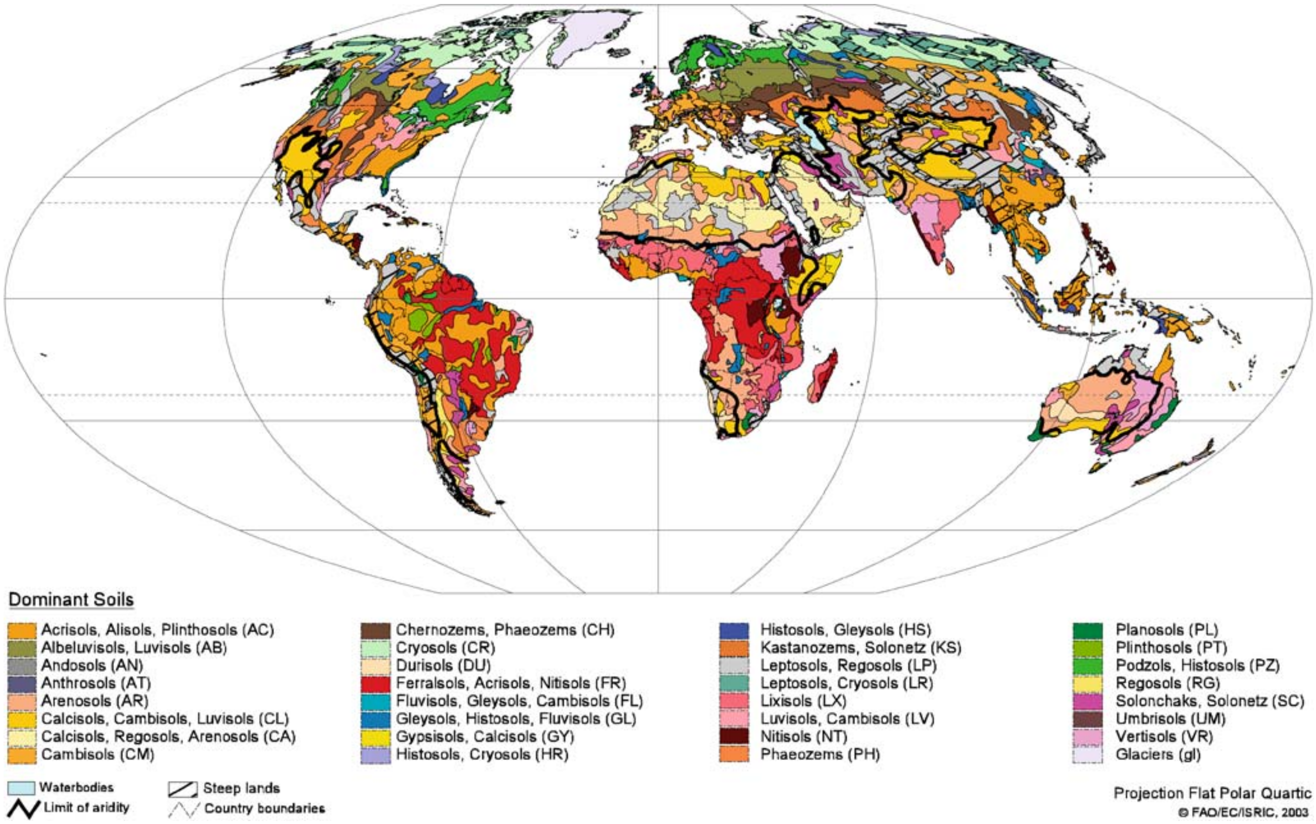


Figure C37 World Soil Resources global map.

Mineral soil whose formation is conditioned by the particular properties of their *parent material* are sub-divided into the *Andosols* of volcanic regions, the sandy *Arenosols* of desert areas, beach ridges, inland dunes or areas with highly weathered sandstone and the swelling / shrinking heavy clayey *Vertisols* of back-swamps, river basins, lake bottoms and other areas with a high clay content.

Mineral soils whose formation was influenced by their topographic setting (for example, soils associated with recurrent floods or on steep terrain) range from the *Fluvisols*, which

Table C12 Simplified key to the WRB Reference Groups (modified from Deckers et al., 2002)

1	Organic matter $>$ 40 cm deep ↓ no	Yes →	HISTOSOLS
2	Cryric horizon ↓ no	Yes →	CRYOSOLS
3	Soils with long and intensive agricultural use ↓ no	Yes →	ANTHROSOLS
4	Soils containing many artefacts ↓no	Yes →	TECHNOSOLS
5	Depth $<$ 25 cm ↓ no	Yes →	LEPTOSOLS
6	>35% clay vertic horizon ↓ no	Yes →	VERTISOLS
7	Fluvic materials ↓ no	Yes →	FLUVISOLS
8	Salic horizon ↓ no	Yes →	SOLONCHAKS
9	Gleyic properties ↓ no	Yes →	GLEYSOLS
10	Andic or vitric horizon ↓ no	Yes →	ANDOSOLS
11	Spodic horizon ↓ no	Yes →	PODZOLS
12	Plinthite or petroplinthite within 50 cm ↓ no	Yes →	PLINTHOSOLS
13	Ferralic horizon ↓ no	Yes →	FERRALSOLS
14	Natric horizon ↓ no	Yes →	SOLONETZ
15	Abrupt textural change ↓ no	Yes →	PLANOSOLS
16	Structural or moderate textural discontinuity ↓no	Yes→	STAGNOSOLS
17	Chernic or blackish mollic horizon ↓ no	Yes →	CHERNOZEMS
18	Brownish mollic horizon and secondary $CaCO_3$ ↓ no	Yes →	KASTANOZEMS
19	Mollic horizon ↓ no	Yes →	PHAEOZEMS
20	Gypsic or petrogypsic horizon ↓ no	Yes →	GYPSISOLS
21	Duric or petroduric horizon ↓ no	Yes →	DURISOLS
22	Calcic or petrocalcic horizon ↓ no	Yes →	CALCISOLS
23	Argic horizon and albeluvic tonguing ↓ no	Yes →	ALBELUVISOLS
24	Argic horizon with $CEC_c > 24$, $Al_{sat} > 60\%$ ↓ no	Yes →	ALISOLS
25	Argic and nitic horizons ↓ no	Yes →	NITISOLS
26	Argic horizon with $CEC_c < 24$, $BS < 50\%$ ↓ no	Yes →	ACRISOLS
27	Argic horizon with $CEC_c > 24$, $BS > 50\%$ ↓ no	Yes →	LUVISOLS
28	Argic horizon with $CEC_c < 24$, $BS > 50\%$ ↓ no	Yes →	LIXISOLS
29	Umbric horizon ↓ no	Yes →	UMBRISOLS
30	Cambic horizon ↓ no	Yes →	CAMBISOLS
31	Coarse texture $>$ 100 cm ↓ no	Yes→	ARENOSOLS
32	Other soils	→	REGOSOLS

show stratification or other evidence of recent *alluvial* sedimentation, non-stratified *Gleysols* in *waterlogged areas* and shallow *Leptosols* over hard rock or highly calcareous material, to the deeper *Regosols*, which occur in unconsolidated materials that have a minimal profile development because of low soil temperatures, prolonged dryness or erosion.

Soils that are only moderately developed on account of their young pedogenetic age or because of *rejuvenation* of the soil material are referred to as *Cambisols.*

The wet tropical and subtropical regions where high soil temperatures and ample moisture promotes rock weathering, rapid decay of soil organic matter, and a long history of dissolution and transport of weathering products have five types of deep and mature soil types. *Plinthosols* are marked by the presence of a mixture of clay and quartz ('plinthite') that hardens irreversibly upon exposure to the open air while deeply weathered *Ferralsols* have a very low cation exchange capacity and are virtually devoid of weatherable minerals. *Alisols* have high cation exchange capacity and much exchangeable aluminum, *Nitisols* have deep profiles in relatively rich parent material, *Acrisols* develop on acid parent rock with a clay accumulation horizon, low cation exchange capacity and low base saturation while *Lixisols* possess a low cation exchange capacity but high base saturation percentage.

Soil in arid and semi-arid regions are differentiated to *Solonchaks* with a high content of soluble salts, *Solonetz* with a high percentage of adsorbed sodium ions, *Gypsisols* with a horizon of secondary gypsum enrichment, *Durisols* with a layer or nodules of soil material that is cemented by silica and *Calcisols* with secondary carbonate enrichment.

Soils that occur in the steppe zone between dry and humid temperate climates where vegetation consists of ephemeral grasses and dry forest classify to three reference soil groups. *Chernozems* with deep, very dark surface soil and carbonate enrichment in the subsoil, *Kastanozems* with less deep, brownish surface soils and carbonate and/or gypsum accumulation at some depth and the *Phaeozems*, the dusky red soils of prairie regions with high base saturation but no visible signs of secondary carbonate accumulation.

The brownish and greyish soils of humid temperate regions show evidence of clay or organic matter redistribution. Eluviation and illuviation of metal-humus complexes produce the greyish (bleaching) and brown to black (coating) colors of soils. Five reference soil groups include the acid *Podzols* with a bleached eluviation horizon over an accumulation horizon of organic matter with aluminum and/or iron, *Planosols* with a bleached topsoil over dense, slowly permeable subsoil, base-poor *Albeluvisols* with a bleached eluviation horizon tonguing into a clay-enriched subsurface horizon, base-rich *Luvisols* with a distinct clay accumulation horizon and *Umbrisols* with a thick, dark, acid surface horizon that is high in organic matter.

All soils of permafrost regions that show signs of 'cryoturbation' (i.e., disturbance by freeze-thaw sequences and ice segregation) are assembled in one reference soil group, the *Cryosols*.

A simplified key to the 30 reference groups is given in Table C12. It is based on the presence, sequence or exclusion of diagnostic horizons and additional diagnostic features. Further characterization of soils is possible with the application of the qualifiers. Each qualifier has a unique meaning generally derived from the definitions of diagnostic features. The qualifiers are listed in table format in priority sequence for each Reference Groups. Two qualifiers may be used in soil unit names. If additional qualifiers are needed, they follow the reference soil group name between brackets. For example: Silti-Calcic Chernozem (Vermic).

Erika Micheli

Bibliography

Deckers, J., Driessen, P., Nachtergaele, F., and Spaargaren, O., 2002. World reference base for soil resources – in a nutshell. In Micheli, E., et al., eds., *Soil Classification 2001.* (*EUR 20398 EN*). Luxembourg: Office for Official Publications of the European Communities.European Soil Bureau.

FAO, 1988: FAO/Unesco Soil Map of the World. Revised Legend (FAO/Unesco/ISRIC). World Soil Resources Reports #60. Rome: FAO.

Nachtergaele, F.O., 2001. The Future of the FAO Legend and the FAO/Unesco Soil Map of the World. Proceedings U.S. Soil Science Congress 2001. Charlotte 21–25 October 2001.

Nachtergaele, F.O., Spaargaren, O., Deckers, J.A., and Ahrens, B., 2000. New developments in soil classification World Reference base for soil resources. *Geoderma*, **96**: 345–357.

Working Group RB, 1998 c: World Reference Base for Soil Resources. (ISSS/ISRIC/FAO). World Soil Resources Reports #84. FAO, Rome.

The WRB and related documents are available online: http://www.fao.org/ag/agl/agll/wrb/.

Cross-references

Classification of Soils: FAO
Classification of Soils: World Reference Base (WRB) Soil Profiles
Classification of Soils: Soil Taxonomy
Horizon Designations in the WRB: See also individual articles on each of the Reference groups

CLASSIFICATION OF SOILS: WORLD REFERENCE BASE (WRB) SOIL PROFILES

Figure C38 displays profiles of all 32 reference groups in the WRB classification.

Otto Spaargaren

CLASTIC

A geological term applied to rocks made up of fragments. The fragments are broken pieces of pre-existing rocks and minerals, and may themselves be referred to as clastic.

CLAY MINERAL ALTERATION IN SOILS

Minerals, organic components, microbial organisms, soil fauna, plants, and aqueous solutions interact in the pedosphere in biogeochemical reactions collectively referred to as weathering. The full complexity of the interactions, especially important in the rhizosphere, and how the interactions relate to important aspects of soil science such as pedogenesis, mineral nutrition,


Acrisol from Madagascar


Albeluvisol from the Netherlands


Alisol from China


Andosol from Mexico


Anthrosol from the Netherlands

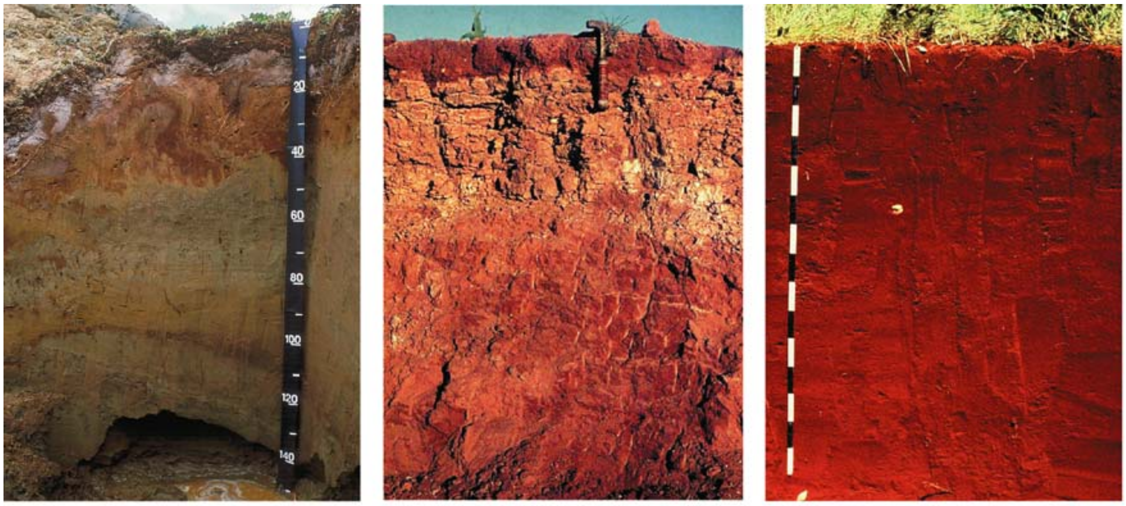

Arenosol from China


Calcisol from Italy


Cambisol from France


Chernozem from Germany

Figure C38 Continued



Cryosol from the Russian Federation

Durisol from South Africa

Ferralsol from Brazil

Fluvisol from the Netherlands

Gleysol from Germany

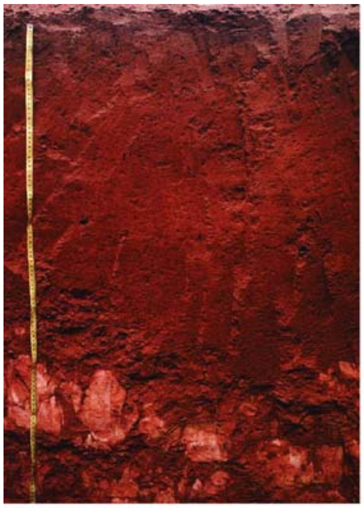
Gypsisol from Israel

Histosol from Ireland

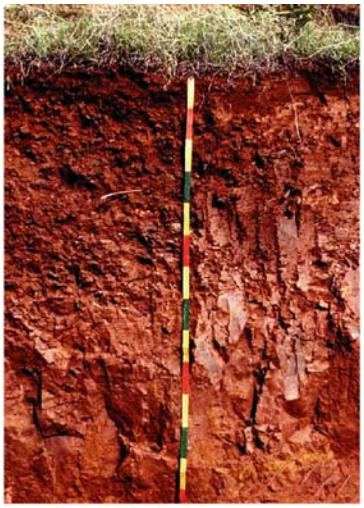
Kastanozem from Kazakhstan

Leptosol from Israel

Figure C38 Continued



Lixisol from Ghana

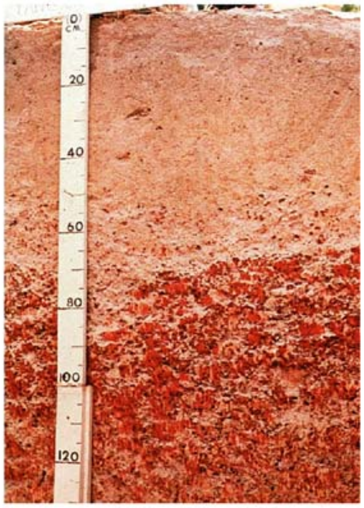


Luvisol from China

Nitisol from Kenya

Phaeozem from South Africa

Planosol from the United States



Plinthosol from Ghana

Podzol from Germany

Regosol from Ghana

Solonchak from China

Figure C38 Continued

D

DATUM LEVEL

The reference level used in defining the height of a topographic feature on a landscape or map. The commonest datum level used for this purpose is the mean sea level at a specified point.

DEBRIS

The material remains of any process of destruction. Applied in the Earth sciences to anything left behind on a landscape as the result of mass wasting. Stone lines in soil or soil parent materials are examples from pedology. Debris flows are common, especially in arid and semi-arid regions (Blatt et al., 1980, p 186), and may become (as colluvium for example) the parent material of soil.

Bibliography

Blatt, H., Middleton, G., and Murray, R., 1980. *Origin of sedimentary rocks*, 2nd ed. Englewood Cliffs, N.J.: Prentice-Hall. 782 pp.

DEGRADATION

The reduction of a component of a rock, soil or landscape into a more rudimentary form by decomposition, disintegration or erosion. The wearing down of a land surface, or the progressive modification of soil by leaching into more acid varieties. In soil mineralogy the word is used to describe the process by which an inherited mineral is transformed into a clay mineral in one or more stages, each stage retaining part of the structure of a preceding stage: for example the sequence vermiculite→smectite→kaolinite (Evans, 1992, fig. 5.3).

Bibliography

Evans, L.J., 1992. Alteration products at the earth's surface – the clay minerals. (Chapter 5) In Martini, I.P., and Chesworth, W., ed., *Weathering, soils & paleosols*. Amsterdam; New York: Elsevier, pp 107–125.

Cross-reference

Clay Mineral Formation

DELTA

The roughly triangular tract of land enclosed and traversed by the diverging distributaries of a river emptying into the sea or other large body of water. So-called from its resemblance in shape to the fourth letter of the Greek alphabet, and first applied as a geographical term to the Nile delta. Figure D1 shows the Lena Delta in Arctic Russia.

Bibliography

Wagner, D., Lipski, A., Embacher, A., and Gattinger, A., 2005. Methane fluxes in permafrost habitats of the Lena Delta: effects of microbial community structure and organic matter quality. *Environmental Microbiology* 7: 1582–1592.

DENITRIFICATION

See *Nitrogen Cycle*.

Figure D1 The Lena Delta is the largest delta in the Siberian arctic. It is a region of permafrost and patterned ground, with Crysols (accompanied by Histosols and Gleysols) as the dominant soil type. The region is highly sensitive to global change, particularly in terms of the genesis of methane, which is anticipated to have a significant positive feedback on global warming (Wagner et al., 2005). Image courtesy of the European Space Agency.

DESALINIZATION

The removal of salt from saline soils. Saline soils can only be used for growing crops, if salts in the soil are leached away. This is normally achieved by using an excess of irrigation water (Beek et al., 1980). In turn this may lead to the salinization of groundwater so that a good drainage system is required to keep the groundwater table below the rooting zone. Worldwide there are almost 200 million hectares of saline soil, and as the human population increases, there will be increased pressure to desalinize more of these soils for agriculture. Scarcity of salt-free irrigation and leaching water is, and will increasingly become, a major problem, making the sustainable use of such soils questionable.

Bibliography

Beek, K.J., Blokhuis, N.A., Driessen, P., Van Breeman, N., Brinkman, R., and Pons, L.J., 1980. Problem soils: their reclamation and management. ILRI Pub. No. 27, Wageningen. pp. 47–72.

Cross-reference

Alkaline Soils
Salt Leaching
Solonchaks

DESERT

Originally an uninhabited and uncultivated wilderness. Now technically defined as an arid region with sparse vegetation and less than 250 mm annual rainfall. In the form “edaphic” desert, the term may be applied to regions of higher rainfall, which because of excessive drainage, have a droughty character. Desert soils are commonly alkaline and usually contain soluble salts within the solum (e.g., Calcisols, Gypsisols, Solonchaks).

Cross-reference

Biomes and their Soils

DESERTIFICATION

The transformation, or degradation by natural processes, human intervention or a combination of the two, human intervention, of fertile land into desert (see Figure D2 and Arnalds and Archer, 2000).

Bibliography

Arnalds, O., and Archer, S., 2000. *Rangeland desertification.* Dordrecht: Kluwer Academic Publishers. 209 pp.

DESICCATION

The removal of moisture, or the drying out, of a substance. Alternating episodes of dessication and rehydration cause expanding clays such as smectites to shrink and swell. Soils with notable amounts of these minerals acquire deep desiccation cracks with slickensides, in the dry season (Ahmad and Mermut, 1996).

Bibliography

Ahmad, N., and Mermut, A., 1996. *Vertisols and technologies for their management.* Amsterdam: Elsevier, 549 pp.

Cross-reference

Vertisols

DESILICATION

Desilication (or desilicification) is the removal of silicon from a soil or soil horizon, relative to some less mobile component or components. Characteristic of pedogenesis in the humid tropics where silicon tends to be more mobile than iron and aluminum in well drained soils. The process is active in the formation of ferrallitic soils, laterites and bauxites. Because silicate parent materials contain a large reservoir of Si, and because the element is commonly present as sparingly soluble quartz, desilication requires a long period of time to produce laterites and bauxites. This would be favored by periods of biostasis on the land surface (Erhart, 1967).

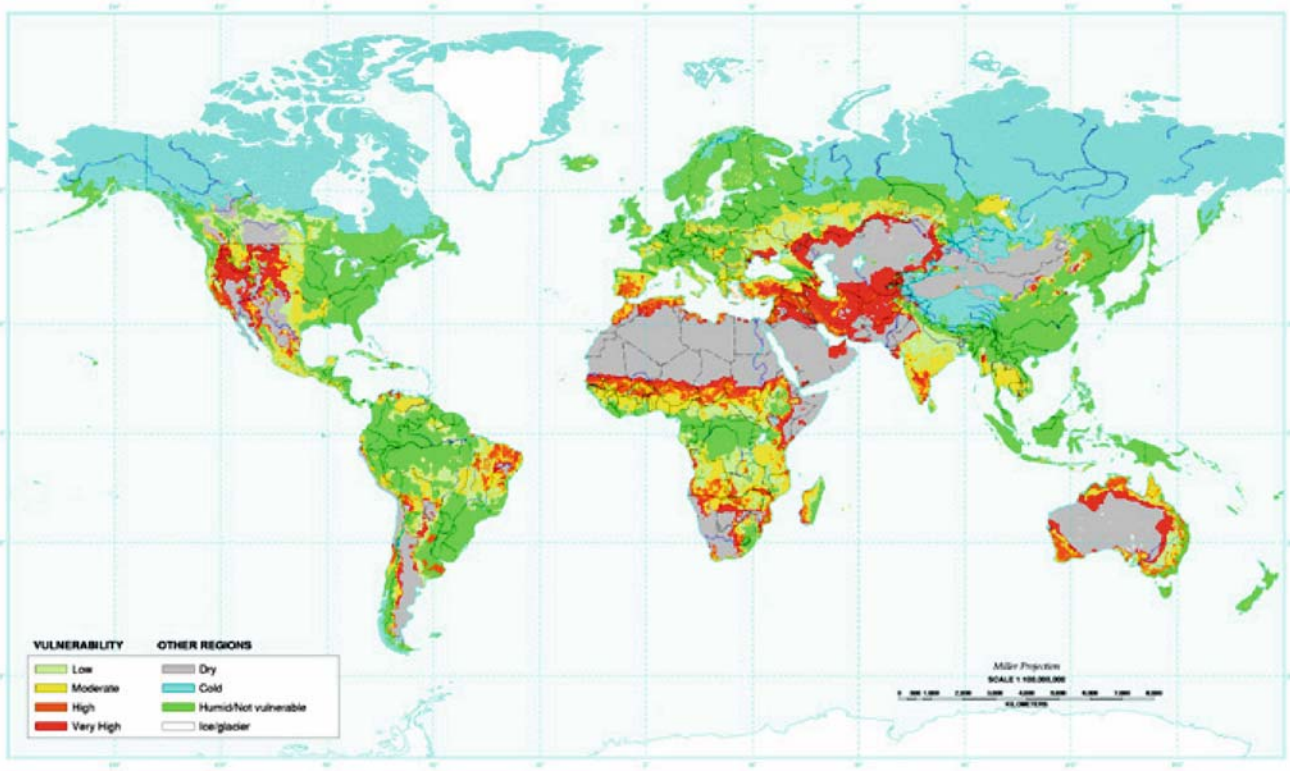


Figure D2 Global desertification vulnerability. Courtesy USDA-NRCS, Soil Survey Division.

Bibliography

Erhart, H., 1967. *La genèse des sols en tant que phénomène géologique; esquisse d'une théorie géologique et géochimique, biostasie et rhexistasie*, 2nd edition. Paris: Masson. 177 pp.

Cross-reference

Tropical Soils

DETRITUS

Matter produced by the wearing down of exposed surfaces of rock and soil, and eroded away as gravel, sand, or clay. Clay minerals that are produced in this way and then inherited by soil parent material, are called detrital clays.

DIFFUSION

The movement of chemical species in gas or liquid, as a response to a chemical gradient, resulting in the limit, to the leveling out of that gradient. Diffusion in the solid state also occurs, but is not significant at the low temperatures of pedogenic processes.

DIFFUSION PROCESSES

Diffusion, an important process in soil, is the name given to the process whereby matter is transported under a gradient of chemical potential, activity or concentration. The chemical composition of a soil is never uniform and static; concentration gradients are formed and modified, particularly around plant roots, fertilizer granules, microorganisms and at the soil surface. Solutes are also transported by mass flow, however for those solutes, which have a low concentration in the soil solution, such as K^+ and phosphate, diffusive flux, dominates transport.

The diffusion coefficient (defined in Equation (1)) of any substance is much greater in the gaseous phase (typically 10^{-5} m^2 s^{-1}) than in the liquid phase (circa 10^{-9} m^2 s^{-1}) and lowest in the adsorbed or solid phase ($D = 10^{-10}$–10^{-27} m^2 s^{-1}, see *Surface Diffusion*, below). When a diffusing substance exists in more than one form in soil, its overall, or effective diffusion coefficient will reflect the mobilities it has in each phase or form. In soils, typical diffusion coefficients are 10^{-6} m^2 s^{-1} for anions or cations which are not strongly adsorbed such as Cl^-, NO_3^-, or Na^+ and 10^{-13} m^2 s^{-1} for strongly adsorbed anions or cations such as phosphate (HPO_4^{2-} and $H_2PO_4^-$) and Cs^+.

Theoretical considerations

The diffusion coefficient, D, is defined by the following empirical relationship (Fick's First Law):

$$F = -D\frac{\mathrm{d}C}{\mathrm{d}x} \tag{1}$$

where F is the flux through unit area in unit time, C the concentration at a given point and x (or r for spherical coordinates) the ordinate in the direction of diffusion. When the flux changes with time it is more appropriate to use the differential equation, Fick's Second Law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \quad \text{or} \quad \frac{\partial \mathrm{C}}{\partial \mathrm{t}} = D\frac{1}{r}\left(\frac{\partial C}{\partial r}\right) + \frac{\partial^2 C}{\partial r^2} \tag{2}$$

Since diffusion arises from random thermal motion it is to be expected that the diffusion coefficient depends on the temperature. They are related by the Nernst-Einstein relation:

$$D = u\mathrm{k}T \tag{3}$$

where u is the absolute mobility of the diffusing molecule, k the Boltzman constant and T the temperature (K).

Furthermore the diffusion coefficient of an ion, i, is related by the Nernst Equation to its molar conductance λ_i:

$$D_\mathrm{i} = \mathrm{R}t\lambda_\mathrm{i} \big/ (\mathrm{F}'^2 z_\mathrm{i}) \tag{4}$$

where R is the gas constant, F′ the Faraday constant and z_i the valence of the ion.

Ion diffusion

When an ion diffuses electroneutrality must be maintained. Either an ion of opposite charge diffuses in the same direction (salt diffusion) or an ion of the same charge diffuses in the opposite direction (counter diffusion). In these cases the flux will depend on the individual diffusion coefficients, the concentration gradients and the gradient of potential, which arises from the tendency of one ion to diffuse faster than another. It is necessary to apply the Nernst-Planck Equation,

$$F_\mathrm{i} = -D_\mathrm{i}\left[\frac{\mathrm{d}C_\mathrm{i}}{\mathrm{d}x} + \left(\frac{z_\mathrm{i}\, C_\mathrm{i}\, \mathrm{F}'}{\mathrm{R}T}\right)\frac{\mathrm{d}\psi}{\mathrm{d}x}\right] \tag{5}$$

where ψ is the potential. Combining Equation (4) and the electroneutrality principle, $\Sigma z_\mathrm{i} F_\mathrm{i} = 0$ yields, in the case of the diffusion of a monovalent cation and a monovalent anion,

$$D_{12} = \frac{D_1 D_2 (C_1 + C_2)}{C_1 D_1 + C_2 D_2} \tag{6}$$

In order to avoid the difficulty in interpreting the results of diffusion experiments, either the diffusing species are chosen so that $D_1 \approx D_2$ and hence $D_{12} \approx D_1 \approx D_2$. The diffusion of an isotope in what is essentially a zero concentration gradient of the element is the best example of this. This process is known as self-diffusion.

Diffusion with chemical reaction

Few substances which diffuse in soil are completely inert. The extent of their reaction modifies their diffusive properties. Assuming that the diffusant exists in two phases, one mobile (1) and the other immobile (2),

$$\frac{\mathrm{d}C_1}{\mathrm{d}t} = D\frac{\mathrm{d}^2 C_1}{\mathrm{d}x^2} - \frac{\mathrm{d}C_2}{\mathrm{d}t} \tag{7}$$

If the reaction is instantaneous, an equilibrium always exists between phases 1 and 2, thus

$$\frac{\mathrm{d}C}{\mathrm{d}t} = D\left(\frac{\mathrm{d}C_1}{\mathrm{d}C}\right)\frac{\mathrm{d}^2 C}{\mathrm{d}x^2} \tag{8}$$

When C_2 is a linear function of C_1, $C_2 = KC_1$, then the effective diffusion coefficient is a constant given by $D_\mathrm{eff} = D/(l + K)$. When C_2 is not a linear function of C_1 the effective diffusion coefficient is also a function of concentration and not constant. In the case of self-diffusion the exchange isotherm is linear, and so the effective diffusion coefficient constant.

If the diffusant is mobile in both phases, again assuming that there is always an equilibrium distribution between the two phases,

$$\begin{aligned}\frac{\mathrm{d}C}{\mathrm{d}t} &= \frac{\mathrm{d}C_1}{\mathrm{d}t} + \frac{\mathrm{d}C_2}{\mathrm{d}t}\\ &= D_1\frac{\mathrm{d}^2 C_1}{\mathrm{d}x^2} + D_2\frac{\mathrm{d}^2 C_2}{\mathrm{d}x^2}\\ &= \left(D_1\frac{\mathrm{d}C_1}{\mathrm{d}C} + D_2\frac{\mathrm{d}C_2}{\mathrm{d}C}\right)\frac{\mathrm{d}^2 C}{\mathrm{d}x^2}\end{aligned} \tag{9}$$

The effective diffusion coefficient thus depends on the diffusion coefficients in the two phases, weighted by the relative concentration in these phases. The same analysis may be made for the diffusion of an element, which exists as two chemical species at equilibrium in solution, for example a hydrated cation and another complex of that cation, or a redox couple.

Diffusion and water flow

Solutes are transported through soil both by diffusion and by mass flow. It is often important to assess the relative importance of mass flow and diffusive flux for the transport of nutrients to plant roots. Mass flow supply is the product of average liquid phase concentration and average water flux arising from root water absorption; the diffusive flux may be estimated using the approximate relation between the diffusion coefficient and the average distance diffused in time t, $x = \sqrt{(Dt)}$. Solute movement and nutrient availability are discussed in greater detail by Barber (1995), Tinker and Nye (2000) and Kirk (2002a,b).

When the concentration of an ion in solution is relatively high with respect to the requirements of the plant, then mass flow dominates, and the effect of diffusion may be ignored. However when the concentration is low, then the root absorbance may exceed the supply by mass flow and a concentration gradient will be set up. When the soil solution concentration is very low, as for phosphate, potassium and many pollutants, then although the diffusion coefficient is often low, uptake is limited by diffusive flux.

Molecular diffusion plays an important role in the hydrodynamic dispersion of species dissolved in water flowing through soil. A solute applied as a pulse to a solution flowing through soil will disperse increasingly as it moves down. This arises from both convection and from molecular diffusion and the relative importance of each depends on the flow rate and packing characteristics of the soil.

The diffusion-dispersion coefficient, D^*, may be given as the sum of the diffusion coefficient and the dispersion coefficient D_h, itself found to be an approximately linear function of the average water flow velocity, U, (Hillel, 1998). Thus,

$$D^* = D + D_h = D + kU \tag{10}$$

where k is a constant.

Measurement of diffusion coefficients

The diffusion coefficient cannot be measured directly. It may be obtained from electrical conductivity data (Palmer and Blanchar, 1980) using the Nernst Equation (Equation (4)), but it is usually calculated by fitting experimental data to a solution to either Fick's First or Second Law. Figure D3 summarizes some of the experimental techniques often used to obtain diffusion coefficients. These methods are applicable only when the diffusion coefficient is constant. Although it is possible to obtain analytical solutions to diffusion equations with time or concentration dependent diffusion coefficients or complex boundary conditions (Crank, 1975), these are now usually solved numerically (for example, Smith, 1985; Barber and Cushman, 1981), see *Modeling Diffusion Systems* below.

The methods used may be divided into two classes: steady state and transient state systems. In the former a concentration gradient is set up across a soil block and a steady state concentration gradient allowed to establish, D is calculated from the measured flux and the average concentration gradient using Fick's First Law. In the latter the concentration gradient changes with time, boundary conditions are chosen to facilitate the analytical solution of Fick's Second Law. Either the rate of change of concentration of the diffusant at some point, usually at a source or a sink, is followed, or else a concentration-distance profile obtained. For the diffusion of gases or diffusion in spherical geometry it is more convenient to monitor the change of concentration. Concentration profiles are usually obtained by slicing a block of soil and analyzing chemically or radiochemically each slice, but have been obtained using ion selective electrodes (Wang and Yu, 1989).

Errors arise because of nonhomogeneity of the soil, poor contact at the source-soil or soil-sink interfaces, leading to a barrier (this is increasingly likely as soil moisture content decreases). The protocol adopted for a given system should minimize experimental error and facilitate the detection of errors and artifacts within the constraints of geometry, time scale and detection limits. For example the unsliced half-cell technique is simple and convenient, especially for slowly diffusing species, but the diffusion coefficient is calculated from a single concentration and it is impossible to detect an interface barrier.

Many of the boundary conditions require that the soil approximates to an infinitely long medium, it is useful to note that this assumption is valid only if $x/V(4Dt)$ is <2 and in the case of the half-cell technique, if the fraction, f (Figure D3, $D = \pi f^2 L^2/t$) of diffusant having crossed the interface after time, t, with respect to that at equilibrium, does not exceed 0.15.

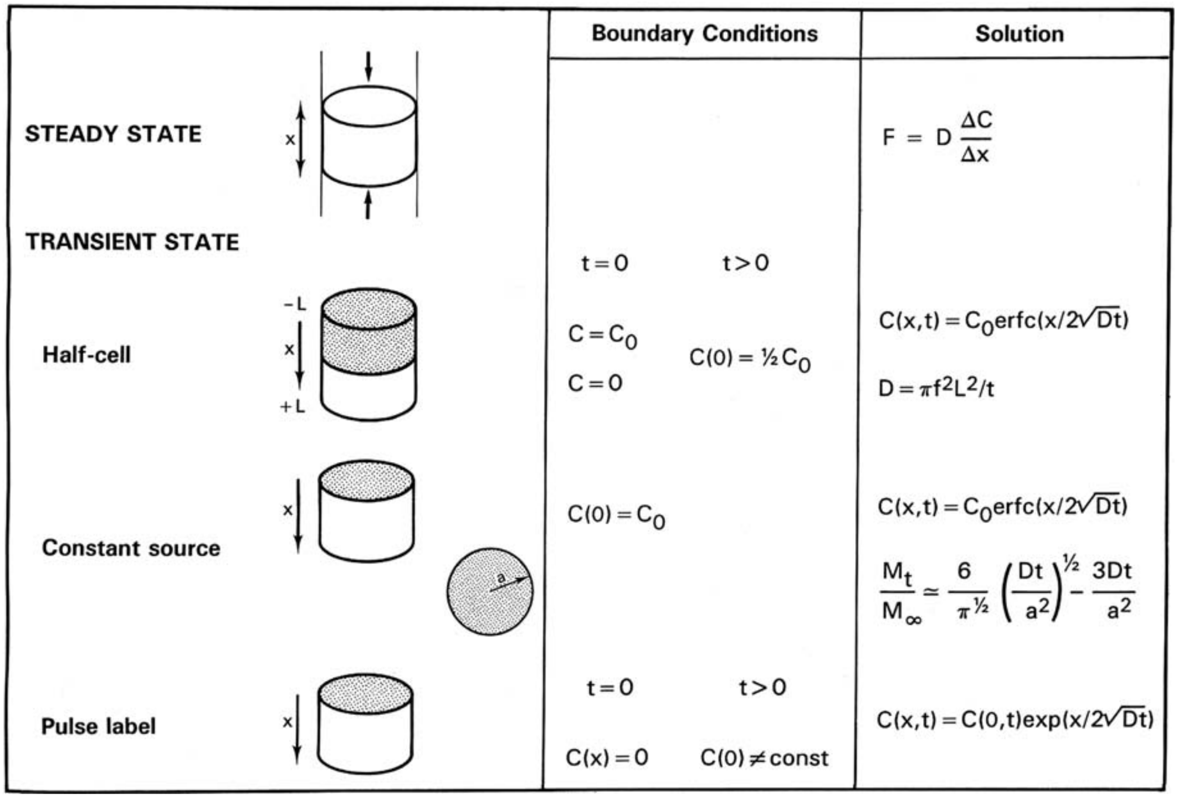


Figure D3 Schema of methods used to obtain diffusion coefficients in soil.

Diffusion in soil

Soil is a complex porous medium consisting of air-filled and water-filled pores and a solid matrix, which has a complex chemistry. As we have seen above, it is possible to calculate the diffusion coefficient of a species, which exists in more than one form. In this section we shall discuss the effect of soil parameters on the effective diffusion coefficient and introduce the various symbols, which have been used in soil science.

Gas diffusion

The diffusion coefficient in the gaseous phase is about 4 orders of magnitude greater than in the liquid phase, therefore the diffusion coefficient of a gas, even a soluble gas, is largely determined by its diffusion in the air-filled porosity of the soil, ε. Thus the diffusion coefficient of a gas in soil, D_{gas} is related to that in ideal conditions, D_0, by an impedance parameter, f_{G},

$$D_{\text{gas}} = D_0 f_{\text{G}} \tag{11}$$

Although it is not possible to predict f_{G} for a given soil, it is known to be a function of ε. Various empirical functions have been used to describe the relationship (Hillel, 1980). The simplest is the linear relation found by Penman (1940) but a range of constants have been reported. Currie (1984) found no single relationship between f_{G} and ε for one soil at a range of compactions. Figure D4 (redrawn from Collin and Ramuson, 1988) illustrates the complexity of the variation of f_{G} with gas filled porosity as a fraction of total porosity over a wide range of the latter. The gas filled porosity almost invariably decreases as the moisture content increases. The corresponding decrease in f_{G} has serious consequences on soil aeration in wet soils. The supply of O_2 to plant roots and microorganisms and the dispersion of respiratory CO_2 may be severely restricted.

Liquid diffusion

The diffusion coefficient of a molecule in the liquid phase, in equilibrium with an immobile adsorbed phase is given by,

$$\begin{aligned} D_{\text{liquid}} &= D_{\text{L}} f_{\text{L}} \theta_{\text{L}} \frac{\mathrm{d}C_{\text{L}}}{\mathrm{d}C} \\ &= \frac{D_{\text{L}} f_{\text{L}} \theta_{\text{L}}}{\theta_L + b} \simeq \frac{D_{\text{L}} f_{\text{L}} \theta_{\text{L}}}{b} \end{aligned} \tag{12}$$

where D_{L} ($\text{m}^2\ \text{s}^{-1}$) is the diffusion coefficient of the species in ideal solution, f_{L} the dimensionless liquid phase impedance factor, θ_{L} the volumetric moisture content ($\text{m}^3\ \text{m}^{-3}$), b (or ρK, where K, ($\text{dm}^3\ \text{kg}^{-1}$), is the ratio of concentrations in the adsorbed and liquid phases, known as the partition coefficient and ρ, kg dm^{-3}, the bulk density) the buffer capacity defined as $C_{\text{s}}/C_{\text{L}}$ with C_{s} (or ρS) the amount adsorbed per unit volume of soil, C_{L} (or L) the amount in solution per unit volume of solution and C the overall concentration. The ratio $\theta_{\text{L}}/(\theta_{\text{L}} + \text{b})$ represents the fraction of time spent in the liquid phase. The first three terms have been combined to give an effective porous diffusion coefficient, $D_{\text{p}} = D_{\text{L}} f_{\text{L}} \theta_{\text{L}} \cdot f_{\text{L}} \theta_{\text{L}}$ is analogous to f_{G} in the gaseous phase.

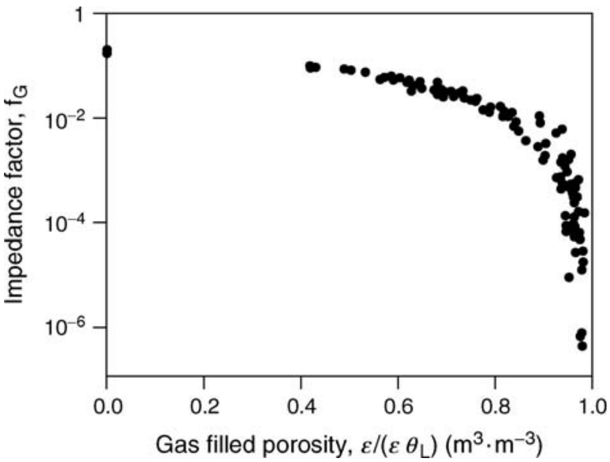


Figure D4 Variation of gas phase impedance factor, *f''*, calculated from the ratio of the measured diffusion coefficient and that in an ideal system, with the gas filled porosity as a fraction of total porosity, $\varepsilon/(\varepsilon + \theta_{\text{L}})$... (redrawn from Collin and Rasmuson, 1988).

The liquid phase impedance factor is an average term that combines the geometric tortuosity of the liquid phase pathway and the deviation from ideality of the soil solution. It is calculated from the value of the diffusion coefficient of a non-adsorbed ion such as chloride, $f_{\text{L}} = D/D_{\text{L}}$. It may be expressed as $a\gamma(L/L_{\text{e}})^2$ where a is a viscosity factor, γ an interaction factor and L/L_{e} reflects the effective path length (Olsen et al., 1965). Anions may be subject to exclusion from the negatively charged surfaces of soil and clay minerals. In principal this could lead to apparent impedance factors that depend on the anion, the degree of compaction (in addition to changes in tortuosity of the liquid filled pore space) and to both pH and ionic strength. However such variation is too small to be detected experimentally in soils. However it is likely to have a greater impact in compacted media where the pore space is proportionally much smaller (Bourg et al., 2003).

D_{L} depends only on the temperature and on the ion or molecule diffusing, particularly on its size and charge; it can often be obtained from standard tables.

Surface diffusion

The mobility of adsorbed ions is linked to their degree of hydration. It is thus reasonable to assume that the mobility of anions such as phosphate that are covalently bound to the surface is negligible with respect to liquid phase diffusion. However adsorbed phase diffusion may be responsible for the slow process of fixation of phosphate by clay minerals (Barrow, 1991; Pavlatou and Polyzopoulos, 1988). Similarly the adsorbed phase diffusion of unhydrated cations may be a rate-limiting step in the weathering of minerals (K^+ in mica) and the adsorption and desorption of Cs^+.

Studies in clay systems have clearly established that adsorbed cations contribute significantly to diffusive flux and electrical conductivity, however in soils systems the evidence was less clear-cut. Mobility of cations in the adsorbed phase is often ignored or introduced as an excess term, however recent work has indicated that the mobility of adsorbed hydrated cations should be included in the diffusion coefficient. Thus, from Equation (9), and using symbols analogous to those in Equation (12),

$$D = D_{\text{L}} f_{\text{L}} \theta_{\text{L}} \frac{\mathrm{d}C_{\text{L}}}{\mathrm{d}C} + D_{\text{L}} f_{\text{s}} \frac{\mathrm{d}C_{\text{s}}}{\mathrm{d}C} \tag{13}$$

The surface phase impedance factor, like its liquid or gaseous phase equivalent is a global factor, which reflects both geometric, and interaction factors, however in the adsorbed state a range of chemical forms (bonding with the surface) may exist, each with differing mobilities. f_s is always less than f_L, often by orders of magnitude, even though a considerable proportion of the flux may be associated with the surface. The variation of f_s for a range of contrasting soils is much less than the difference between cations as is illustrated in Figure D5. For a range of soils and cations, Staunton (1990) has found f_s to be indirectly proportional to the partition coefficient, $S/L(C_s/\rho C_L)$ This suggests that the value of f_s is largely determined by the average energy barrier between the ground state of the cation and the energy level in the diffuse double layer in which they are mobile. It seems unlikely that soil texture, packing density or moisture content will directly affect that value of f_s but this remains to be verified. In compact media, such as clays in geological formations or in the form of engineered barriers, the liquid filled pore space is much less than in soil and the contribution of surface phase mobility to overall diffusion is consequently greater (Bourg et al., 2003).

The second term in the right hand side of Equation (13), which accounts for surface mobility in the diffusion coefficient, is not a constant, nor is the product $D_L f_s$. This implied assumption may explain why surface mobility may have been underestimated by some authors (e.g., Rowell et al., 1967).

It is generally assumed that strongly adsorbed macromolecules, including proteins, are immobilized on adsorption. However, it should be noted that current methods of measurement probably do not allow surface diffusion to be distinguished from other factors including microbial degradation, time dependent adsorption, conformational changes of sorbed species and complex sorption that depends on both concentration and pH. Despite the experimental difficulties of working with soils, recent techniques such as NMR (Nuclear magnetic Resonance) and FRAP (Fluorescence Recovery After Photobleaching) may soon provide new possibilities. For example, FRAP was initially developed to study the mobility of molecules in living cells and on biological membranes (Pawley, 1995), but it is being increasingly applied to other surfaces such as polystyrene, porous glass and silica.

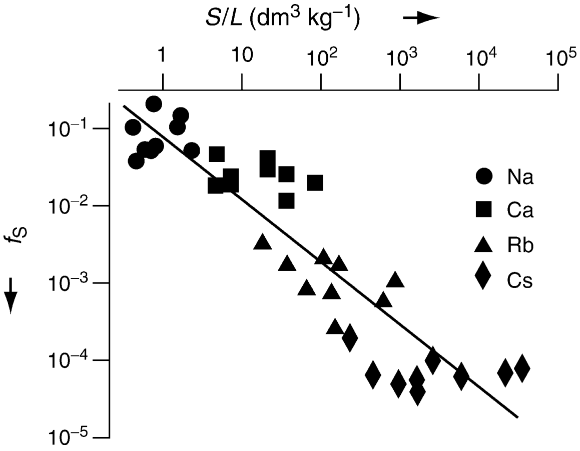


Figure D5 Relation between f_S (calculated from the self diffusion coefficients of Na, Rb, Cs and Ca) and the partition coefficient for a range of soils with contrasting mineralogy and clay content (redrawn from Staunton, 1990).

Important soil parameters

Volumetric moisture content

The soil volumetric moisture content appears directly in Equations (12) and (13), however it may also affect the value of D indirectly. In both the liquid and gas phase the impedance factors are functions of θ_L as illustrated by Figures D6a and D7. As θ_L is decreased the larger pores are drained. This facilitates gas diffusion, but restricts liquid phase diffusion since an increasing proportion of the water-filled pores are narrow or consist of liquid films between air-filled pores and the solid matrix, in which the geometric tortuosity is greater. A lesser effect may arise from changes in the composition of the soil solution on drying and the consequence on the factors a and γ. The value of f_L decreases with decreasing moisture content to a threshold value. The threshold value of θ_L depends on the texture of the soil and to some extent on the size of the diffusing molecule. Barraclough and Nye (1984) have found that f_L decreases more rapidly with decreasing θ_L as molecular weight is increased from 40 (chloride) to 4 000 (polyethylene glycol) to 40 000 (polyvinyl pyrrolidone). In addition, the possibility of slow equilibration with dead-end pores increases, however no experimental evidence of this has been found. It should be added that it is experimentally difficult to obtain diffusion coefficients in dry soil.

Bulk density

The liquid phase impedance factor has been found to be dependent on the bulk density. This probably arises largely from the dependence of the geometric tortuosity on the pore size distribution. Few data are available at constant moisture content. Figure D6b illustrates the decrease in the liquid phase impedance factor with increasing bulk density for two soils, each maintained at constant moisture content. In general, the effect of bulk density, for a given soil, is of minor importance when compared to that of water content (Barraclough and Tinker, 1981; So and Nye, 1989). Similar trends are found for gaseous diffusion, as increasing bulk density usually implies decreasing air-filled porosity.

Soil structure

Soil pore size distribution, and hence the liquid and gas phase impedance factors, are related to soil texture and packing. A comparison of the data for pairs of contrasting soils in Figures D6 and D7 illustrate the effect of soil texture on the variation of f_L with θ_L, ρ and pF. The larger the average pore size the less tortuous is the diffusion pathway, however it is not possible to make precise predictions. The pore size distributions of sieved, repacked soils differ from undisturbed cores and this will be reflected in the impedance factors, however the effect is generally small (Pinner and Nye, 1982). Soil structure contributes to the formation and stability of gas bubbles that may in turn interfere with the diffusive flux of soil gases including methane (Rothfuss and Conrad, 1998).

Chemical speciation

The diffusion coefficient depends on the exact chemical nature of the diffusing species: does calcium diffuse as the simple aqueous cation Ca^{2+} or as $CaCl^+$, phosphate as HPO_4^{2-} or $H_2PO_4^-$ and iron as Fe^{3+} or Fe^{2+} In cases such as the first example the formation of weak inorganic complexes of the alkali and alkaline earth cations is usually ignored, and if necessary all interference may be removed by working in a perchlorate background. The

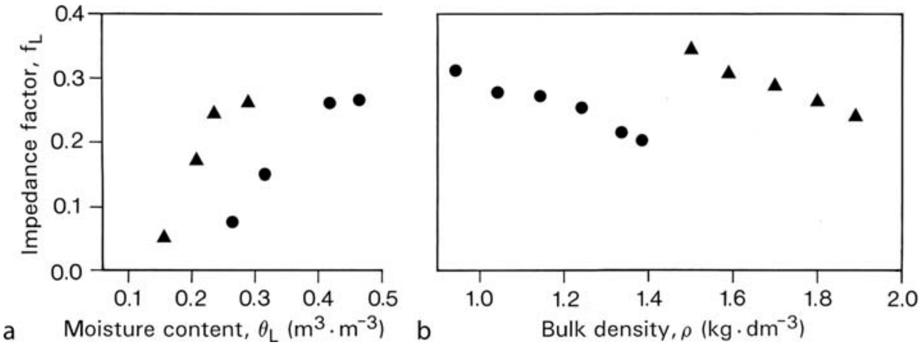


Figure D6 Liquid phase impedance factor of two contranting soils as a function of **(a)** volumetric moisture content, at constant bulk density and **(b)** bulk density, at constant volumetric moisture content (redrawn from Barrclough and Tinker, 1981). Wobum Sandy Loam: (a) $\rho = 1.76$ kg dm^{-3}, (b) $\theta_L = 0.23$ m^3 m^{-3}; Rothamsted Silty Clay Loam: (a) $\rho = 1.20$ kg dm^{-3}, (b) $\theta_L = 0.44$ m^3 m^{-3}.

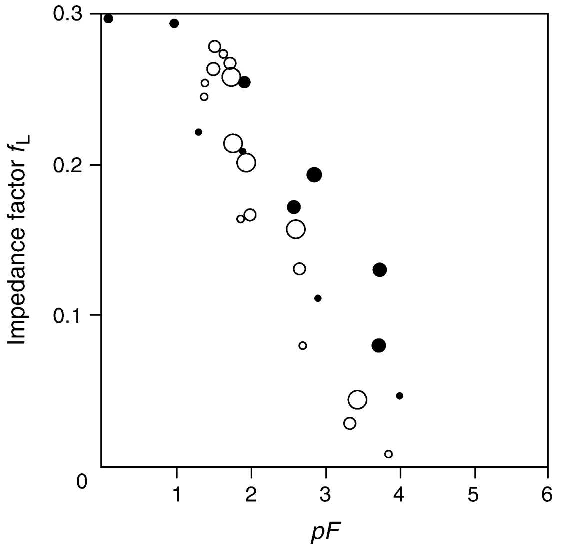


Figure D7 Liquid phase impedance factor of two contrasting soils at a range of bulk densities as a function of *pF*. The increasing size of the symbols indicates increasing bulk density. (Redrawn from So and Nye, 1989). Evesham Silty Clay (●), ρ: 0.75–0.85; 0.85–0.95; 0.95–1.05; 1.05–1.2 kg dm^{-3}; Begbroke sandy Loam, (○), ρ: 1.1–1.2; 1.2–1.3; 1.3–1.4; 1.4–1.53 kg dm^{-3}.

presence of organic complexing ligands such as EDTA, citrate and malate, is more important. High concentrations of such ions may be released into soil solution by roots and microorganisms, causing the diffusion coefficient to differ considerably from that of the hydrated ion (Erich et al., 1987; O'Connor et al., 1971).

The phosphate couple depends on the pH of the medium, it is therefore often necessary to consider coupled H^+/phosphate (Nye, 1984). Redox conditions are important for many transition metals, and also iodine (I^-/IO_3^-) and technetium, which may be present in radioactive waste (Tc^{4+}/TcO_4^-).

Modeling diffusion systems

The aim of this section is to draw attention to those situations in which it is preferable or essential to use numerical models, not to provide an exhaustive review of models containing a diffusion component. The methods for measuring diffusion coefficients described above are suitable only for systems with simple geometry, particular boundary conditions and a constant diffusion coefficient (ideally a self-diffusion coefficient). They are rarely suitable for salt or counter diffusion, nor for most cases of diffusion with chemical reaction. The following are some examples of systems that should be investigated by comparing experimental data with the simulations of an appropriate mathematical model.

1. Diffusion with non-instantaneous reaction
   - Isotopic exchange of phosphate (Staunton and Nye, 1989)
   - Fe^{2+}/Fe^{3+} (Kirk et al., 1990), I^-/IO_3^- and other redox couples
2. Diffusion of any species with a nonlinear adsorption isotherm
   - Bulk diffusion of phosphate (Kirk and Nye, 1986)
3. Coupled diffusion (including salt or counter diffusion when the diffusing species do not have very similar diffusion coefficients)
   - Phosphate diffusion with a pH gradient (Nye, 1984)
   - Counter diffusion of exchangeable cations (Rhue, 1992)
4. Diffusion when convenient boundary conditions do not exist, e.g., root exudation, non-homogenous distribution of source (fertilizer granules), sink term (plant uptake, chemical or microbiological degradation).
   - Root absorption or microbial population dynamics limited by diffusion (Kirk and Staunton, 1989; Darrah, 1991; Kirk, 2002a, b)
5. Diffusion accompanied by mass flow.

Siobhán Staunton

Bibliography

Barber, S.A., 1995. *Soil Nutrient Bioavailability. A Mechanistic Approach.* New York: Wiley, 414 pp.

Barber, S.A., and Cushman, I.R., 1981. Nitrogen uptake model for agronomic crops. In Iskandar, I.K., ed., *Modelling wastewater renovation-land treatment.* New York: Wiley-Interscience. pp. 382–409.

Barraclough, D., and Nye, P.R., 1979. The effect of molecular size on diffusion characteristics in soil. I. *Soil Sci.*, **30**: 29–42.

Barraclough, P.B., and Tinker, P.B., 1981. The determination of ionic diffusion coefficients in field soils. I. Diffusion coefficients in sieved soils in relation to water content and bulk density. I. *Soil Sci.*, **32**: 225–236.

Barrow, N., 1991. Testing a mechanistic model. XI. The effects of time and level of application on isotopically exchangeable phosphate. I. *Soil Sci.*, **42**: 277–288.

Bourg, I.C., Bourg, A.C.M., and Sposito, G., 2003. Modeling diffusion and adsorption in compacted bentonite: a critical review. *J. Contaminant Hydrology*, **61**: 293–302.

Collin, M., and Rasmuson, A., 1988. A comparison of gas diffusivity models for unsaturated porous media. *Soil Sci. Soc. Am. 1.*, **52**: 1559–1565.

Crank, I., 1975. *The mathematics of diffusion.* Oxford: Clarendon Press, 414 pp.

Currie, I.A., 1984. Gas diffusion through soil crumbs: the effects of compaction and wetting. I. *Soil Sci.*, **35**: 12–10.

Darrah, P.R., 1991. Models of the rhizosphere. II. A quasi-three-dimensional simulation of the microbial population dynamics around a growing root releasing soluble exudats. *Plant Soil*, **138**: 147–158.

Erich, M.S., Duxbury, I.M., Bouldin, D.R., and Cary, E., 1987. The influence of organic complexing agents on iron mobility in a simulated rhizosphere. *Soil Sci. Soc. Am. I.*, **51**: 1207–1214.

Hillel, D., 1998. Environmental Soil Physics. London: Academic Press, 413 pp.

Kirk, G.J.D., 2002a. Modelling root-induced soubilization of nutrients. *Plant & Soil*, **247**: 49–57.

Kirk, G.J.D., 2002b. Use of modelling to understand nutrient acquisition by plants. *Plant & Soil*, **247**: 123–130.

Kirk, G.J.D., Ahmad, A.R., and Nye, P.R., 1990. Coupled diffusion and oxidation of ferrous iron in soils. II. A model of the diffusion and reaction of O_2, Fe^{2+}, H^+ and HCO_3^- in soils and a sensitivity analysis of the model. I. *Soil Sci.*, **41**: 411–431.

Kirk, G.J.D., and Nye, P.R., 1986. The dissolution and dispersion of dicalcium phosphate dihydrate in soils. III. A predictive model for regularly distributed particles. I. *Soil Sci.*, **37**: 511–524.

Kirk, G.J.D., and Staunton, S., 1989. On predicting the fate of radioactive caesium in soil beneath grassland. I. *Soil Sci.*, **40**: 71–84.

Nye, P.H., 1984. pH changes and phosphate solubilization near roots – an example of coupled diffusion processes. In *Roots, Nutrient and Water Influx, and Plant Growth.* Madison, WI: Soil Science of America Society, Crop Science of America Society, and American Society of Agronomy, pp. 89–100.

O'Connor, G.A., Lindsay, W.L., and Olsen, S.R., 1971. Diffusion of iron and iron chelates in soil. *Soil Sci. Soc Am. Proc.*, **35**: 407–410.

Olsen, S.R., Kemper, W.D., and Van Schaik, I.C., 1965. Self diffusion coefficients of phosphorus in soil measured by transient and steady-state methods. *Soil Sci. Soc. Am. Proc*, **29**: 154–158.

Palmer, C.I., and Blanchar, R.W., 1980. Prediction of diffusion coefficients from the electrical conductance of soil. *Soil Sci. Soc. Am. I.*, **44**: 925–929.

Pavlatou, A., and Polyzopoulos, N.A., 1988. The role of diffusion in the kinetics of phosphate desorption: the relevance of the Elovich Equation. I. *Soil Sci.*, **39**: 425–436.

Pawley, J.B., 1995. *Handbook of Biological Confocal Microscopy*, 2nd edn. New York: Plenum Press.

Penman, H.L., 1940. Gas and vapor movements in the soil: I The diffusion of vapors through porous solids. *I Agr. Sci.*, **30**: 437–461.

Pinner, A., and Nye, P.H., 1982. A pulse method for studying effects of dead-end pores, slow equilibriation and soil structure on diffusion of solutes in soils. I. *Soil Sci.*, **33**: 25–35.

Rhue, D., 1992. Coupled diffusion of exchangeable cations in soil. *Soil Sci. Soc. Am. I.*, **56**: 683–689.

Rothfuss, F., and Conrad, R., 1998. Effect of gas bubbles on the diffusive flux of methane in anoxic paddy soil. *Limnology & Oceanography*, **43**: 1511–1518.

Rowell, D.L., Martin, M.W., and Nye, P.H., 1967. The measurement and mechanism of ion diffusion in soils. III. The effect of moisture content and soil-solution concentration on the self-diffusion of ions in soils. *I. Soil Sci.*, **18**: 204–221.

Smith, G.D., 1985. Numerical solution of partial differential equations. Oxford: Clarendon Press. 337 pp.

So, H.B., and Nye, F.H., 1989. The effect of bulk density, water content and soil type on the diffusion of chloride in soil. *I. Soil Sci.*, **40**: 743–749.

Staunton, S., 1990. A comparison of the surface impedance factors of Ca, Na, Rb and Cs derived form their self-diffusion coefficients in various soils. *I. Soil Sci.*, **41**: 643–653.

Staunton, S., and Nye, F.H., 1989. Three approaches to the self-diffusion and non-instantaneous exchange of phosphate in soil. *I. Soil Sci.*, **40**: 761–771.

Tinker, P.B., and Nye, P.H., 2000. Solute Movement in the Rhizosphere. New York: Oxford University Press.

Wang, E.I., and Yu, T.R., 1989. Diffusion of ions in variable-charge soils: 1. Determining diffusion coefficients with miniature ion-selective electrodes. *Soil Sci.*, **147**: 34–39.

DISPERSION

The breakdown of soil aggregates into constituent particles of colloidal size, and their suspension in a fluid such as water. A necessary condition for the downward movement of clays in suspension, and their accumulation lower down the soil column as a Bt horizon, for example in a Luvisol. See *Flocculation*.

DISSECTION

The breaking up by erosion of a flat surface such as a plain or plateau into uplands, and valleys. A special kind of erosional surface called an etchplain, is produced in shield regions that have been dissected over a long period as a peneplained surface, never far from base level, is slowly uplifted and simultaneously eroded.

Bibliography

Budel, J., 1982. *Climatic geomorphology* (trans. Fischer, L., and Buscher, D.). Princeton, N.J.: Princeton University Press, 443 pp.

DISSOLVED MATERIAL

Material held in solution in a liquid such as soil water.

DIVIDE

A watershed: a ridge or line of high ground between two river valleys, marking the division between two separate systems of drainage. The Great Continental Divide is the term applied the height of land in the Rocky Mountains in the USA that divides westward from eastward draining waters.

DOLINE

A relatively extensive depression in a region of limestone bedrock, caused by the subsidence or collapse of a land surface as a consequence of the removal of material at depth. The mechanism of removal is commonly the slow dissolution of the limestone, though in glaciated terrain, the flushing of debris from fissures in the bedrock may also cause the surface to subside. In the classic Adriatic area of karst formation, dolines are funnel shaped.

DRAINAGE

The removal of water from higher to lower levels on and in a landscape, as a consequence of flow along natural or artificial channels or drains. The system of drains, natural or artificial, which conducts water by gravity from one locality to another. An area drained by a river and its tributaries is a drainage basin or catchment area. The river and tributary channels are the environment of Fluvisols.

DRUMLIN

Hills on a glaciated landscape molded by an ice sheet that has overridden an existing mound or obstruction. Drumlins are commonly pear-shaped in plan and have a relatively gentle slope towards the upstream direction of ice movement, and a steeper slope at the downstream end.

Cross-reference

Ice Erosion

DRY DEPOSITION

The fallout from the atmosphere of particles and non-dissolved materials. Generally applied to acidifying constituents.

Cross-reference

Acid Deposition Effects on Soils

DUNE

A mound, ridge, or hill of drifted sand. Characteristic of sand deserts, seacoasts, or of extensive sandy deposits resulting from glacial and periglacial processes. Barchan dunes are crescent shaped and form in desert regions where the wind blows form a more or less constant direction. The horns of the crescent point downwind, the direction of dune-migration. Sief dunes are ridge-like with the axis of elongation parallel to the prevailing wind.

Cross-reference

Wind Erosion

DURICRUSTS AND INDURATION

Typical of soils in the semi-arid regions, the duricrust (from Latin *durus*, hard; and German *Kruste,* crust) is a product of an "induration" process at or near the surface that is associated with strong seasonality when the wet season leads to solution and the dry season to capillary action and evaporation (Duchaufour, 1978, 1982; Finkl, 2005; Goudie, 1973; Retallack, 1990). Induration implies long-term stability where the cements are siliceous or ferruginous, but may be quite rapid for calcareous ones. Cementation often creates "hardpan" or pisolitic, nodular horizons. Eolian action may introduce elements not present in the underlying soil profile, being often derived as dust from remote deserts or seacoasts. Saline components are traced to oceanic wave froth, and some iron or silica components are derived from the extra-terrestrial "rain" of cometary debris.

A word or two is needed, regarding the use (and misuse) of the terms "mantle", "regolith" and "saprolite". In an earlier encyclopedia of this series ("Field and General") the terms are discussed by Finkl (1988). Briefly, it should be established that "*mantle*" should only be used in a very general sense and care should be taken to avoid confusion with the internal planetary mantle that envelopes the Earth's core. "*Regolith*" (based on the Greek word *rhegos*, blanket) was proposed by Merrill (1897) for any superficial deposit, which is either *(a)* "sedentary" or in situ, e.g., soil, lag gravel, organic matter and peat, although Merrill also confused the situation by some misunderstandings. Or *(b)* "*transported*", e.g., cliff talus, colluvium, solifluction material, eolian and alluvial deposits. Local terms like "grus", "head" and grèzes litées are only appropriate in their special settings.

In contrast, there is "*saprolite*" (based on the Greek word "*sapros*", rotten) proposed by Becker (1895) for any decomposed rock in situ, and is characteristically soft, and in the tropics may attain a thickness of up to 200 m. It may retain traces of original structures, but is chemically altered, leached, and may be pallid or mottled.

It should be understood that although duricrusts of all varieties are a product of induration, the process of induration introduces several soil-related lithologic types that are not technically duricrusts, and in this entry these will also be treated briefly. The induration processes include *lateritization* and *bauxitization*, also *silicification* and *calcification*, as well as the general processes of *lithification*, that usually involves oxidation and other reactions associated with the weathering (Merrill, 1897, p. 254) and diagenesis of freshly accumulated sediments, a process which when they are exposed to soil-forming elements may be identified as "epidiagenesis" (Fairbridge, 1966). Such freshly exposed sediments are commonly found as *flood plain alluvium, lacustrine* and *littoral* accumulations, as well as volcanic deposits such as *ash* or *tephra* (Middleton, 2003). The precise boundary between a freshly deposed sediment and the initial soil indication is evidently a blurred one. One might say that the first flowering plant to appear on a freshly erupted lava marks that magical moment.

The U.S. Soil Taxonomy and other classifications appear to have no collective term for duricrusts, although a common ferallic form is called *plinthite* when soft or *petroplinthite* when dehydrated and hard (Duchaufour, 1978, 1982; Retallack, 1990; Nahon, 1991: Martini and Chesworth, 1992). Once formed, a hardpan may be thickened by veneers from above or additional capillarity from below, or sideways.

The term duricrust was introduced by Woolnough (1927), as a collective term to cover a variety of cementing solutions, that include *calcrete*, *ferricrete*, *silcrete* (terms proposed by Lamplugh, 1902) and others proposed from time to time, including, *alucrete*, *dolocrete*, *gypcrete* and *salcrete*. Each has distinctive environmental constraints, as indicated below. They were little used in the U.S. until near the end of the 20th century (Fairbridge, 1968), but are more familiar to workers in the southern hemisphere.

Calcrete

Where the cementing agent is $CaCO_3$ (usually calcite), the duricrusts are created by rainwater mobilization of the bicarbonate.

a. This is provided by porous lime-rich sands, which may be derived from eolian-transported deposits. The latter are clastic products of reef corals and their associated biota or crushed neritic mollusca, calcareous algae and foraminifera. The carbonate sands may also be derived from erosion of pre-existing *eolianite* formations (lithified, i.e., indurated dunes).
b. Lime-rich clastics may also be produced by fluvial or aeolian erosion and transport from ancient limestone formations, of any age; a major source is the outwash of glacial origin that is distributed by wind as *loess* (Ruhe, 1965), although the corresponding climate belts are rarely sufficiently arid to permit more than a little nodular accumulation. Wind distribution of carbonate dust is also suspected in regions like the Rocky Mt foothills in western Texas (Brown, 1956).
c. Travertine "soil pavements" are sometimes affected by shrinkage cracks during dehydration, and may create a *carbonate breccia* (Playford and Leech, 1985).
d. Sharp oscillations of the water table, especially in coastal areas due to eustatic fluctuations, may lead to karst-type tubes and *vertical pipes* lined by veneers of travertine (Fairbridge and Teichert, 1953).
e. Organic activity, tree-roots and burrows introduce vertical or irregular channels for the percolating rainwater, resulting in *rhizomorphs* or *rhizoconcretions* (Fairbridge, 1968).

There are numerous regional names that are appropriate for the calcrete varieties in different parts of the world. Thus there is *caliche* in the U.S. Southwest and in the Spanish-speaking world; another form of caliche in the Atacama Desert region of Chile and Peru is nitrate-rich or iodine-rich, transported thanks to the spray in onshore winds from the Pacific. In Mexico an old Aztec name *tepetape* is used. In Arabic-speaking countries, the name is *nari*, and in India, *kunkar* or *Kankar*.

Calcrete or "caliche" can play a role in the global problem of rising atmospheric CO_2 because a dry-warming climate favors sequestration of CO_2, while a cool-wet climate leads to weathering and release of CO_2 to the soil, atmosphere and oceans. Alternations of dune building (dry) and soil building (humid) phases are typical features of recent eolianites (Fairbridge and Teichert, 1953).

Dolocrete

In certain regions of warm shallow waters favorable to coral reef growth, there is a dominance of calcareous algae, which preferentially secrete a magnesium-rich calcite. During diagenesis, even in beachrock, a proto-dolomitic cement develops and hence the term "*dolocrete*". It is found also in the Persian Gulf sabkhas (described below under "gypcrete").

Phoscrete

A cement of calcium phosphorite is associated with insular limestones (e.g., raised coral reefs) in the form of collophane, a possible amorphous precursor of apatite. The islands have served as sea-bird sanctuaries and now have guano deposits (Glenn et al., 1994; Burnett and Riggs, 1990). These have been extensively exploited as a source of agricultural phosphate.

Ferricrete

Iron-cemented paleosols are widespread in the old Gondwanaland countries: Brazil, Africa, India and Australia, but only sporadically in North America and Europe. They closely define the geomorphic landscapes (King, 1967; Thomas, 1974; Twidale and Campbell, 1993). As originally defined by Lamplugh (1902) ferricrete is a sandstone or conglomerate with a ferruginous cement, that is most often hematite (Fe_2O_3) or the colloidal, hydrated sesquioxides of iron and aluminum, thus limonite, goethite and gibbsite. It is often associated with the ferrallitic soils and sometimes with the latosol or lateritic soils (Brady and Weil, 2004; Tardy, in Middleton, 2003. Tardy recognizes that practically all laterites are polygenetic because of the gross climatic fluctuations and climatic effects of continental drift over long periods of time.

Opaline silica (an amorphous hydrated silica gel) is often present, and on dehydration, this creates an extremely hard crust that plays an important role in geomorphology, crowning many prominent plateaus. In French-speaking parts of North Africa the ferricretes and laterites are collectively called the Cuirasse-de-Fer (the iron breast-plate of medieval warriors; Maignien, 1958; Nahon, 1991). In this way, the geomorphic plateau-forming crust of ferricrete, laterite and silcrete tends to merge (see the article on Tropical Soils in this volume).

As usual in the Gondwana countries there is the long-term inheritance problem, going back lengthy periods, in the order of 10^6 to 10^8 yr, during which climatic fluctuations and plate migrations have provided a background theme (Douglas and Spencer, 1985; Beckmann, 1983; Finkl and Churchward, 1976; Goudie, 1973, Mabbutt, 1965; Tardy in Middleton, 2003, p. 410). To identify the present-day or at least Quaternary soil-forming processes it may be helpful to consider tectonically active or youthfully emergent landscapes. Thus the insular variety of Indonesia provided a rich background for the original and comprehensive studies by Mohr, Van Baren and Van Schuylenborgh. In a smaller field area, but one expanded by elevation and climate, there are the studies of Bremer and her colleagues Schnütgen and Späth (1981) in Sri Lanka. In particular, Schnütgen's attention to microstructure is illuminating.

A particular form of ferricrete, the ferralitic pisolite gravels, is widespread in the inner coastal plain of Western Australia (Finkl, in Alexander, 1999). They are visually similar to those on the planet Mars. Tardy (in Middleton, 2003, p. 409) believes these concretions originated as kaolinite, which may be of considerable thickness, becoming progressively enriched by iron as they are reorganized in the pisolitic (hard) form. They have been referred to as "low-level laterites". However, this is not quite accurate because they are also found in the paleodrainage depressions of the plateau margins. There, they have been widely exploited as aluminum ores. The term "*alucrete*" has been mentioned. "*Lateritic bauxite*" is more usual, the principal ore being gibbsite ($Al(OH)_3$), best developed in the Weipa deposits of northern Queensland (Wilke and Schwermann, 1977; Middleton, 2003). Elsewhere on the West-Australian plateau the source rocks have furnished nickel-rich ores.

Coastal outcrops of lateritic ferricrete are to be seen in southern India, on the coasts of Goa and Kerala. They are commonly affected by *piping*, a phenomenon that points to solution during brief ice-age episodes of heavy precipitation, the pipes disappearing below sea level. Another ice age phenomenon is the *fluting*, or erosion of very steep slopes leaving knife-edge ridges of distinctive form, reminiscent of carbonate solution in tropical karst landscapes. Examples are seen in the Seychelles in the deeply weathered granitic basement.

Coastal laterites are also seen in Hong Kong and its offshore islands where the fluting can be seen passing directly below present sea level (Wang, 2003).

The former coastline of the Guyana borders of South America, possibly of pre-Miocene (even Cretaceous) age presents an interesting relationship with the commercial bauxite deposits, which are concentrated about 200–300 m above present sea level, but at a eustatically reasonable elevation for the Late Cretaceous sea level. This tropical belt was probably fringed by mangrove swamps, where the low pH would have favored the concentration of kaolinite, but subsequent exposure to fluctuating climates could remove silica and concentrate gibbsite.

Another factor that may be considered is the role of wind in building thick accumulations of smectite (montmorillonite) on non-volcanic islands, as could be the case in Jamaica. Here a massive mantle of bauxite is exploited but there is no obvious source of alumina in this insular location unless through its position downwind from the volcanic Leeward Islands (Lesser Antilles), which would provide abundant ash and thus smectite.

Wind transport of volcanic ash may also help to explain the karst bauxites of the Alpine belt in Europe. Plentiful source of volcanic ash are available, but the classical idea of limestone solution seems quite inadequate.

Silcrete

A duricrust of silica, (SiO_2, that may be either unhydrated, calcedonic quartz or opaline silica, the hydrated form. Silica solubility rises at very low pH and very high (>9) pH, increasing with temperature, as H_4SiO_4. (In other words, plotted against pH, the solubility curve is like a capital "U".) The opaline form is about 10–20 times more soluble than quartz.

The basic field studies and theoretical analyses have been undertaken, in most cases, quite independently and apparently often under the impression that their authors were dealing with unique situations (but see Ullyott, Nash and Shaw, 1998). Countries involved include England, France, Australia and South Africa. In the European investigations the questions were first raised by archaeologists who were faced by the origin of "standing stones" or "megaliths", such as at Stonehenge (on Salisbury Plain, Wiltshire, U.K.) and those of Brittany (as at Carnac, in NW France) and in Corsica. These stones had been erected by Bronze Age ("Megalithic") people, ca. 5 000–3 000 yr BP apparently in religious rites associated with the summer solstice or other astronomic events. The "standing stones" are referred to in Britain as "*druid stones*" or "*sarcens*" (a derivative from "saracen", a Moslem or exotic stranger), or in France as "menhirs" (from the Breton, meaning "long stone"). It is believed that the megalith sarcens originated in a thin veneer of Eocene sand, which once overlapped the chalk surface of Salisbury Plain (or comparable settings) that became silicified on exposure. The silcrete may form regular jointing in the same way that calcrete can develop in beach rock which commonly breaks up into rectangular blocks. Such ready-made building blocks would have been ideal megaliths, and required no long-distance transportation. (In contrast, the smaller "bluestones" of Stonehenge had to be conveyed in some way from South Wales.)

In the Paris Basin (France) there are several Cenozoic formations of quartz-rich sands, the weathering of which during the cold-dry oscillations of Pleistocene climates (periglacial but not glaciated), that generated very high pH and thus favored SiO_2 solution. These products include:

a. *Pudding stones* (English) or "Pondingue" (French) which in the Paris Basin are well-rounded pebbles of the Cretaceous chert (flints) in a cement of whitish silica. A fine illustration of an example from Larchant (Seine-et-Marne) is given in Cayeux, aka Cailleux (1981, p. 154) (Figure D8).
b. *Meulières* (Fr. for millstones), a quartzitic limestone that formed on the West-European planation surface in the Oligocene-Miocene. Segments of this surface are preserved in the Plateau de Brie, also of Beauce, Valois, etc. In Embleton's *Geomorphology of Europe* (1984), it is remarked that this surface was very comparable with that of the Kalahari Desert in southern Africa.
c. *Giant siliceous concretions* of homogenous silica, which were probably emplaced as ground-water spring deposits, such as those found in parts of the Paris Basin (France).

Silcretes in the modern desert regions were first studied in Australia, later in South Africa. They are clearly invaluable paleoclimatic indicators (Martin and Chesworth, 1992: see Milnes and Thierry). Two distinctive categories are recognized in soil processes: *(a)* alkaline groundwater silcretes associated with semi-arid conditions, and *(b)* pedogenic silcretes

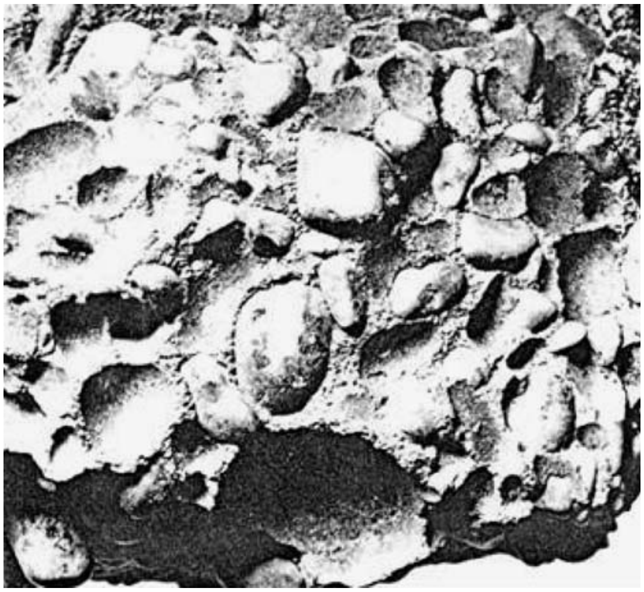


Figure D8 *Pudding stones* from Larchant (Seine-et-Marne) (from Cayeux, aka Cailleux (1981, p. 154).

associated with deep weathering under warm-wet climates. Primary sedimentation adds a third category of silicification, which transcends surface processes.

A key factor in this context is the diagenetic habit of silica to form biologically in opaline form as a colloid or hydrous gel (3–9% H_2O). The classic examples are the chert or flint concretions within the Upper Cretaceous Chalk formations, which are widely known in Europe, Asia, North America and Australia. The main source of the silica is the unicellular plankton Radiolaria, which is mobilized during burial to reassemble as concretions in particular (porous) horizons. Since mid-Tertiary times, diatoms have become more abundant and tend to dominate. Another source is provided by siliceous spicules in sponges, which often provide nuclei for the concretions. The rotting of the organic matter in the sponges (and other organisms, such as pelecypods), appears to have lowered the local pH and thus assisted the silica migration (Fairbridge, 1983). The rate of silicification can be judged by an interesting relationship to be seen at Moens Klint in Denmark, at the Cretaceous/Tertiary boundary. The Cretaceous Chalk was briefly exposed by the boundary event, partly desiccated and then developed vertical joints, some being filled with chert, all being abruptly truncated by the erosion surface which was immediately followed by the Danian Formation of the Lower Tertiary. The silica-emplacement rate may then be estimated here as in the range of 10^5 yr.

Radiolarian chert, in a finely bedded structure, in contrast to the nodular forms, is a typical deep-sea "ooze", formed at 3 000–4 000 m depth. The opaline state was probably the progenitor of both radiolarites and diatomites, the dehydration being favored by burial and heat.

The source of biogenic silica is by no means limited to the marine realm, but is seen actively forming today in some subtropical lakes such as Lake Chad. The silica is commonly found as "acritarchs" on the extensive swamp vegetation. Seasonally exposed to desiccation, the vegetation dies back and the "harmattan" winds pick up the minute grains and thence carrying them into the upper atmosphere, some being rained out in remote places such as Florida or New York.

The Miocene silcretes of argillaceous playa deposits in the Madrid Basin of Spain have been studied in depth and a convenient synthesis is provided by Mrs. Bustillo in Middleton (2003, p. 659–660), recognizing that the basic controls were hydrologic and climatic.

Non-marine cherts are also found in the Rift Valley lakes of East Africa. A hydrous Na-silicate (e.g., magadiite) is precipitated during seasonal evaporation in these alkaline lakes, creating varve-like sequences.

Siliceous induration is a geomorphic phenomenon that transcends the time frame of most soil-forming duricrusts, but the boundary is a blurred one. It is associated with the growth of peneplains and pediplains (Adams, 1975) and thus intimately connected to the Mesozoic/ Cenozoic history of Gondwanaland, but less clearly with that of Laurasia (Fairbridge, 1965; Stephens, 1971; Finkl and Fairbridge, 1979).

Let us consider the history of the Appalachian belt following the initial rifting of the proto-Atlantic (Adams, 1975). Paleosols and erosion surfaces can be dated by "denudation chronology", i.e., by stratigraphically dated truncation or overlap relationships (King, 1962, p. 355). A sub-Triassic planation, with paleosols, can be inferred in New Jersey, but recently resurrected and visible on the west side of Manhattan. The paleolatitude of this belt in the Triassic-early Jurassic time frame lay in the intertropics and equatorial zone. An extensive etchplain existed at that time, all across Gondwanaland. Progressive fracturing began with widespread diabase emplacement and volcanism, creating initial marine troughs or isolated rift depressions. This led to the isostatic uplift of the rift shoulders similar to those of the present Red Sea (as in Yemen and Eritrea). The eastern rifts evolved into the proto-Atlantic and the western side began its stabilization phase (the "Gondwana Cycle" of King, 1967) with an extensive etchplain, leading to deep groundwater circulation and silica transport. This was favored by the porosity of some of the late Paleozoic sediments – very high in the case of the sandstones of Oriskany type. By early Cretaceous a "Post-Gondwana cycle" could be dated by marine transgressions along the Atlantic seaboard. Deep drilling discloses thick paleosols beneath them. In many places the exact relationships are confused by multiple overlaps, collectively known as the "Schooley" surface. Late Cretaceous upwarping caused valley incision and by the Oligocene an "African cycle" was widely established over the now isolated cratonic units. In the Appalachians it is identified as the Harrisburg Surface. However, the silicified remnants of the post-Gondwana cycle now remained as insoluble quartzite-supported ridges or steps in the uplifted land surfaces. Since that time only small periglacial features have slightly modified it.

On the other side of the world, the region of southwestern Australia (the "Darling Peneplain" of Woolnough, 1918) seems to possess traces of planation and paleosols of closely analogous chronology, while distributed on a totally distinctive bedrock, the West-Australian Craton (Finkl and Churchword, 1976). Whereas the bedrock lithology of the Appalachians consisted of the various Paleozoic stratigraphic components, an orogenic belt subjected to later rifting, the bedrock of the West-Australian Craton was a heterogeneous mix of Precambrian crystalline rocks. Its fracturing began in early Paleozoic times, initiating a Red Sea-type graben-gulf, while its faulted margin (Darling Fault) became repeatedly incised by deep river valleys. The erosive process of such incision into ancient crystalline rocks was glacially slow and only possible after lengthy "pre-soaking" in the subsoils of repeated fluvial or estuarine cycles.

Following the early Permian glaciation of Gondwanaland, the late Permian stream beds in SW Australia carried distinctive faceted and striated boulders (Fairbridge and Finkl, 1978). This alluvium became silicified and now occupies an inverted relief on ridge tops of the cratonic (Darling) plateau. Incised into them are younger braided stream deposits of Mesozoic age and in turn these are incised by Late Cretaceous-Eocene dendritic alluvium (also silicified) that terminates at 280 m elevation (today), the highest level of mid-Eocene eustasy. At this point in time southern Australia was rifted from eastern Antarctica (Veevers and Cottrill, 1978) and then drifted northward into a subtropical environment where deep weathering led to >50 m of latosol. The West-Australian Craton had by then developed an extensive network of W-directed streams that today are still preserved as ephemeral lakes (Van de Graaff et al., 1978). In the south, however, the Eocene rifting caused a downward tilt that led to extensive stream piracy, with valleys that became deeply incised during the low sea level of the Oligocene, although the climate became increasingly seasonal and drier. Desiccation converted the upper surfaces from soft latosols to hard lateritic (ferralitic) duricrust, which today spans much of the higher ground of the interior plateau. The Miocene sea-level rise generated deep rias and other estuaries that brought marine deposits far into the southern interior ("Plantagenet Group" of Fairbridge and Finkl, 1978).

Subsequently there was progressive emergence during the Pliocene and Quaternary, although the silicified crests of former Precambrian features protected them from further erosion, so that they were preserved as inselbergs. Some of them offshore (Recherche Archipelago) are today drowned inselbergs, washed today by the waves of the Southern Ocean.

The Earth’s continents of today comprise clusterings of former cratonic blocks, for which the Western Australian example provides a convenient model, labeled by Finkl a “cratonic regime” (Fairbridge and Finkl, 1979). In a nutshell, each craton has a nucleus of Archaean crystalline rocks, peneplaned or etchplaned and overlapped by “stacked veneers” of younger sediments, separated by paleosols and duricrusts. The duricrusts best preserved are the silcretes and laterites.

Gypcrete and salcrete

These two examples of duricrust with gypsum or salt cements are exclusively associated with the semi-arid climate belts and then mainly in the coastal regions, though interior salt lakes may offer comparable settings. The usual situation is what is called a “*sabkha*”, “sebkhe” or “sabkhat” in Arabic, or “saline” or “playa” in Spanish. Unfortunately, neither is used with a very strict definition. Sometimes an English terms “salt flat” is employed. Best known in geological terminology as the *sabkha* (the other spelling “sebkha” is the French variant), meaning a salt-encrusted mudflat, the desiccated surface of which alternates seasonally with seepage or an inundation phase by either oceanic tides or fluvial flooding. Evaporite minerals form in the capillary zone above the saline water table (Hardie, in Middleton, 2003).

One of several very different settings are commonly cited for the “standard” model. These are:

a. The tidal mudflats of the SE Persian Gulf (called “Arabian Gulf” by some of the Arabs), notably Abu Dhabi in the Arab emirates, once known as the “Trucial Coast”. The mudflats are seasonally inundated by a change in the wind system (Kinsman, 1969).
b. Saline lagoons of the Gulf of Aqaba (Elat, in Hebrew) located on the W. side, now under Egyptian control. The sabkha is fed from the sea by seepage through a sand bar, and the brines are concentrated by evaporative “pumping” (Figure D9). Dense brines seep down and seawards by a “reflux” process (Gavish, in Gvirtzman and Buckbinder, 1978).
c. The Schott-el-Djerid in Tunisia (“djerid” is Arabic for “dry”), which is isolated from the Mediterranean by a belt of beach ridges, which are porous and provide the seasonal saline influx. Fresh water on the other hand comes in from seasonal rivers fed by rains from the mountainous interior (Tricart and Cailleux, 1973).
d. The Colorado Delta in the northernmost Gulf of California. Winds from the south seasonally bring saltwater into the mudflat areas and these phases alternate with fresh water input from the Colorado (Thompson, 1968). In places layered halite (NaCl) is forming (Shearman, 1970).

None of these examples attracted much interest until the second half of the 20th century when the importance of dolomitization became apparent to the oil and gas industry. Many supratidal coastal lagoons in the semi-arid latitudes were found to precipitate *gypsum* ($CaSO_4 \cdot 2H_2O$), usually as a cement in coastal sands, but in places as elegant crystals. Where these gypsum-rich layers are found in Cenozoic geological formations, there has been dehydration associated with increasing burial load to create *anhydrite* ($CaSO_4$). Eventually, these formations may become uplifted and the anhydrite exposed to rainwater; the process is then reversed and an inversion to gypsum takes place. However, an increase in volume is involved (by about 40%) and curious contorted structures are seen. The type area for the gypsum formation today is the southern Persian Gulf, e.g., in the Abu Dhabi region, but the process had been going on discontinuously since the middle Tertiary, and where it is tectonically emerged, as in northern Iraq and Syria, the expansion features can be observed as a structural aspect of the regional soil (by RWF in 1939).

The waters of the southern coast in the Abu Dhabi area are extremely shallow and, although the tides are not very important, there is a seasonal shift in the wind systems and a persistent norther sets in, resulting in a widespread flooding of the mudflats which are in places over 10 km across.

What drew worldwide attention to the sabkhas was a report of “proto-dolomite”, which of course would be expected in this setting, but set up a “sabkha syndrome” among the multitude of new researchers (Carozzi, 1975, p. 5). Many of the papers are reproduced, at least in part, in the “Benchmark volumes”

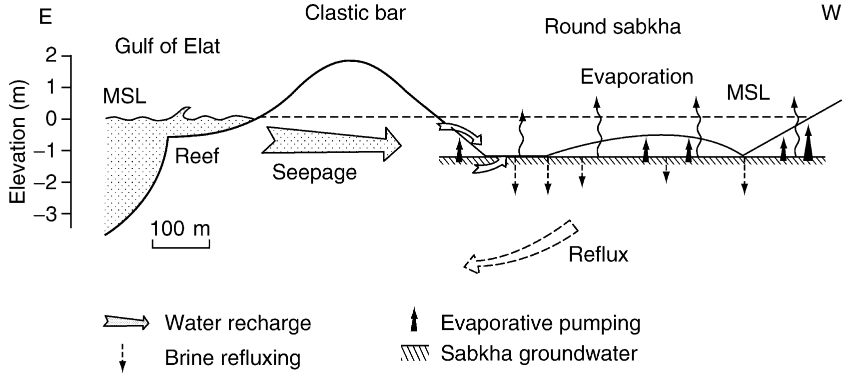


Figure D9 Saline lagoons of the Gulf of Aqaba (Elat, in Hebrew).

(which the writer edited), notably that by Kirkland and Evans (1973: "*Marine Evaporites: Origin*, *Diagenesis*, *and Geochemistry*"; and by Zenger and Mazzullo, 1982: "*Dolomitization*". An abundant literature was involved, most recently reviewed by Marshall and Fairbridge (1999).

Rhodes W. Fairbridge

Acknowledgments

Appreciation is expressed to all those who led field trips in Britain, France and Germany, to the Persian Gulf, in North America, Jamaica, Brazil, Australia, New Guinea and the Pacific. For logistic support at the NASA-GISS in New York, Dr. James Hansen, is due enduring gratitude, as well as the Columbia University Center for Climate Systems Research.

Bibliography

Adams, G.F., 1975. *Planation Surfaces: Peneplains, Pediplains and Etchplains.* Stroudsburg: Dowden, Hutchinson & Ross (Benchmark Papers in Geology, **22**), 476 pp.

Alexander, D.E., and Fairbridge, R.W., 1999. *The Encyclopedia of Environmental Science.* Dordrecht: Kluwer Academic (now: Springer), 741 pp.

Becker, G.F., 1895. Reconnaissance of the gold fields of the southern Appalachians. *U.S. Geol. Surv.,* 16th Ann. Rept., pt. 3, 251–331.

Brady, N.D., and Weil, R.R., 2004. *Elements of the Nature and Properties of Soils.* 12th edn. Upper Saddle River: Prentice Hall. 606 pp.

Bremer, H., Schnütgen, A., and Späth, H., eds., 1981. *Zur Morphogenese in den feuchten Tropen.* Berlin: Gebruder Borntraeger. 296 p.

Brown, C.N., 1956. The origin of caliche on the north-eastern Llano Estacado, Texas, *Jour. Geol.*, **64**: 1–15.

Burnett, W.C., and Riggs, S.R., eds., 1990. *Phosphate Deposits of World*, vol. 3. Cambridge Univ. Press. 553 pp.

Carozzi, A.V., ed., 1975. *Sedimentary Rocks: Concepts and History. Stroudsburg*, Pa.: Dowden, Hutchinson & Ross (Benchmark, v. 15). 468 pp.

Catt, J.A., 1986. *Soils and Quaternary Geology.* Oxford: Clarendon Press. 267 p.

Cayeux, A. de (aka Cailleux), 1981. *La Terre.* Paris: Bordas. 838 pp.

Douglas, I., and Spencer, T., eds., 1985. *Environmental Change and Tropical Geomorphology.* London: Allen and Unwin Co. 378 pp.

Duchaufour, P., 1978. *Ecological Atlas of Soils of the World.* New York: Masson (transl. from French by G.R. Mehuys et al.), 178 pp.

Duchaufour, P., 1982. *Pedology* (transl. from French of 1977). London: Allen and Unwin. 448 pp.

Elhaï, H., 1967. Colloque sur les argilles á silex du Bassin de Paris. *Mém. Soc. Géol. France,* h.s.4.

Embleton, C., 1984. *Geomorphology of Europe.* New York: Wiley-Intersci., 465 pp.

Fairbridge, R.W., 1965. The Indian Ocean and the status of Gondwanaland. *Progress in Oceanography.* **3**: 83–136.

Fairbridge, R.W., 1966. *The Encyclopedia of Oceanography.* New York: Reinhold Publ. Co., 1021 pp.

Fairbridge, R.W., ed., 1968. *The Encyclopedia of Geomorphology.* New York: Van Nostrand Reinhold, 1295 pp.

Fairbridge, R.W., 1983. The Pleistocene-Holocene boundary: *Quaternary Science Reviews*, **1**: 215–244.

Fairbridge, R.W., and Finkl, C.W., Jr, 1978. Geomorphic analysis of the rifted cratonic margins of Western Australia. *Zeitschr. f. Geomorph.*, N.S. **22**(4): 369–389.

Fairbridge, R.W., and Teichert, C., 1953. Soil horizons and marine bands in the coastal Limestones of Western Australia. *Royal Soc. New South Wales, Jour. & Proc.*, **86**: 68–87.

Finkl, C.W., ed., 1988. *The Encyclopedia of Field and General Geology.* New York: Van Nostrand Reinhold, 911 pp.

Finkl, C.W., 2005. Coastal soils. In Schwartz, M.L., ed., *Encyclopedia of Coastal Science.* Dordrecht: Springer, pp. 278–302.

Finkl, C.W., and Churchward, H.M., 1973. The etched land surfaces of southwestern Australia. *Jour. Geol. Soc. Australia*, **20**(3): 295–307.

Finkl, C.W., and Fairbridge, R.W., 1979. Paleogeographic evolution of a rifted cratonic margin: S.W. Australia. *Palaeogeogr., Paleoclim., Palaeoecol.*, **26**(3/4), 221–252 (with discussion by W.F.E. Van de Graaff, 1981) *ibid.,* **34**: 163–172.

Glenn, C.R., et al., 1994. Phosphorus and phosphorites: sedimentology and environments of formation. *Eclogae Geologicae Helvetiae*, **87**: 747–788.

Goudie, A., 1973. *Duricrusts in Tropical and Subtropical Landscapes.* Oxford: Clarendon Press. 174 pp.

Gvirtzman, G., and Buchbinder, B., 1978. *Recent and Pleistocene Coral Reefs and Coastal Sediments of the Gulf of Elat.* Jerusalem: Tenth Internat. Congr. on Sedimentology. Exc. Y-4.

King, L.C., 1967. *The Morphology of the Earth.* 2nd edn. Edinburgh: Oliver & Boyd. 726 pp.

Kinsman, D.J.J., 1969. Modes of formation, sedimentary associations and diagnostic features of shallow water and supratidal evaporites. *Amer. Assoc. Petroleum Geol. Bull.*, **53**: 830–840.

Kirkland, D.W., and Evans, R., 1973. *Marine Evaporites: Origin, Diagenesis and Geochemistry.* Stroudsburg: Dowden Hutchinson & Ross (Benchmark, **7**). 426 pp.

Lamplugh, G.W., 1902. Calcrete. *Geol. Mag., Dec. IV*, **9**: 575.

Mabbutt, J.A., 1965. The weathered land surface in Central Australia. *Zeitschr. f. Geomorph.*, **9**(1): 82–114.

Martini, I.P., and Chesworth, W., eds., 1992. *Weathering, Soils and Paleosols.* Amsterdam: Elsevier, 618 pp.

Merrill, G.P., 1897. *A Treatise on Rocks, Rock-Weathering and Soils.* New York, London: Macmillan, 411 pp.

Middleton, G.V., 2003. *Encyclopedia of Sediments and Sedimentary Rocks.* Dordrecht: Kluwer (now Springer), 821 pp.

Milnes, A.R., and Thierry, M., 1992. Silcretes. In Martini, I.P., and Chesworth, W., eds., *Soils and Paleosols.* Amsterdam: Elsevier, 349–377.

Nahon, D.B., 1991. *Introduction to the Petrology of Soils and Chemical Weathering.* New York: Wiley, 313 pp.

Retallack, G.J., 1990. *Soils of the Past.* London: Harper Collins Academic, 520 pp.

Ruhe, R.V. 1965. Quaternary paleopedology. In Wright, H.E., Jr, and Frey, D.G., eds., *The Quaternary of the United States*. Princeton, NJ: Princeton Univ. Press, 755–764.

Shearman, D.J., 1970. Recent halite rock, Baja California, Mexico. *Institute of Mining and Metallurgy, Transactions*, **B79**: 155–162.

Stephens, C.G., 1971. Laterite and silcrete in Australia: a study of the genetic relationships of laterite and silcrete and their companion materials, and their significance in the formation of the weathered mantle, soils, relief and drainage of the Australian continent. *Geoderma*, **5**(1): 3–52.

Thomas, M.F., 1994. *Geomorphology in the Tropics.* London, New York: J. Wiley. 460 pp.

Twidale, C.R., and Campbell, E.M., 1993. *Australian Landforms.* Adelaide: Gleneagles Co., 560 pp.

Ullyott, J.S., Nash, D.J., and Shaw, P.A., 1998. Recent advances in salcrete research and their implications for the palaeoenvironmental significance of sarcens. *Proc. Geol. Assoc.* (London), **109**: 255–270.

Van de Graaff, W.F.E., et al., 1978. Relict Early Cainozoic drainages in arid Western Australia. *Z. Geomorph.* N.F. **21**: 379–400.

Veevers, J.J., and Cotterill, D., 1978. Western margin of Australia: Evolution of a rifted arch system. *Geol. Soc. Amer. Bull.* **89**: 337–355.

Wang, P., 2003. Carbon reserve changes preceded major ice-sheet expansion at the mid-Brünhes Event. *Geology*, **31**: 239–242.

Woolnough, W.G., 1918. The Darling peneplain of Western Australia. *Jour. Proc. Roy. Soc. New South Wales*, **32**: 385–396.

Woolnough, W.G., 1927. The chemical criteria of peneplanation. (II) the duricrust of Australia. *Jour. Roy. Soc. New South Wales*, **61**: 1–23, 24–53.

Cross-references

Calcareous Soils
Calcisols
Ortstein
Pan
Tropical Soils

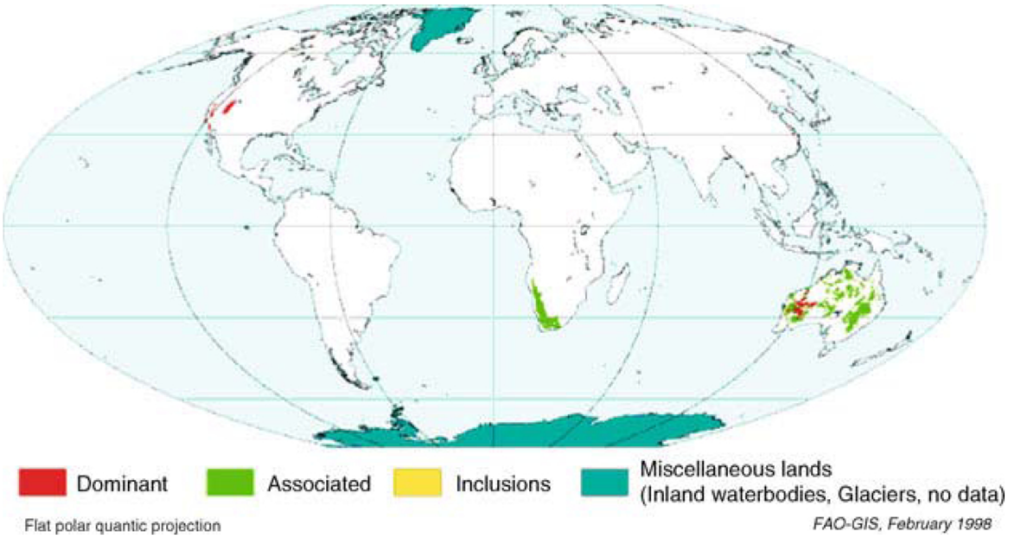


Figure D10 Distribution of Durisols.

DURISOLS

Durisols are fairly deep, free-draining soils of dry environments with a cemented layer (secondary silica being the cement) in the upper meter of soil.

Connotation. Soils with hardened secondary silica; from L. *durus*, hard.

Synonyms. Known as hardpan soils (Australia) or Dorbank (South Africa) or as the "duripan phase" of other soils, e.g., of Calcisols (FAO).

Definition. Durisols are defined by FAO (2001) as free-draining soils with a layer or pan (a duric or petroduric horizon) in the upper meter of the soil in which the grains are cemented by silica.

Parent material. Mainly alluvial and colluvial deposits of all texture classes.

Environment. Level and slightly sloping alluvial plains, terraces and gently sloping piedmont plains in arid, semi-arid and Mediterranean regions.

Profile development. AC or ABC profiles; eroded Durisols with exposed *petroduric* horizons are common in (gently) sloping terrain.

Origin. In humid climates or during the wet season in drier zones (see Figure D10), weathering and acidification take place in the surface horizon, clay is translocated to a lower section of the profile (illuviation) and silica is transported downward in solution. The leached silica accumulates and precipitates at depth to form a duric horizon containing patches in which the grains are cemented with silica. With time the patches become continuous and the horizon is referred to as petroduric (duripan).

Use. Most Durisols can only be used for extensive grazing. Arable cropping of Durisols is limited to areas where irrigation water is available (a continuous petroduric horizon at shallow depth must be broken up).

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. (World Soil Resources Reports, 94). Rome: Food and Agriculture Organization of the United Nations. 334 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. Soils of the World. Heidelberg Berlin: Springer-Verlag, 130 p.

Cross-references

Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils
Tropical Soils

DUST

Finely divided mineral or other particles, light enough to be transported by wind see Figure E10.

E

E HORIZON

See *Horizon, Profile, Horizon Designations*.

EARTH CYCLES

Cycles in the major *chronological* sense of affecting the planet Earth are *(a)* rather strictly defined within an astronomic framework; *(b)* in an *evolutionary sense,* that is, taken loosely in a birth/death or youth/maturity/old age system; *(c)* in a *stochastic or random sense* within a window, with feedback between certain constraints; and *(d)* on a small scale *dynamic sense*, like a ball bouncing to and fro.

Astronomic chronological cycles

Three distinct but interlocking systems in astronomy are well known, the galactic cycle of the Milky Way, the solar cycle involving the Sun and its various planets, and the Earth-Moon system involving only two celestial bodies (see below). All three involve spinning bodies, with known spin-rates, revolving in known orbits that in the second and third categories can be predicted with a high-degree of mathematical precision, although the first one, the galactic, is still poorly quantified. During the last century, geochemical dating methods have been developed to such refinement that it is possible to consider at least the last two billion years of Earth history as an established framework that demonstrates *three fundamental facts* (note *facts*, NOT hypotheses):

a. The long-term stability of the Earth within its place in the Solar System, orbital periods being essentially constant. This is a crude but long-term stability within a history marked by periodic asteroid impacts, ice ages, and plate-tectonic rearrangements, which fail to even nudge the Earth's long-term stability.
b. Despite revolutionary chapters in the planet Earth's geochemical history, the atmospheric composition has changed relatively slowly and the essential element water has always remained liquid. Soil formation, reflecting biological activity at more or less constant temperatures (15±10 °C on average), has led to mineral and rock weathering, and thus permitted normal water erosion and sedimentation for at least the last billion years.
c. The "Law of Biologic Continuity" (Fairbridge, 1980) states that at no point in geologic time has there ever been a total destruction of the Earth's biota, followed by a "re-creation". In short, biologic evolution has been a continuum, albeit "punctuated" with accelerations and slow-downs (Eldredge and Gould, 1972; Rampino and Stothers, 1984; Rampino and Haggerty, 1996). There is no place for "Intelligent Design" in this scientific setting, although *Homo sapiens* has evolved its own spiritual world which ought not to be confused with the totally distinct physical world.

Solar cycles

In their orbits around the Sun, the planets develop distinctive cycles, most important of which is the regular alignment of the two largest planets, the Jupiter and Saturn Lap (called SJL) with an average periodicity of 19.8593 yr (but with a variance of about ±2 yr; though over a century or two, the average is always maintained: Fairbridge and Sanders, 1987). Other planets combine with these two, eventually to create an "All-planet Concordance" at 6 672 yr (that is 336 × SJL).

When these two largest planets are aligned a torque is applied to the spinning Sun (spin-rate about 25 days) which generates disturbance in the photosphere, notably sunspots (Schove, 1983). The *sunspot cycle* has an average of 600 returns in 6 672 yr, a mean cycle of 11.1212 yr. This affects the Earth's weather in various ways, but always adjusted to the annual cycle.

The sunspot cycle is not very regular, being ±6 yr. One of the modifiers is the QBO or Quasibiennial Cycle Oscillation of 2.1721 yr, which is observed in both the Sun's rotations and the Earth's climate. It is an exact fraction of the 6 672.73 yr planetary resonance (1/3072), and the tree-ring ^{14}C flux cycle (1/96 × 208.5226).

Other planetary alignments contribute to a complex array of cycles, some of which seem to have important links with the

Earth's climatic systems. The ancient Mayan astronomers of pre-Columbus Mexico, even without telescopes, managed to establish a complex calendar based on alignments of Jupiter, Earth and Venus. A seasonal program of planting and harvesting for the Mayan people was established that was apparently very successful.

Short-term cycles among the planetary "competition" are uneven, as shown by the El Niño examples. Only their long-term analyses disclose systematic links, e.g., a 69.5 yr cycle is exactly 1/96 × 6 672 yr. Actual El Nino Southern Oscillations average about 3.3 yr but are constrained by the annual seasonality "strait jacket". U.S. west coast tree-ring spectra show a major spike at 3.3 yr.

Lunar cycles

The tide raising force of the Moon is on average 2.17 times that of the Sun, reminding us of the QBO. Babylonian astronomers (also without telescopes) two and a half millennia ago discovered what they called the "Saros" period, 18.0303 yr, which is 18 yr + $11^1/_3$ days, the return period of lunar eclipses, each recurring at intervals of about 120° E longitude. After three (360°) it returns to almost the same spot. (Predictive tables were available in the 4th century BC) On a more than decadal scale the 18.03 yr cycle is the most important ocean tide (Wood, 2001). It should be recognized also that the Earth-Moon pair behaves more or less as a single planet, and the Saros is in an exact ratio (1 : 370) to the All-Planet Concordance of 6 672.73 yr.

The Moon's orbit around the Earth varies from the Sun-side to the shade-side to create the full-moon/new moon alternation every two weeks, executing a spiral trajectory around the Earth's orbit. At each "full and change" peak there will be a maximization of the ocean tide (the "springtide"). However, the Moon's orbit is tilted at up to $23^1/_3$° to the Earth's, which explains the polar seasons ("midnight sun" and "long night"). And furthermore its orbital plane inclination varies through an 18 yr cycle (the 18.6 yr declination period, close to the Saros) with the Moon reaching a zenith position once in each hemisphere, thus creating a 9 year cycle. Tide is highest at the zenith state, but this zenith shifts to and fro over about 1 200 km in each of the tropics. Tidal currents are then accelerated and due to the Coriolis effect as the sea surface tilts. As the zenith location shifts polewards, along the coast the sea level falls, but offshore (as in Bermuda) it rises. A warm pulse is added to the Gulf Stream (and other geostrophic currents around the world). The effect reaches even into the Arctic, which affects in particular the weather north of Russia. It also has a biological effect, measured by the commercial fisheries. Another branch of the current reaches into the Baltic where the fisheries have been recorded for nearly 800 years (Pettersson, 1930). Seasonality is important in an 18.6 yr cycle, because of sea-ice formation in winter, so it only returns in full force every 93 years. This periodicity is also recorded in air temperatures and agricultural crops. An Italian book on agronomy, some 400 years ago, recorded this 18.6 yr cycle as useful for farmers.

On a global scale it has been found that the 18 yr Saros period shows up in the spectra of world sea-level records. As the Earth spins, the Moon passes overhead and creates a "tidal wave" that follows it. The Pacific waters always tend to flow into the Indian Ocean, but there is a "choke point" in the narrow openings of the East Indies that is hemmed in by two of the world's largest continental shelves, the Sunda and Sahul, each more than 1.5×10^6 km^2. The westward current at times flows more than 10 knots in the narrowest constrictions (made narrower by coral reefs). The rising tide brings cold, offshore water onto the shelves and gives a minute cool pulse to the rising columns of air (amplified already by the cone-shaped altitudes of the volcanic islands). In this way, the cyclic returns of rare extra-high tides are transmitted into the stratospheric circulation. An example was observed at the summer solstice, June 21, 2005, which coincided with full moon and extreme spring tides, high and low.

A regular return is the perigee-syzygy cycle of about 4.42 yr, that records closest approach of Earth and Moon (perigee), coinciding with closest alignment with the Sun (syzygy). It is just half the lunar apsides period (8.849 yr). Full tables for the last 400 yr are provided in Wood (2001). U.S. tree-ring power spectra show a major peak at 42 yr.

A combination of both solar and lunar forcings is suggested by the geomagnetic signals. These can be read over about 8 centuries using the proxy of auroras, as observed in Scandinavia by rural clergy, who pointed to the celestial displays as measures of religious significance (warnings against sin, and so on). Ekholm and Arrhenius (1898) found both the Solar 22 yr and Lunar 18.6 yr periodicities with approximately equal power. Both occur distinctively on the Hudson Bay, Canada, where a "staircase" of 183 glacioisostatically emerged beach ridges reflect open-water storminess cycles of c. 45 yr, with longer resonances at ratios of 34 : 57 and fractions (Fairbridge and Hillaire-Marcel, 1977).

For rainfall records over periods of less than 12 months, perhaps the most remarkable observation was that of the Rev. R. Everest in India (1834) who recorded the maximum daily precipitation at the time of the new moon and about 6 days before or 6 days after (±1–2 d). Since then, countless papers have been devoted to this subject, relating the rainfall to the dew point (atmospheric pressure), solar radiation, lunar declination and so on. It is still a problem that defies simplistic solutions.

Luni-solar orbital cycles

A special category of chronologic cycles relates to the small but regular changes in the orbital parameters of the Earth-Moon-Sun system. They are often referred to as the Milankovitch parameters. In the 19th century several suggestions of orbital controls of terrestrial climates were put forward (Adhémar, Croll, Ball and others), but the data were imperfect and the idea had to wait for Milankovitch, who of Serbian origin was captured during WWI but treated kindly and was able to work out the complex mathematics (long-hand). His first version, in French, attracted some attention, but then came WWII, and again he was captured and again able to polish his earlier results. This time he published in German, which was translated into English in Israel and made available by Washington, although the gist had been explained in English before WWII by Zeuner (latest ed., 1959), then a Jewish refugee in London. Still not accepted by the conservative establishment, the ideas suddenly came into the limelight with the deep-sea coring explorations of Columbia University (see Imbrie and Imbrie, 1979). A Czech student in Prague (Kukla) had measured the magnetic orientations of loess paleosols in Moravia, but there was a Russian invasion in 1968. Fortunately he was "liberated" to Columbia, where he was soon to recognize that the climate cycles of the deep-sea deposits and those of the Moravian loess were exactly the same (Kukla, 1970). The paleosol profiles were extended to China and further locked in to the deep-sea sections. Even the doubters were now convinced, and 1984 saw a general acceptance (Berger et al., 1984). (The writer of this entry has had the honor of knowing all the personalities concerned, even visiting the Moravian loess, and would note the extraordinary role played by the dedication of a few in the face of daunting adversities. R. W. F.)

The orbital variations demonstrated by Milankovitch could only be approximated at first, because each of the cycles was slightly different. Only very long-term series could establish the precise averages, and in the geological sequences, the dating precision falls off in time which is measured in up to 10^8 yr periods. The best-established value for the general precession is 25 694 yr (pers. comm. Berger, 1992), which the writer (R. W. F.) is able to determine is equivalent to 2 010.0 × 12.78 297, the Neptune-Jupiter "Lap" (beat frequency). This demonstrates that the fundamental lunar orbital parameter is precisely in tune with two key planets. The general resonance of the planetary orbits is discussed in another Encyclopedia (*Planetary Sciences*: Shirley and Fairbridge, 1998).

Very approximately, the principal Milankovitch periodicities are as follows:

Eccentricity:	410 kyr
	94 kyr
Obliquity:	40–41 kyr
Precession:	23 kyr
	19 kyr

Evolutionary cycles

Cycles in this sense are not defined mathematically but clearly exist in a growth and decline sense (Small, 1970). Thus, an oak tree starts with an acorn, sprouts, grows to a sapling, eventually to a full-grown tree, but eventually passes into an old-age state, which may last 500 years or more, until disease, decay, and lightning-strike or whatever, terminates its life cycle.

A youth-maturity-old age evolutionary theory was developed for geomorphology by W. M. Davis, a celebrated Harvard professor of a century ago. In a two-volume compendium on landforms by Chorley, with Beckinsale and Dunn (1964, 1973) the volumes are divided into pre-Davis and post-Davis, which reflects his former importance. Since then, the popular thrust in geomorphology has turned to a quantitative, process-approach. Youth-maturity-old age was set aside. Nevertheless, it is clearly a conceptual tool, as in *(a)* the theoretical emergence of a new land surface from the ocean, *(b)* the initiation of a rill and drainage system, *(c)* evolution of "youthful" valleys with fast-running streams, rapids and waterfalls, *(d)* gradient reduction, flood plains, meandering water-courses, and *(e)* reduction of the entire landscape to a peneplain. It was a beautiful, idealized model, but no example could ever be found. The explanation is that the Earth's surface is immensely complex, its tectonics active, and lithology varied, while paleoclimates and their inherited traces are great in number. Accordingly, soil classifications cannot be fit into convenient generalizations, except in a non-genetic way.

The freshly erupted ash of Mt. Pinatubo in the Philippines was quickly affected by rain, carrying also spores and seeds. Within 12 months a "youthful soil" is initiated. New highway cuts in the central valley of Mexico disclose numerous Holocene and late Pleistocene ash formations, each with a capping of paleosol. Most of those examples never got out of the youthful stage, but some reached maturity, with distinctive characteristics. In contrast, on the West-Australian Craton there are the so-called lateritic soils (Ferralsols), some inherited from the remote geologic past. Silicification, a soil-related process, tends to be a terminal experience, that is to say, once a soil is strongly silicified it will usually be insoluble, except in the equatorial tropics, so that it passes from maturity to old age and cannot evolve further unless tectonically revived (Fairbridge and Finkl, 1978).

In the southern hemisphere, there are extensive Gondwanaland surfaces of this advanced maturity. Even so, in regions of moderate to heavy precipitation, tropical weathering will continue on a buried front, the so-called etchplain (Fairbridge, 1968, p. 331; Bremer, 1981; Büdel, 1982). Where tectonism leads to topographic contrasts the etchplain will continue to evolve over multi-million-year "cycles". It is commonly exhumed (Twidale, 1971).

From the pedologic viewpoint it is important to recall that the southern hemisphere lands, during plate tectonic spreading, have all moved away from Antarctica and partly into the northern hemisphere (King, 1967; Fairbridge, 1973). Since the end of the Permian glaciation, this 250 Myr plate migration has exposed the great Gondwana surfaces to continuous, almost uninterrupted weathering while slowly passing through the tropical belts. No northern hemisphere soil has evolved over anything like such long periods.

Stochastic or random series

To speak of a "stochastic cycle" would be a contradiction in terms (oxymoron), but there are nevertheless stochastic series or sequences that oscillate within an envelope or framework of limiting constraints. Much of the computer modeling of modern meteorology and weather prediction proceeds on the assumption that it is a random system, but there are very rigid boundaries. For example, water and water vapor play a key role, while at OEC there is a recognizable limit. Even this, however, varies with the salinity of that water, and the freezing point of sea water (avg. 3.5% salts) is a few degrees lower. The dew point varies with atmospheric pressure and the latter varies not only with the elevation or altitude, but also with the inherited features of the air mass concerned (Oliver and Fairbridge, 1987).

The northern and southern hemisphere circulations are characterized by westerly jet streams which circle the globe at about 45° E, N and S, but are displaced N and S with the seasons. The northern one is particularly unpredictable, being sensitive to *(a)* surface water temperature over the Pacific and Atlantic with their geostrophic currents, the Kuroshio and Gulf Stream (both responsive to the lunar declination cycles and other potentials); and *(b)* the albedo and other inputs from the unequal-sized North American and Eurasian continents where the seasonal variance of snowfall or late-summer aridity play important roles. The number of "wiggles" on the jet is always changing, even by the hour. The world's greatest computers strive to keep pace with all the variables. However, the solar radiation and seasons are securely locked into the annual cycle, and constrain the degrees of freedom displayed by those variables.

Dynamic cycles

These are the rhythmic cycles, compared to the bouncing of a tennis ball, or the pendulum of a clock or children's swing. Energy is required to provide that little extra nudge from time to time. In the environment the annual cycle is clearly dependent on the astronomical controls, already discussed. And dependent upon it are the seasons, the lunar input, and the day/night rhythms. This last factor tends to develop a rhythm of its own, as displayed by the biological response, as measured by the hours on a clock and by the waking/sleeping behavior of many organisms. In the cold latitudes, many mammals (polar bears, for example) prepare a den and go into hibernation for the winter, when their pulse-rate, body temperature, and general metabolism fall to a minimum. Certain frogs and other amphibia are known to lapse into a total freeze-up that can last indefinitely.

In soils, the active season is dictated as a rule by air temperature, as in the temperate latitudes, but in the subtropics it is the wet season, dictated for example by the arrival of the monsoon. Most of the soil biota responds almost instantly to these triggers.

In the semiarid and hyperarid regions the question of a wet season is not usually relevant, and the energy is provided by wind. Here the dynamic influence is usually a fluctuating turbulence, the net effect being the construction or maintenance of a dune. Its mobility inhibits soil formation. The same wind energy is that which produces waves at sea, where they will lead to the rhythmic rocking of a boat. Where the waves impact on a beach (and are not complicated by multiple fetch), the gradient developed evolves a pattern to create a rhythmic series of beach cusps. This elegant example of rhythmic dynamics is a transient process and may disappear within a few days.

Rhodes W. Fairbridge

Bibliography

Berger, A., et al., 1984. *Milankovitch and Climate.* New York: Reidel, 895 pp.

Büdel, J., 1982. *Climatic Geomorphology* (transl. from German of 1977). Princeton, NJ: Princeton University Press, 443 pp.

Chorley, R.J., Dunn, A.J., and Beckinsale, R.P., 1964/73. *The History of the Study of Landforms.* London: Methuen, Vol. 1, 678 pp.

Ekholm, N., and Arrhenius, S.A., 1898. Uber den Einfluss des Mondes auf die Polarlichter und Gewitter. *Kongl. Svenska Vetenskaps Akademiens Handlingar (Stockholm)*, **31**(2): 77–156.

Eldredge, N., and Gould, S.J., 1972. Punctuated equilibria: an alternative to phyletic gradualism. In Schopf, T.J.M., ed., *Models of Paleogeology.* San Francisco: Freeman Cooper, pp. 82–115.

Everest, R., 1834. On the influence of the Moon on atmospherical phenomena. *Proc. Asiatic Soc. Bengal*, 345–359; and a further notice at 631–635.

Fairbridge, R.W., ed., 1968. *The Encyclopedia of Geomorphology.* New York: Van Nostrand Reinhold, 1295 pp.

Fairbridge, R.W., 1973. Glaciation and plate migration. In Tarling, D.H., and Runcorn, K., eds., *Implications of Continental Drift to the Earth Sciences.* London: Academic Press, Vol. 1, pp. 503–515.

Fairbridge, R.W., 1980. The estuary: its definition and geodynamic cycle. In Olaussen, E., and Cato, I., eds., *Chemistry and Biogeochemistry of Estuaries.* New York: John Wiley & Sons, pp. 1–35.

Fairbridge, R.W., and Sanders, J.E., 1987. The Sun's orbit, A.D. 750–2050: basis for new perspectives on planetary dynamics and Earth-Moon linkage. In Rampino, M.R., et al., eds., *Climate-History, Periodicity, and Predictability.* New York: Van Nostrand Reinhold, pp. 446–471 (bibliography, pp. 475–541).

Imbrie, J., and Imbrie, K.P., 1979. *Ice Ages: Solving the Mystery.* Short Hills, NJ: Enslow Publ., 224 pp.

King, L.C., 1967. *The Morphology of the Earth*, 2nd edn. Edinburgh: Oliver & Boyd. 726 pp.

Kukla, G.J., 1970. Correlation between loesses and deep-sea sediments. *Geol. Föen. Förh., Stockholm*, **92**: 148–180.

Oliver, J.E., and Fairbridge, R.W., eds., 1987. *The Encyclopedia of Climatology.* New York: Van Nostrand Reinhold, 986 pp.

Pettersson, O., 1930. The tidal force. *Geogr. Annaler*, **12**: 261–322.

Rampino, M.R., and Haggerty, 1996. Impact crises and mass extinctions; a working hypothesis. *Geol. Soc. Am., Sp. Pap.*, 307.

Rampino, M.R., and Stothers, R.B., 1984. Geological rhythms and cometary impacts. *Science*, **226**: 1427–1431.

Schove, D.J., ed., 1983. *Sunspot Cycles.* Benchmark Papers in Geology, Vol. 68. Stroudsburg: Hutchinson Ross Publ. Co., 392 pp.

Shirley, J.H., and Fairbridge, R.W., eds., 1998. *The Encyclopedia of Planetary Sciences.* London: Chapman & Hall (now Springer), 990 pp.

Small, K.J., 1970. *The Study of Landforms*. Cambridge: Cambridge University Press. 486 pp.

Twidale, C.R., 1971. *Structured Landforms.* Cambridge, MA/London: MIT Press, 247 pp.

Wood, F.J., 2001. *Tidal Dynamics*, 3rd edn, 2 Vols. West Palm Beach: Coastal Education and Research Foundation.

Zeuner, F.E., 1959. *The Pleistocene Period.* London: Methuen, 444 pp.

Cross-reference

Biogeochemical Cycles

ECOLOGY

A branch of biology which deals with the relations of living organisms to their surroundings, their habits and modes of life. Agroecology is the application of the principles of ecology to agricultural systems – the branch of agricultural science which deals with the relations of the farmers' crops and stock with that part of the biosphere that has been modified in the interests of food production for human society.

Bibliography

Paul, E.A., ed., 2007. Soil microbiology, ecology, and biochemistry. 3rd ed. Amsterdam; Boston: Academic Press. 532 pp.

EDAPHIC

Pertaining to, produced or influenced by, the soil.

EDAPHIC CONSTRAINTS ON FOOD PRODUCTION

Here we consider edaphic constraints to food production to be those conditions of soil, land, and climate that adversely affect agricultural productivity. This article is based largely on a paper by Eswaran et al. (2003).

Virtually all global land resources are affected by edaphic constraints to some degree, and as a consequence of a steadily increasing population and demand for food, as well as the impact of the current episode of climatic change, the situation is likely to become more acute.

Types of constraints

The major edaphic constraints fall into two groups: those that are natural in origin, and those that are anthropogenic. Some stresses (soil acidity and erosion, for example) may fall into both categories.

Natural stresses

Natural stresses may be either intrinsic (i.e., a consequence of characteristics specific to the soil and its internal processes), or extrinsic (i.e., a consequence of ambient conditions in the external environment of the soil).

a. Intrinsic stresses
   1. Chemical stress conditions. Nutrient deficiencies; excess of soluble salts; acidity, alkalinity, salinity; low base

saturation; toxicities, Al, Mn and minor elements; acid sulfate condition; anion retention, especially P species; calcareous or gypsiferous conditions, low redox (hydromorphic conditions).
2. Physical conditions. High erosivity; steep slopes; shallow soils; surface crusting and sealing; low water-holding capacity; impeded drainage; low structural stability; root restricting layer; high swell/shrink potential.
3. Biological conditions. Low or high organic matter content.
4. Ecosystem conditions. Low soil resilience; natural soil degradation.

b. Extrinsic stresses
   1. Climate-controlled conditions. Extreme climatic regimes; extreme high and low temperatures; insufficient length of growing season; waterlogging; excessive nutrient leaching; global climate change.
   2. Biological conditions. Frequency of pests and diseases; high population of termites.
   3. Catastrophic events. El Niño and extreme storm events; floods; droughts; landslides; earthquake activity; volcanic eruption.
   4. Ecosystem conditions. Impairment of ecosystem functions and services; diminished soil quality and soil health.

Anthropic stresses

1. Chemical conditions. Acidification by acid rain, acidifying fertilizers, drainage of wetlands, exposure to mine wastes; contamination with toxins.
2. Physical conditions. Accelerated soil erosion; soil compaction; subsidence of drained organic soils.
3. Biological conditions. Diminished biodiversity; loss of predators; high incidence of pests and diseases; allelopathy.

This basic scheme requires some elaboration. For instance, a constraint for one type of land use may be an advantage for another. A water-saturated condition for example, is considered an impediment for most crops, yet paddy rice benefits from it. Similarly, high exchangeable Al is toxic to many temperate region crops, notably grain cereals, but in tropical and subtropical regions, where the condition is common in oxisols and ultisols, natural selection has produced Al-tolerant plants. Also, both adverse and favorable effects may arise from similar causes. Thus, crop production normally benefits from a moderate organic matter content in soil, and may be impaired if it is too low or too high.

A further point regarding the stress factors listed above. Rather than singly, it is common to find them in combinations, a great number of which are possible. For example, a soil with moisture stress may simultaneously have nutrient deficiencies, surface crusting, and a shallow solum. A further consideration to be taken into account is level of severity, which controls the degree of adverse impact, of course. Finally, some constraints are not currently quantifiable. The recent concepts of soil quality, soil health, and the resulting soil resilience, are not yet sufficiently quantified in a way that would allow them to be used operationally as potentially limiting factors of crop production.

Land quality stresses

Table E1 presents a matrix in which we have used stress factors to define 25 stress classes. These are ranked according to their degree of negative impact on crop production. We consider the most limiting factor to be continuous moisture stress, with a high shrink/swell potential to be the least. By using the stress factors as a key, nine Inherent Land Quality Classes are established, with Class I having the most, and Class IX the least favorable attributes. The matrix also indicates the criteria used in Soil Taxonomy to define Stress and Land Quality Classes. Table E2 adds detail with regards to the attributes of the Land Quality Classes.

Construction of Table E1 depended upon correlations with taxonomic classes and since some of the edaphic factors listed above are not taxonomic criteria (e.g., soil resilience, termite activity, susceptibility to erosion, allelopathy, steep slopes, and pest and disease incidence, catastrophic events) no conclusive inferences can be made regarding these conditions. Such conditions are therefore not considered in the matrix.

Geographic extent of edaphic constraints

Areas and percentages of the global ice-free land resources represented for each of the 25 stress factors, and the corresponding Inherent Land Quality Classes, are shown in Table E3. "Inherent" implies land quality prior to human interference. Commonly, however, human activities have caused a deterioration of the land resource on a planet-wide scale, and it is not always possible to make an accurate assessment of the anthropogenic imprint. Consequently the estimates in Table E3 are best considered to be minimal ones.

Even so, the estimates clearly show the precarious state of the world's land resources. Over half of global land (54%) exhibits severe or prohibitive constraints for food production (i.e., areas falling in Classes VII, VIII, and IX). Nearly a third of the land (30%) has serious limitations (i.e., areas grouped in Classes V and VI). Land with moderate limitations (about 13%) – Classes II, III, and IV – makes up a meager 13%. The best land for food production with no or few constraints (Class I) makes up a minuscule 3%.

Three stress classes, namely 25, 24, 11, all of which are climate controlled, make up 52% of the world's land resource. On a small-scale map, no other classes occupy a large enough area to be meaningfully displayed. A brief description of their respective limitations is described next.

Class 25 is based on the aridic soil moisture regime, wherein the soil, during a year, is *(a)* dry for more than half of the time when soil temperature is above 5 °C and *(b)* moist for fewer than 90 consecutive days when soil temperature is above 8 °C. This means that water is unavailable to mesophytic plants for long periods, and that moisture is continuously available for plant growth for fewer than 90 consecutive days. Aridisols are characteristic of such conditions, and are found bordering the deserts of the world. Crop production is only possible under irrigation.

Soils of Class 24 are found in arctic and subarctic regions, predominantly in the zone of permafrost in the northern hemisphere. The surface soil thaws in the summer and a tundra or taiga vegetation is supported. However, low temperatures preclude crop production.

Class 11 comprises soils with an ustic or xeric soil moisture regime. The moisture stress in both regimes is unfavorable for plant growth during times when other conditions may be favorable. Ustic soils are dry for more than 90 consecutive days of the growing season. Xeric soils are typical of areas with Mediterranean climates, where moist, cool winters contrast with warm, dry summers. The ustic and xeric suborders of

Table E1 Matrix for defining stresses

Stress class	Land quality class	Major land stress factor	Criteria for assigning stress
25	IX	Extended periods of moisture stress	Aridic SMR, rocky land, dunes
24	VIII	Extended periods of low temperatures	Gelisols
23	VIII	Steep lands	Slopes greater than 32%
22	VII	Shallow soils	Lithic subgroups, root restricting layers <25 cm
21	VII	Salinity/alkalinity	"Salic, halic, natric" categories;
20	VII	High organic matter	Histosols
19	VI	Low water holding capacity	Sandy, gravelly, and skeletal families
18	VI	Low moisture and nutrient status	Spodosols, ferritic, sesquic & oxidic families, aridic subgroups
17	VI	Acid sulfate conditions	"Sulf" great groups and subgroups
16	VI	High P, N, organic compounds retention	Anionic subgroups, acric great groups, oxidic, families
15	VI	Low nutrient holding capacity	Loamy families of Ultisols, Oxisols
14	V	Excessive nutrient leaching	Soils with udic, perudic SMR, but lacking mollic, umbric, or argillic
13	V	Calcareous, gypseous conditions	With calcic, petrocalcic, gypsic, petrogypsic horizons; carbonatic and gypsic families; exclude Mollisols and Alfisols
12	V	High aluminum	pH < 4.5 within 25 cm and Al saturation $>60\%$
11	V	Seasonal moisture stress	Ustic or Xeric suborders but lacking mollic or umbric epipedon, argillic or kandic horizon
10	IV	Impeded drainage	Aquic suborders, 'gloss' great groups
9	IV	High anion exchange capacity	Andisols
8	IV	Low structural stability and/or crusting	Loamy soils and Entisols except Fluvents
7	III	Short growing season due to low temperatures	Cryic or frigid STR
6	III	Minor root restricting layers	Soils with plinthite, fragipan, duripan, densipan, petroferric contact, placic, <100 cm
5	III	Seasonally excess water	Recent terraces, aquic subgroups
4	II	High temperatures	Isohyperthermic and isomegathermic STR excluding Mollisols and Alfisols
3	II	Low organic matter	With ochric epipedon
2	II	High shrink/swell potential	Vertic subgroups
1	I	Few constraints	Other soils

Table E2 Properties of the inherent land quality classes

Land Quality Class	Properties
I	This is prime land. Soils are highly productive, with few management-related constraints. Soil temperature and moisture conditions are ideal for annual crops. Soil management consists largely of sensible conservation practices to minimize erosion, appropriate fertilization, and use of best available plant materials. Risk for sustainable grain crop production is generally <20%.
II & III	The soils are good and have few problems for sustainable production. However and particularly for Class II soils, care must be taken to reduce degradation. The lower resilience characteristics of Class II soils make them more risky, particular for low-input grain crop production. However, their productivity is generally very high and consequently, response to management is high. Conservation tillage is essential, buffer strips are generally required and fertilizer use must be carefully managed. Due to the relatively good terrain conditions, the land is suitable for national parks and biodiversity zones. Risk for sustainable grain crop production is generally 20–40% but risks can be reduced with good conservation practices.
IV, V, & VI	If there is a choice, these soils must not be used for grain crop production, particularly soils belonging to Class IV. All three Classes require important inputs of conservation management. In fact, no grain crop production must be contemplated in the absence of a good conservation plan. Lack of plant nutrients is a major constraint and so a good fertilizer use plan must be adopted. Soil degradation must be continuously monitored. Productivity is not high and so low input farmers must receive considerable support to manage these soils or be discouraged from using them. Land can be set aside for national parks or as biodiversity zones. In the semi-arid areas, they can be managed for range. Risk for sustainable grain crop production is 40–60%.
VII	These soils may only be used for grain crop production if there is a real pressure on land. They are definitely not suitable for low-input grain crop production; their low resilience makes them easily prone to degradation. They should be retained under natural forests or range and some localized areas can be used for recreational purposes. As in Class V & VI, biodiversity management is crucial in these areas. Risk for sustainable grain crop production is 60–80%.
VIII & IX	These are soils belonging to very fragile ecosystems or are very uneconomical to use for grain crop production. They should be retained under their natural state. Some areas may be used for recreational purposes but under very controlled conditions. In Class VIII, which is largely confined to the Tundra and Boreal areas, timber harvesting must be done very carefully with considerable attention to ecosystem damage. Class IX is mainly the deserts where biomass production is very low. Risk for sustainable grain crop production is >80%.

alfisols, andisols, inceptisols, mollisols, ultisols, and vertisols, and the ustic suborder of oxisols, are the main soil types in Class 11. Supplemental irrigation is employed in cropping these soils.

Causes and consequences of the constraints

Essentially all of the intrinsic chemical, physical and biological stress conditions we have considered, can be interpreted in terms of particular combinations of Jenny's (1941) factors of

Table E3 Global land areas of major stress classes and land quality classes

Class code	Land resource stress			Inherent land quality class		
	Kind	Area (1 000 km^2)	Percent	Class	Area (1 000 km^2)	Percent
25	Continuous moisture stress	36 480	27.94	IX	36 480	27.94
24	Continuous low temperatures	21 776	16.68	VIII		
23	Steep lands	484	0.37	VIII	22 260	17.05
22	Shallow soils	7 358	5.64	VII		
21	Salinity/alkalinity	3 068	2.35	VII		
20	High organic matter content	1 221	0.94	VII	11 647	8.92
19	Low water holding capacity	3 363	2.58	VI		
18	Low moisture & nutrient status	3 462	2.65	VI		
17	Acid sulfate conditions	112	0.09	VI		
16	High anion retention	2 498	1.91	VI		
15	Low nutrient holding capacity	7 788	5.96	VI	17 223	13.19
14	Excessive nutrient leaching	4 471	3.42	V		
13	Calcareous, gypseous conditions	2 471	1.89	V		
12	High exchangeable aluminum	4 062	3.11	V		
11	Seasonal moisture stress	10 342	7.92	V	21 346	16.35
10	Impeded drainage	2 829	2.17	IV		
9	High anion exchange capacity	913	0.70	IV		
8	Low structural stability	1 369	1.05	IV	5 111	3.91
7	Seasonal low temperatures	3 009	2.30	III		
6	Minor root restricting layer	1 517	1.16	III		
5	Seasonal excess water	1 362	1.04	III	5 888	4.51
4	High temperatures	2 506	1.92	II		
3	Low organic matter content	3 101	2.37	II		
2	High shrink/swell potential	925	0.71	II	6 532	5.00
1	Few constraints	4 088	3.13	I	4 088	3.13
	TOTAL	130 575	100		130 576	100

soil formation: climate, organisms, relief, parent material and time. A few examples may suffice to illustrate this. A parent material inherently poor in plant nutrients (quartz-rich sand for instance) will inevitably produce a soil with nutrient deficiencies. A similar consequence may arise even if the parent material is rich in one or more plant nutrients, if the potential source is resistant to weathering (feldspathic sands for example, where the feldspar is commonly potassic). Weathering over the very long term, as in the humid tropics may produce soils in which prolonged leaching has resulted in relatively infertile conditions. Landscape factors may also be conducive to soil problems – erosion and mass movement on steep slopes for example, impeded drainage in topographic lows, together with possible accumulations of organic matter or soluble salts. Like all things, soils are subject to the second law of thermodynamics following the laws of thermodynamics, and a natural degradation can be expected, the result being diminished soil quality and resilience.

Catastrophic events also play a role by imposing a new set of edaphic conditions onto an agroecosystem. Volcanic eruptions are a prime example and may totally change the landscape and cover productive agricultural land with volcanic ash, as Mount St. Helens in the USA and Pinatubo in the Philippines have recently shown. Similarly, catastrophic landslides and episodes of soil erosion may be triggered by the intense rainfall associated with hurricanes and typhoons.

Such conditions are essentially beyond human control, but other impediments to food production are clearly the result of human activity. Examples include: soil acidification caused by acid-producing fertilizers, acid rain or mine wastes; nutrient depletion due to continuous farming without replacing the harvested nutrients by fertilizers; surface crusting, sealing and compaction caused principally by use of heavy machinery and by animals pastured on soils with a low structural stability, and accelerated soil erosion on slopes as a consequence of inappropriate cultivation techniques.

A specific and dramatic example of irreversible land deterioration is provided by the salt ponds near Dowerin north of Perth in western Australia. Wheat production there was preceded by forest clearance, after which the water table rose and brought salt to the surface from a geologic layer originally above the aquifer. This resulted in salt scalds, and some 10% of the wheat belt of Western Australia, or about 1.8 million ha, has now been affected by salt. Within a few decades as much as 40% may be affected.

Whether natural or human-induced, adverse edaphic conditions unless corrected, result in the suboptimal performance of food production systems. Underlying reasons are usually clear. The land at the production site may be too dry, too wet, too cold, too steep, too shallow, too infertile, too acid, or too alkaline. However, some cases are not so clear. For example, subsoil acidity may prevent roots from growing thereby limiting access to sources of moisture and nutrients at depth. Similarly, moisture stress at depth may occur even in areas of ample precipitation if surface crusting and sealing prevents rainfall from entering the root zone. Tillage and the emergence of seedlings may also be hindered in such cases.

Coping with constraints

There are essentially three coping strategies for farmland compromised by edaphic constraints: *(a)* deal with constraints by means of traditional methods of soil and land management; *(b)* grow crops that are tolerant to the constraints or develop tolerance as a result of bioengineering; and *(c)* find other uses for the land.

In principle the farmer is required to match the land and soil characteristics with the requirements of the crop. Usually the match is less than perfect and remedial measures are needed. In some cases this may not be possible – cold climates and catastrophic events clearly lie outside of human control. Even where techniques for correcting constraints are available, they may prove unworkable for economic or environmental reasons.

The most extensive constraint is continuous moisture stress and irrigation is mandatory on about 20% of the global area farmed. However, many irrigation schemes are unsustainable over the long term and waterlogging and salinization may result. The Aral Sea in Kazakhstan and Uzbekistan provides a tragic example. In the 1930s diversion of the Amu Darya and Syr Darya Rivers was engineered to provide irrigation water for cotton production. Bureaucratic incompetence and ecosystem mismanagement resulted in widespread salinization and a consequent rapid decline of productivity. The Aral Sea, formerly the fourth largest inland lake in the world, has lost 55% of its surface area and 80% of its volume, and has become a toxic desert of salts and agrochemical degradation products. Numerous examples, though less extreme, point to the fact that irrigation is no more than a short term answer to the problem it attempts solve, and always threatens to lead to greater problems in the long run.

Some three-quarters of agricultural land worldwide suffer from low soil fertility. There are of course well known remedial techniques using fertilizers, farm manure, composts and crop rotations. Yet the environmental price tag must always be considered – fertilizer production for example is heavily fossil fuel intensive.

With regard to the use of crops tolerant of specific constraints, few food crops currently serve the purpose. Genetic engineering is set to change the farming system radically however. It may now be technically feasible to design crops that are drought resistant, aluminum or salt tolerant, nitrogen-fixing, disease immune, or capable of dealing with any constraint that the farmer encounters. The ultimate constraint here may be socio-political. Certain communities, particularly in Europe and parts of the developing world, are currently hostile to the idea of genetically engineered foods.

Removing land with severe constraints from agricultural production seems to be an attractive proposition in that it might then be used to provide ecosystem services. Such land for example could be used as a reservoir for carbon sequestration, as a biodiversity reserve, and or for recreational and touristic purposes. In many countries, however, demand for food rules out this option, and with a growing population, especially in the developing world, it will become increasingly difficult to employ.

Conclusion

Agriculture is practiced on more than 25% of the Earth's land surface. This is about the same area under forest, and contrasts with the grasslands, which make up 40%. All agricultural land suffers some degree of degradation, though hard numbers are difficult to find. For example the World Resources Institute estimates that 40% of the global agroecosystem is strongly to very strongly degraded – a number that is based on a qualitative (and judgmental) study of the International Soil Reference and Information Centre (Oldeman et al., 1991). Better data are obviously required; the real situation may be less dire than currently perceived.

The need to feed the augmented population of the future (a 50% increase is projected by 2050) is an enormous challenge made all the more difficult by the long-term decline in agricultural capacity of farmland. However, in spite of accumulating constraints on the soil component of the agroecosystem, improvements in crop varieties, pest and soil fertility management, and other technological advancements, food production continues to outpace population growth. Yet the burden on developing nations will be great.

The ultimate critical factor limiting food production is likely to be water. At 70% usage, agriculture is by far the biggest consumer of the Earth's fresh-water resource. Current irrigation practices commonly return only 30–60% for downstream use. For the projected increase in population, more efficient use will be necessary, if agriculture (to say nothing of industrial and domestic consumption) is to grow by the requisite amount. In addition, it is a sobering thought that from the earliest civilizations in Mesopotamia, to the cotton fields of the Aral Sea in modern times, irrigation systems have never been sustainable over the long term.

Finally, global change is the wild card in the mix. No doubt higher temperatures, the fertilizing effects of CO_2 increase, and augmented rainfall in some areas, may increase productivity, but increases in drought, major storms and other meteorological extremes, are at least as likely to bring about the opposite outcome. As usual, the future is unpredictable, but no matter what, the farmer (also as usual) will have a difficult row to hoe.

Friedrich H. Beinroth, Hari Eswaran, and Paul F. Reich

Bibliography

Brady, N.C., and Weil, R.R., 1996. *The Nature and Properties of Soils*, 11th edn. Upper Saddle River, NJ: Prentice Hall. (This textbook covers all basic aspects of soil science.)

Eswaran, H., Beinroth, F.H., and Reich, P.F., 2003. A global assessment of land quality. In Wiebe, K., ed., *Land Quality, Agricultural Productivity, and Food Security: Biophysical Processes and Economic Choices at Local, Regional, and Global Levels.* Northampton, MA: Publ. Edward Elgar, pp. 111–132.

FAO-Unesco, 1995. The digital soil map of the world and derived soil properties. Land and Water Digital Media Series 1 (CD-ROM), Rome: FAO. (The map at a scale of 1:5,000,000 is the only soil map that covers the entire world.)

Foth, H.D., and Ellis, B.G., 1997. *Soil Fertility*, 2nd edn. Boca Raton, FL: Lewis Publishers. (This textbook provides comprehensive current coverage of the factors of soil fertility.)

Oldeman, L.R., Hakkeling, R.T.A., and Sombroek, W.G., 1991. *World Map of the Status of Human-Induced Soil Degradation: An Explanatory Note.* Wageningen, Netherlands: ISRIC. (The map constitutes the only global assessment of anthropogenic soil degradation.)

Parfit, M., 2000. Australia – a harsh awakening. *Natl Geogr.*, **198**(1): 2–31. (This illustrated article describes human-induced land degradation and current efforts to repair the damage.)

Soil Survey Staff, 1999. *Soil Taxonomy*, 2nd edn. *U.S. Dept. Agric., Natural Resources Conservation Service, Agric. Handbook 436*, Washington, DC: USDA. (This book describes and illustrates the U.S. system of soil classification.)

Sumner, M.E., ed., 2000. *Handbook of Soil Science.* Boca Raton, FL: CRC Press. (This 2000-page book provides authoritative and up-to-date references information on all aspects of soil science.)

World Resources Institute, 2000. *World Resources, 2000–2001*. Amsterdam: Elsevier. (This book provides an excellent assessment of the current state of the world's ecosystems.)

Cross-references

Anthrosols
Classification of Soils
Soil

EDAPHOLOGY

Study of the community of microflora and microfauna in the soil (edaphon), and the processes that govern their existence and development (edaphogenesis).

Bibliography

Porta, J., Lopez-Acevedo, M., and Roquero, C., 1994. Edafologia. Madrid: Editions Mundi-Prensa. 807 pp.

Cross-reference

Soil

EFFECTIVE

Said of that portion of an agency or force which is actually brought to bear on a particular object. Examples: effective cation exchange capacity is the sum of the cations a soil can adsorb at its natural pH; effective soil depth is the depth to which plant roots can penetrate to obtain water and nutrients; effective stress is the stress transmitted through the soil by intergranular contact.

EFFLUENT

a. A stream flowing from a larger stream, lake, or reservoir.
b. Discharged waste as in the outflow from a sewage tank, or from land that has been irrigated or used for the disposal and filtration of sewage and other wastes.

ELECTRICAL DOUBLE LAYER

An idealized model used to describe the electrical state of a surface, and commonly used to describe the physical behavior of clay particles in soil. The clay surface and its surface charge constitute one layer, while aqueous solution in contact with the solid is a second (Stern) layer. The latter is held in place by counterions to the ions on the charged surface, the two together forming a kind of molecular capacitor. Ions further from the surface, and less strongly held, form a more diffuse (or Gouy) layer.

ELECTROCHEMISTRY

Electrochemistry is the branch of chemistry that deals with the chemical effects of electrical phenomena and the electrical effects of chemical reactions. Hydrolysis and the electrochemical nature of cells and batteries are studied.

Cross-reference

Redox Reaction and Diagrams in Soil

ELECTRO-OSMOSIS

See *Osmosis*.

ELUTRIATION

The action of separating lighter from heavier particles in a granular mixture, by washing in water. Panning for gold is a classical example, and in nature is mirrored by the sedimentary process that leads to the accumulation of heavy minerals in placer deposits.

ELUVIATION

The lateral or vertical movement of material in solution or suspension through the soil. The direction of displacement depends on the direction of water movement. In Podzols for example, prolonged eluviation produces a bleached horizon (albic, Ae or E) where all but the most intractable minerals (quartz being the dominant one) are removed from that level of the solum.

Cross-references

Podzol
Solonetz

ENDOGENOUS

In geology, formed within the Earth, the interior parts of which constitute the endogene or hypogene. Endogenous processes (volcanic activity and mountain building for example) are ultimately responsible for maintaining the fertility of the soils of the biosphere over the long term, by providing fresh, weatherable, nutrient-rich materials to the surface of the earth.

Bibliography

Chesworth, W., 1991. Geochemistry of micronutrients. Chapter 1 in Mortvedt, J.J., et al. *Micronutrients in Agriculture* 2nd ed. Madison, Wisconsin: Soil Science Society of America. pp. 1–30.

Cross-reference

Biogeochemical cycles

ENERGY BALANCE

An *energy balance* for the soil is an analysis equating the increase in heat content over time of a given volume of soil to the difference between inflow and outflow of heat. The energy balance at the soil surface is of particular interest because heat flux into and out of the soil is an important component of the energy balance of the Earth's surface and therefore influences weather patterns, crop production, and microclimates of plants and animals. Heat flow in soil cannot be analyzed without knowing either soil surface temperature or heat flux across the soil surface as a function of time. Neither of these can be specified without solving the entire energy budget for the soil surface to determine the input of radiant energy and the loss of sensible and latent heat. An analysis of heat flow in soil requires knowledge of the energy budget at the soil surface, the distribution of moisture and composition of solids in the soil profile, and a simultaneous solution of the moisture balance in the soil because moisture flow and distribution influence heat flow.

The differential equations governing heat transfer in soil are similar to heat-transfer equations for any solid medium. Horizontal temperature variations a few centimeters below the soil surface are generally small compared to variations normal to the surface, so it is usually necessary to consider only one-dimensional heat flow. Heat flux density across any plane parallel to the soil surface is given by Fourier's law

$$G = -k\frac{\mathrm{d}T}{\mathrm{d}z} \tag{1}$$

where G is the soil heat flux density, k is the thermal conductivity of the soil, and T is temperature. The energy balance for any location in the soil is obtained by combining Equation (1) with the continuity equation:

$$C\frac{\partial T}{\partial t} = -\frac{\partial G}{\partial z} \tag{2}$$

where t is time and C is the volumetric heat capacity of the soil. Solutions to Equation (2), subject to appropriate boundary and initial conditions, describe the soil energy balance and the temperature distribution in the soil.

The novel feature of soil heat-flow analysis is not the basic equations describing the process, but rather the behavior of the thermal conductivity and heat capacity functions. Soil is a mixture of solids, water, and air. The volume fraction of solids remains fairly constant with time, but the volume fractions of air and water are constantly changing. The heat capacity and thermal conductivity of the soil are therefore variable in space and time. The functional relationship between heat capacity and water content is

$$C = x_o C_o + x_m C_m + x_w C_w + x_a C_a \tag{3}$$

where x denotes the volume fraction, C is the volumetric heat capacity, and the subscripts o, m, w, and a denote organic, mineral, water and air. Table E4 gives some values for volumetric heat capacity of these constituents.

The thermal conductivity function for the soil has two components. Sensible heat is conducted through the mineral grains of the soil and across water or air bridges between the grains. Latent heat is transferred by distillation of water from warm to cold regions of the soil. Since the thermal conductivity of water is 20 times that of air (Table E4), the thermal conductivity of the soil depends strongly on water content. Figure E1 shows how thermal conductivity of a soil increases as the water content is increased. The thermal conductivity of a saturated soil can be ten times the conductivity of a dry soil.

Table E4 Thermal properties of soil materials, water, and air at 20 °C

Substance	C (MJ m^{-3} K^{-1})	K (W m^{-1} K^{-1})
Quartz	2.3	8.8
Other minerals	2.3	2.9
Organic matter	2.5	0.25
Water	4.2	0.6
Air	1.25×10^{-3}	0.025

The rate of distillation, and therefore the latent heat flux in soil, is a function of pore space, (see *Soil pores*) soil temperature, and soil moisture. Since temperature gradients induce moisture flow in soils the energy balance problem cannot be solved without simultaneous solution of the moisture balance problem. For moist soils the apparent thermal conductivity due to latent heat transport within a soil pore is

$$k_v = LD\frac{\mathrm{d}\rho_v}{\mathrm{d}T}$$

where ρ_v is the saturation vapor density (g m^{-3}), L is the latent heat of vaporization for water (J g^{-1}), and D is the diffusion coefficient for water vapor in air (m^2 s^{-1}). The effect of latent heat flux on soil heat flow is accounted for by replacing the thermal conductivity of air by the sum of the conductivity of air and the apparent conductivity due to latent heat transport with vapor. At low temperatures k_v is near zero, so latent heat transfer has little effect on soil thermal conductivity. However, at 60 °C, k_v is about equal to the thermal conductivity of water, so the thermal conductivity of the soil becomes independent of water content. Figure E2 shows the effect of temperature on thermal conductivity of soil. This effect is mainly the result of temperature effects on the latent heat transport. The temperature effects disappear at low water content because water ceases to circulate in the pores (evaporation on the hot side of the pore, condensation on the cold side of the pore, then liquid return flow to the hot side).

Campbell (1985) gives empirical equations, which are useful for estimating thermal conductivities of soils. Thermal conductivity is calculated from

$$k = A + b\theta - (A - D)\exp[-(C\theta)^4] \tag{4}$$

where θ is volumetric water content (m^3 m^{-3}), and A, B, C and D are constants whose values are determined by the clay and mineral fractions of the soil. The equations for these constants, for a mineral (non organic) soil, are

$$A = \frac{0.57 + 1.73x_q + 0.93x_m}{1 - 0.74x_q - 0.49x_m} - 2.8x_s(1 - x_s) \tag{5}$$

$$B = 2.8x_s \tag{6}$$

$$C = 1 + 2.6m_c \tag{7}$$

$$D = 0.03 + 0.7x_s^2 \tag{8}$$

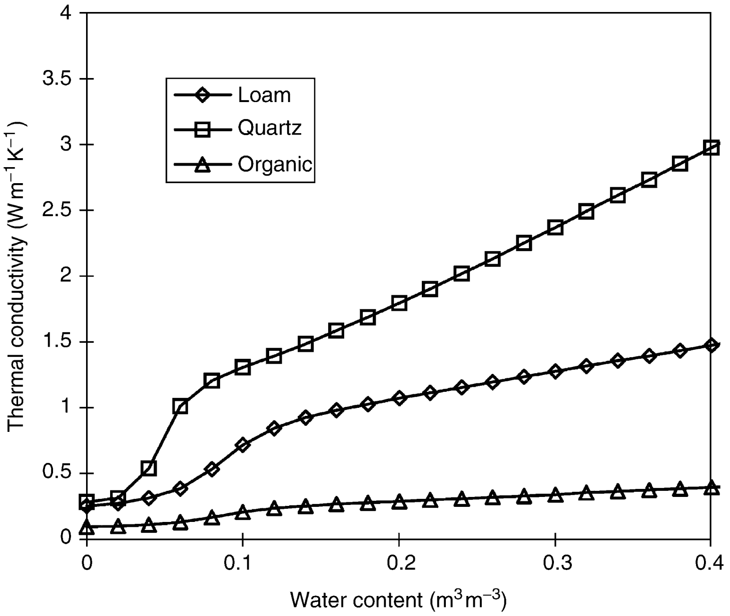


Figure E1 Typical thermal conductivities for quartz sand, loam and organic soils as functions of volumetric water content.

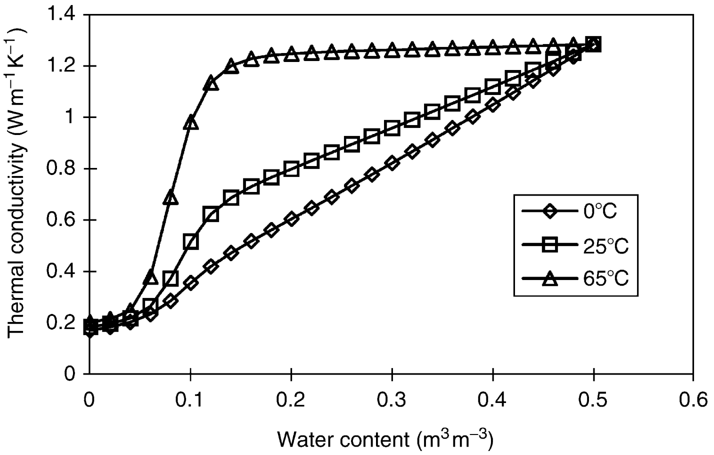


Figure E2 Thermal conductivity as a function of water content for a loam soil at three temperatures. Temperature mainly affects the latent heat transport in soil pores. At 65 °C the apparent conductivity due to vapor transport is equal to the conductivity of liquid water, so at high water content addition of water does not result in increasing conductivity.

where x_q is the quartz fraction, x_m is the remainder of the mineral fraction, $x_s = x_q + x_m$ is the total mineral fraction, and x_c is the clay fraction. These equations apply for soils around 20 °C. Since they have no temperature dependent terms, they can't predict temperature effects. The more complete theory given in Campbell and Norman (1998) is needed to predict the effect of temperature on thermal conductivity.

Gaylon S. Campbell

Bibliography

Campbell, G.S., 1985. *Soil Physics with BASIC: Transport Models for Soil–Plant Systems.* New York: Elsevier, 150 pp.

Campbell, G.S., and Norman, J.M., 1998. *An Introduction to Environmental Biophysics*, 2nd edn. New York: Springer, 286 pp.

de Vries, D.A., 1966. Thermal properties of soils. In van Wijk, W.R., ed., *Physics of Plant Environment.* Amsterdam: North Holland, pp. 210–235.

de Vries, D.A., 1975. Heat transfer in soils. In de Vries, D.A., and Afgan, N.H., eds., *Heat and Mass Transfer in the Biosphere, I. Transfer Processes in Plant Environment.* New York: Wiley, 594 pp.

Cross-references

Conductivity, Thermal
Heat Capacity
Thermal Regime
Transport Processes
Water Budget in Soil
Water Content and Retention

ENVELOPE-PRESSURE POTENTIAL

The envelope-pressure potential is the difference in the potential of the water in a non-rigid porous medium, such as a swelling soil, between a loaded and the unloaded state, everything else being equal. According to the definition given by the International Soil Science Society (Anon., 1975), the envelope-pressure potential is the increment of the equilibrium liquid pressure (as measured, for example, by a tensiometer) caused by an outside mechanical pressure on a soil sample. For natural swelling soils the envelope pressure is equal to the overburden, being the sum of the weight of the overlaying layer of soil and the surface load. The envelope-pressure potential is then called the overburden potential, Ω. The overburden potential can be calculated from the slopes of the bundle of curves relating the moisture ratio to the void ratio. A model presented by Groenevelt and Bolt (1972) provides an excellent fit for this bundle of shrinkage curves. A method for the calculation of the overburden potential from shrinkage data can be found in Groenevelt and Grant (2001).

Piet H. Groenevelt

Bibliography

Anon., 1975. Soil physics terminology. *Int. Soil Sci. Soc. Bull.*, **48**: 16–22.

Groenevelt, P.H., and Bolt, G.H., 1972. Water retention in soil. *Soil Sci.*, **113**: 238–245.

Groenevelt, P.H., and Grant, C.D., 2001. Re-evaluation of the structural properties of some British swelling soils. *Eur. J. Soil Sci.*, **52**: 469–477.

Cross-references

Soil Physics
Water Budget in Soil
Water Content and Retention

ENVIRONMENT

The surroundings of an object of interest such as an organism or a population of organisms, the physico-chemical system within which organisms function. The soil is a porous complex of inorganic, and dead organic solids, aqueous solution, and gas. It constitutes the environment of a biodiverse population of organisms dominated by bacteria.

Bibliography

Porta, J., Lopez-Acevedo, M., and Roquero, C., 1994. Ecologia del Suelo. Chapter 16 in Edafologia. Madrid: Editions Mundi-Prensa. pp. 403–429.

Cross-references

Fauna
Soil Biology
Soil Microbiology

ENZYME ACTIVITY

See *Enzymes and Proteins, interactions with soil-constituent surfaces*.

ENZYMES AND PROTEINS, INTERACTIONS WITH SOIL-CONSTITUENT SURFACES

There are several reasons for studying soil proteins and their fate in soil: *(i)* their constituent amino acids are an important source of soil nitrogen, *(ii)* enzymes secreted by microorganisms and plant roots with hydrolytic properties can be involved in the biogeochemical cycles of soil organic matter (Quiquampoix, 2000; Quiquampoix and Mousain, 2005), *(iii)* pathogenic proteins such as prions involved in transmissible spongiform encephalopathies (Brown and Gajdusek, 1991; Revault et al., 2005; Vasina et al., 2005; Rigou et al., 2006) or insecticidal toxins expressed in transgenic plants (Tapp and Stotzky, 1998; Pagel-Wieder et al., 2004) represent a growing environmental concern.

The strong and often largely irreversible adsorption of proteins on the mineral phase of the soil has important consequences not only on their mobility, but also on their resistance to breakdown and catalytic activity. The mechanisms, which control the interaction between proteins and soil constituents, will be discussed.

Enzymes can be secreted into soil solution by microorganisms. This process makes possible the degradation of the soil organic matter since polymers cannot usually pass through the membranes of the microorganisms and need to be hydrolyzed into soluble low molecular weight compounds which can reach membrane permeases specific for monomers (sugars, amino acids) or occasionally oligomers. An important consequence of the adsorption of these extracellular enzymes on mineral surfaces is a shift of the optimal pH of the catalytic activity toward more alkaline values and a general decrease of the activity.

Other proteins are released into soil along with various other cellular constituents by biological membranes lysis accompanying the decomposition of dead organisms. As proteins are rich in nitrogen, they play an important role in the cycle of this element (see *Nitrogen cycle*). The adsorption on clay mineral surfaces plays a role in the protection of proteins against biodegradation, particularly if the formation of interlayer complexes with clays occurs.

The side chains of the amino acids, which are the constituents of the polymeric chain of the proteins, show a great diversity in their physico-chemical properties. They can be hydrophobic or polar, bear a positive, a negative or no electrical charge. Thus, the different proteins released in soil may exhibit a wide range of types of interactions with the mineral surfaces or the organo-mineral complexes. Nevertheless some general tendencies may be identified.

Influence of pH on adsorption of proteins on clay minerals

Knowledge of the influence of pH is essential to the understanding of the interactions of proteins in general, and enzymes in particular, with the solid phase of soil. Since the pioneering works of Mc Laren et al. (1958) it is well established that for most proteins the maximum of adsorption occurs near their isoelectric point (i.e.p.). Early interpretations of this fact included, for pH > i.e.p. a repulsive electrostatic interaction between the negatively charged protein and the negatively charged clay surface, and for pH < i.e.p., either a competition of the protons of the solution for adsorption sites (Mc Laren et al., 1958), or a decrease in the amount of protein required to satisfy the negative charge of the clay since the net positive charge of the protein increases as pH decreases (Armstrong and Chesters, 1964). Alternatively the possibility of an artifact resulting from protein precipitation, more likely to occur at the i.e.p., has been proposed (Durand, 1964).

More recently the fact that the adsorption of proteins on clay mineral surfaces is accompanied by a release of charge compensating cations (Mc Laren et al., 1958; Albert and Harter, 1973) has been exploited to obtain both the clay surface coverage and the quantity of protein adsorbed, which has led to a different interpretation (Quiquampoix and Ratcliffe, 1992). The latter study is based on the detection by nuclear magnetic resonance (NMR) spectroscopy of the release of a paramagnetic cation, manganese, on adsorption of bovine serum albumin (BSA) on montmorillonite. The fraction of Mn^{2+} released is assimilated to the fraction of the clay surface covered by the protein. Figure E3 shows a maximum adsorption near pH 4.7 which is the i.e.p. of BSA, but the quantity of Mn^{2+} released show a different pattern. Above the i.e.p., both the quantity of protein adsorbed and the quantity of Mn^{2+} released decrease in the same proportion when pH increases, indicating a lowering of the surface coverage of the clay surface and confirming the early interpretation of electrostatic repulsions. But below the i.e.p. the quantity of Mn^{2+} released remains constant when the quantity of protein adsorbed decreases, indicating an unfolding which increases the specific interfacial area of the protein as pH decreases.

Structural studies of adsorbed proteins

No method currently exists which enables the direct measurement of the conformation of proteins in an adsorbed state. Only two methods are suitable for the determination of the tertiary structure of the proteins, and neither can be employed when proteins are adsorbed. One method, X-ray diffraction, necessitates the preparation of protein crystals, which is impossible for adsorbed proteins. The other, NMR spectroscopy, is confined to molecules with a sufficiently high tumbling rate to obtain narrow line widths, a condition not compatible with the adsorption on a surface larger in dimensions than the protein itself. In addition the determination of a tertiary structure has a sense only if all the protein molecules have the same structure. In reality it seems probable that the proteins are adsorbed in multiple states (Horbett and Brash, 1987).

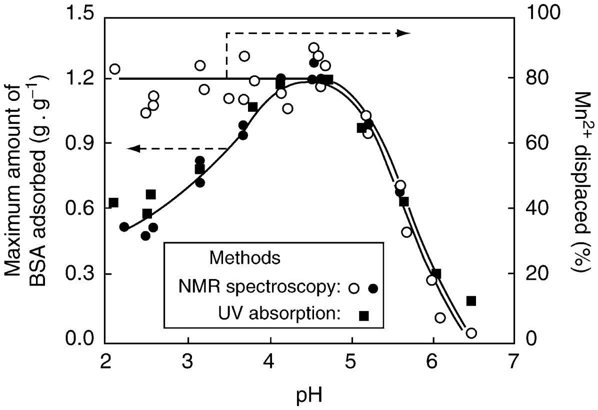


Figure E3 Effect of pH on the maximum amount of bovine serum albumin adsorbed on montmorillonite and on the clay surface coverage followed by the release of Mn^{2+} on protein adsorption. This figure illustrates the maximum adsorption at the isoelectric point (i.e.p.), the decrease of the surface coverage of the clay above the i.e.p. and the unfolding of the protein below the i.e.p. (modified after Quiquampoix and Ratcliffe, 1992).

For these reasons the secondary structures (α-helices, β-sheets, random parts) are probably the higher order structures on which information can be obtained. Circular dichroism (Kondo et al., 1991) and infrared spectroscopy (Tarasevich et al., 1975; Quiquampoix et al., 1993; Baron et al., 1999; Servagent-Noinville et al., 2000; Noinville et al., 2004) have been applied to the resolution of these structures for protein adsorbed on mineral surfaces. Circular dichroism can be used only for the study of adsorption on very small mineral particles due to problems arising from light scattering effects. Kondo et al. (1991) have studied by this technique the modification in α-helix content of proteins adsorbed on ultrafine silica particles (diameter of 15 nm) and found a greater decrease for the proteins whose adiabatic compressibility is high, i.e., whose flexibility of the structure is high in water. For example BSA retained only 60 to 80% of its native α-helix content, depending on pH. Infrared spectroscopy does not suffer from light scattering perturbations and has thus been used for the study of the adsorption of BSA on montmorillonite. A decrease in the α-helix content and an increase in intermolecular β-sheet content have been observed for the BSA by FTIR investigations (Servagent-Noinville et al., 2000; Quiquampoix et al., 2002).

Intercalation of proteins between clay sheets

The suspected protective effect of protein intercalation in clay interlayer position (Loll and Bollag, 1983) has led to a vast number of studies by X-ray diffraction on d(001) spacing of clay-protein complexes (Mc Laren et al., 1958; Armstrong and Chesters, 1964; Albert and Harter, 1973; Harter and Stotzky, 1973). Early interpretations of these results were that the proteins could penetrate between the interlayer spaces by a process of lateral diffusion (Mc Laren et al., 1958). However such a process is not compatible with the strong, largely irreversible aspect of protein adsorption, which implies a large activation energy for surface diffusion (Norde, 1986). A more convincing process of intercalation has been proposed (Larsson and Siffert, 1983), where adsorption of proteins occurs on the external surfaces of the clay, but the shear stress induced by the stirring of the suspension may induce an opening of tactoids exposing a new clay surface which is then free to interact with a clay surface already bearing a protein monolayer.

However the above mechanism does not consider the possibility of intercalated bilayers of proteins, thought by some authors to occur at high protein:clay ratios (Armstrong and Chesters, 1964), therefore a slight improvement could be suggested. Figure E4 compares the evolution of Mn^{2+} release on adsorption of BSA on montmorillonite by a NMR method and the quantity of BSA effectively adsorbed as determined by a classical depletion method (Quiquampoix and Ratcliffe, 1992). Since both breaks in the slopes of these parameters occur at the same protein:clay ratio, it could be concluded that at the maximum of adsorption a monolayer of protein is formed. Multilayer formation would have led to a break in the protein adsorption measurement at a higher protein:clay ratio than for the cation release measurement which represents the surface coverage.

Thus the evidence of multilayers obtained from X-ray diffractometry may arise from an artifact introduced by the dehydration process. At high protein:clay ratio, monolayers are nearly complete, on dehydration two monolayers will be brought into contact, resulting in an interlayer space corresponding to a bilayer. If the protein:clay ratio is low, the monolayers are not complete and the dehydration could lead to an apparent monolayer as a protein molecule adsorbed on a clay surface is unlikely to find a counterpart on the other clay surface. Finally it should be emphasized that the above mentioned unfolding of proteins at pH $<$ i.e.p. will probably reduce the basal spacing of the clay-protein complexes and the drastic manner of dehydration commonly employed, heating at 110 °C or even 200 °C, could introduce an additional artefactual denaturation of the protein.

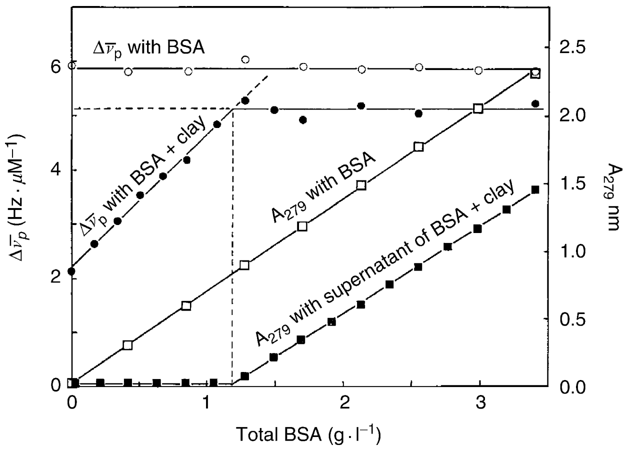


Figure E4 Effect of the addition of bovine serum albumin on the release of Mn^{2+}, as detected by its line broadening effect, Δ_{vp}, on orthophosphate by NMR, and on the UV absorption A_{279nm} of the protein. When present, the montmorillonite suspension is at 1 g dm^{-3}, pH 4.65. This figure illustrates the progressive completion of a protein monolayer on the clay surface (modified after Quiquampoix and Ratcliffe, 1992).

Consequences of electrostatic interactions on enzyme activity

Two main hypotheses have been proposed to explain the shift of the optimal pH of the catalytic activity of enzymes adsorbed on negatively charged surfaces such as clay minerals.

The first hypothesis considers that the pH in the region of the active site of the adsorbed enzyme is lower than the pH in the bulk of the solution which is effectively measured with a glass electrode and this explains the observed shift (Mc Laren and Estermann, 1957; Durand, 1964; Goldstein et al., 1964; Aliev et al., 1976; Douzou and Petsko, 1984). Indeed the negative charge originating in the isomorphic substitution in the crystalline lattice of the clay is compensated by cations, including protons, which make up a diffuse double layer, and thus the activity of the protons near the surface is higher than in the bulk. But this hypothesis has three serious drawbacks.

1. The shift in the optimal pH of activity should give rise to a higher rate of catalytic activity for the adsorbed enzyme than for the enzyme in solution in the alkaline range of pH. This has never been observed. When the absolute values of catalytic activity are reported, they invariably show that the values for the adsorbed enzyme are contained in the envelope of the values for the enzyme in solution (Aliev et al., 1976; Quiquampoix, 1987a; Quiquampoix, 1987b; Quiquampoix et al., 1989; Leprince and Quiquampoix, 1996). Figure E5 illustrates this fact. A misleading presentation of the results which is partly responsible for the popularity of this hypothesis in soil science and biotechnology is the normalization of enzyme activity values to the maximum value attained for each case, free and bound (Mc Laren and Estermann, 1957; Durand, 1964; Goldstein et al., 1964; Douzou and Petsko, 1984). This masks the occurrence of the general decrease in catalytic activity.
2. The hypothesis implies that the conformation of the adsorbed enzyme is similar to the conformation of enzyme in solution and can act as a "molecular pH-meter". Ample evidence to the contrary has been presented above.

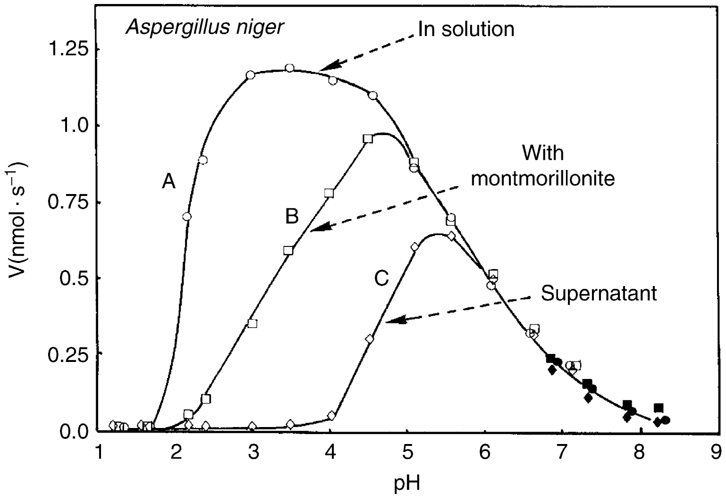


Figure E5 Effect of pH on the activity of *Aspergillus niger* β-D-glucosidase in solution (A), in presence of montmorillonite (B) where both the activities of the free and of the bound enzyme are measured, and in the supernatant (C) where the bound fraction has been eliminated by centrifugation. This figure illustrates the absence of pH shift effect on absolute values of catalytic rates (modified after Quiquampoix et al., 1989).

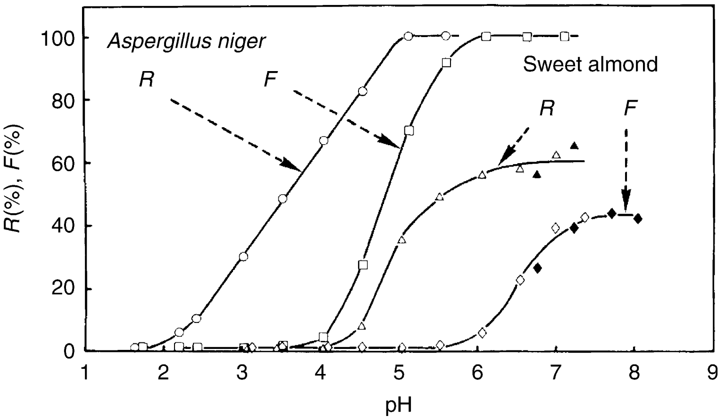


Figure E6 Effect of pH on the relative catalytic activity *R* in the adsorbed state and on the relative quantity *F* in the non-adsorbed state of two *β*-D-glucosidases from *Aspergillus niger* and sweet almond. This figure illustrates the unfolding of the enzymes due to electrostatic attraction at low pH, the decreased adsorption due to electrostatic repulsion at higher pH, and the variability of adsorption and stability properties of enzymes according to the species which produces them (modified after Quiquampoix et al., 1989).

3. Finally the basis of this theory is far from being assured since, as some authors have pointed out (Rouxhet, 1990; Rouxhet and Mozes, 1990; Fletcher, 1991), the tendency of a proton to react with the active site of the enzyme is not given by the proton activity but by its molar free enthalpy, namely its electrochemical potential:

$$\mu = \mu_0 + RT\ln[H^+] + F\psi$$

And since the system is in a state of thermodynamical equilibrium, the molar free enthalpy of the proton is the same in the bulk of the solution and at the clay surface.

The second hypothesis is based on evidence of pH dependent modifications of protein conformation. Figure E6 can be used as an illustration of this hypothesis. An *Aspergillus niger* *β*-D-glucosidase exhibits decreasing relative activity, *R*, defined as the ratio of activity in the adsorbed state and activity of an equal amount in solution, with decreasing pH. The attractive electrostatic interactions between the positively charged protein and the negatively charged clay surface, which lead to the unfolding of the enzyme, play a major role. The fraction of the enzyme, which is not adsorbed, *F*, increases with increasing pH. Again electrostatic forces are the main determinant of this behavior, but this time between a negatively charged enzyme and the negatively charged clay surface. The *Aspergillus niger* *β*-D-glucosidase is an example of enzyme for which electrostatic interactions probably completely regulate the interactions with clay surfaces. Figure E6 shows also results obtained with a sweet almond *β*-D-glucosidase, for which *R* and *F* do not reach 100% when pH increases. Interactions of another nature are probably implied in addition to the electrostatic ones to explain this observation and will be presented later.

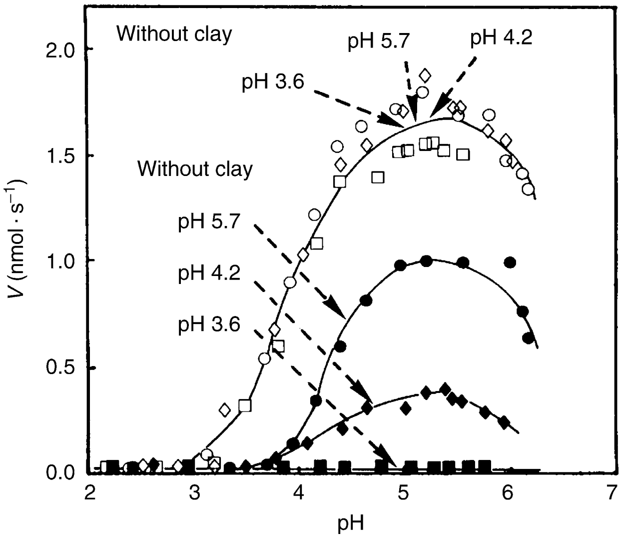


Figure E7 Effect of the pH of adsorption on montmorillonite on the pH profile of activity of sweet almond *β*-D-glucosidase. This figure illustrates the irreversibility of the unfolding of the enzyme at acid pH (modified after Quiquampoix, 1987a).

Irreversibility of the structural alteration of adsorbed enzymes

Further evidence for the theory of the pH-dependent modification of conformation of adsorbed enzymes which relies purely on catalytic activity measurements, and which is independent of the information obtained by the physical methods presented above, can be obtained. Figure E7 shows the effect of the adsorption of an enzyme at a given pH followed by the measurement of its catalytic activity on a wider range of pH. It can be observed that, the lower the pH of adsorption on montmorillonite, the lower is the measured catalytic activity of the enzyme at a given pH. This result cannot be explained by the surface pH effect since, according to this theory, no lasting effect of the pH at the moment of adsorption should be detected when the catalytic activity is measured at another pH. The change in activity cannot therefore be due to a modification of local pH.

Conversely, a modification of conformation is compatible with this observation, since the higher extent of unfolding at the lower pH values creates a higher number of contact points between the protein and the clay surface. The consequence is that, in order to return to its original conformation, the adsorbed enzyme would require an energy of activation corresponding to the energy of adsorption of all the additional amino acids brought into contact with the solid surface. It is likely that this activation energy is higher than the thermal energy available to the system.

Effect of the hydrophobicity/hydrophilicity of the surfaces on enzyme activity

Adsorption of proteins on artificial organic surfaces is known to involve hydrophobic interactions (Norde, 1986). The occurrence of this type of interaction can also be shown on some mineral surfaces. Figure E8 shows the destabilizing effect of different surfaces on a sweet almond β-D-glucosidase conformation as estimated by the effect on its relative activity *R*. It can be observed that the minimal destabilization of the enzyme structure is obtained with adsorption on goethite in a citrate buffer (Quiquampoix, 1987a). This surface is hydrophilic and with a low electric charge due to the complexation of the citric acid with the hydroxyls of the oxide surface. The occurrence of hydrophobic interactions is shown by the larger destabilizing effect of the uncharged hydrophobic talc surface (Quiquampoix et al., 1989). Compared to the goethite and talc surfaces, the negatively charged surface of montmorillonite confirms the strength of electrostatic interactions since the most important denaturation of the enzyme structure is observed on this surface at pH below 4 when the enzyme bears a net positive charge.

An interesting additional observation is that the effect of an increase of the ionic strength does not suppress the unfolding of the enzyme at pH below 4, as could be expected for an electrostatic interaction. The absence of an effect of the ionic strength on the interaction between a cationic polymer and a negatively charged surface has been observed with the adsorption of ammonium substituted galactomannans (Gu and Doner, 1992) on illite surfaces and has been attributed to a surface charge neutralization of the negative charge of the illite which is independent of the ionic strength. In contrast the anionic carboxyl substitued galactomannans (Gu and Doner, 1992) show an adsorption behavior dependent on the ionic strength, like the adsorption of the sweet almond β-D-glucosidase above its i.e.p. (Quiquampoix, 1987a). Thus attractive and repulsive electrostatic interactions between polymers and clay surfaces seem to show different sensitivities to the ionic strength.

Finally the relative activity of the enzyme on montmorillonite at high ionic strength and high pH is similar to that observed on the hydrophobic talc. The decrease in the repulsive electrostatic interactions and the fact that the hydrophilic nature of the montmorillonite surface is due to the hydration properties of the exchangeable cations, and not to the siloxane surface which is hydrophobic (Chassin et al., 1986; Skipper et al., 1989; Bleam, 1990; Jaynes and Boyd, 1991), are two factors which may explain this convergence. Additional evidence for the occurrence of hydrophobic interactions between proteins and montmorillonite surfaces is the increase in adsorption when proteins are methylated (Staunton and Quiquampoix, 1994).

Interfacial competition of adsorption of enzymes on natural clay-humic complexes

The real situation in soil is not represented by the presence of "clean" uncoated mineral surfaces as adsorbent surfaces for enzymes, but by the presence of organo-mineral complexes, and above all clay-humic complexes (Theng, 1979; Fusi et al., 1989; Rao et al., 1996). The heterogeneity of the soil organic matter is such that the study of better-defined artificial clay-organic complexes is helpful to understand the mechanisms implied.

Figure E9 shows the effect of different clay-organic complexes on the relative activity of a sweet almond β-D glucosidase. The lysozyme-montmorillonite complex involves a protein with a high i.e.p. (11.7). For this reason it is strongly held on the clay surface and renders the surface electropositive. As a result there is no evidence of the unfolding observed with the uncoated montmorillonite surface, which was caused by attractive electrostatic interactions. The enzyme appears to unfold on the polyethylene glycol-montmorillonite complex at low pH, as on the uncoated clay surface. This occurs because the adsorption of the positively charged enzyme on the electronegative clay surface is energetically more favorable than that of polyethylene glycol, which is thus displaced. As the pH increases the enzyme loses its positive charge and hence its ability to

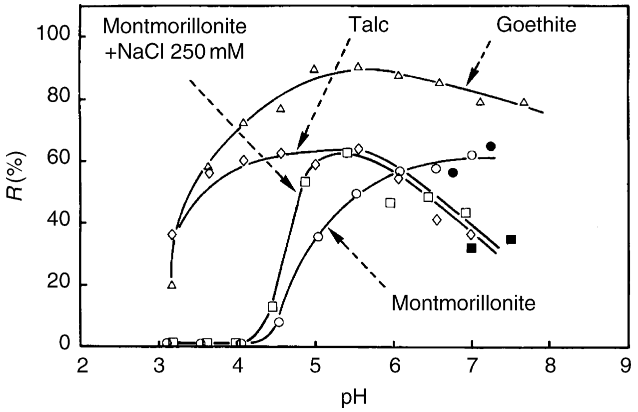


Figure E8 Effect of different mineral surfaces on the relative activity *R* of adsorbed sweet almond β-D-glucosidase. This figure illustrates the increasing destabilizing effect of a hydrophilic surface (goethite), a hydrophobic surface (talc) and a negatively charged surface (montmorillonite) on enzyme conformation (modified after Quiquampoix, 1987a).

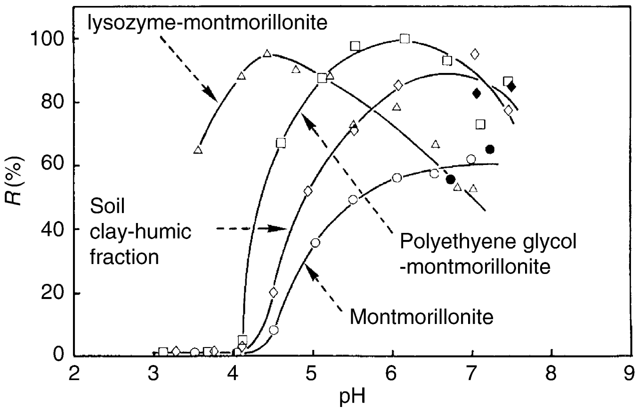


Figure E9 Effect of different organic coatings on mineral surfaces on the relative activity *R* of adsorbed sweet almond β-D-glucosidase. This figure illustrates the interfacial competition of adsorption between the enzyme and organic matter and the protective effect when organic matter is not displaced by the enzyme (modified after Quiquampoix, 1987b).

displace the polyethylene glycol. The higher relative activity in this pH range may be explained by a reduction in the destabilizing hydrophobic interactions because a hydrated polymer layer is intercalated between the enzyme and the surface (Quiquampoix, 1987b).

A natural clay-humic fraction (mineral fraction composed of smectite, interstratified minerals, illite and kaolinite; organic fraction composed of 21% fulvic acid, 29% humic acid and 50% humin) shows an intermediate destabilizing effect on the enzyme. It has been proposed that there is a lower energy of interaction for some of the natural humic substances with the clay surfaces, which are thus more easily exchanged than polyethylene glycol (Quiquampoix, 1987b). Thus the interaction of an enzyme with a mixture of several natural clay minerals, coated with poorly defined natural organic matter, can be adequately explained by taking in account of electrostatic interactions, hydrophobic interactions and interfacial competition of adsorption observed on a very simple model such as a polyethylene glycol-montmorillonite complex.

Conclusions

Adsorption of proteins on soil mineral surfaces is dependent on the nature of the interactions, which can be established between them. With clay minerals, electrostatic interactions usually override hydrophobic interactions. This results in an unfolding of the proteins on the surfaces below their i.e.p. and a decreased adsorption above their i.e.p. If the protein is an enzyme this results in a decrease in its catalytic activity at low pH. Finally the organic matter associated with mineral surfaces in soil can protect the enzyme from these destabilizing interactions if it is not displaced by an exchange mechanism. More detailed descriptions of the interactions of proteins and mineral surfaces can be found in Quiquampoix (2000) and Quiquampoix et al. (2002).

Hervé Quiquampoix

Bibliography

Albert, J.T., and Harter, R.D., 1973. Adsorption of lysozyme and ovalbumin by clay: effect of clay suspension pH and clay mineral type. *Soil Sci.*, **115**: 130–136.

Aliev, R.A., Gusev, V.S., and Zvyagintsev, D.G., 1976. Influence of adsorbents on the optimum pH of catalase. *Vestn. Mosk. Univ. Biol. Pochvoved.*, **31**: 67–70.

Armstrong, D.E., and Chesters, G., 1964. Properties of protein–bentonite complexes as influenced by equilibration conditions. *Soil Sci.*, **98**: 39–52.

Baron, M.H., Revault, M., Servagent-Noinville, S., Abadie, J., Quiquampoix, H., 1999. Chymotrypsin adsorption on montmorillonite: enzymatic activity and kinetic FTIR structural analysis. *J. Colloid Interface Sci.*, **214**: 319–332.

Bleam, W.F., 1990. The nature of cation-substitution sites in phyllosilicates. *Clays Clay Min.*, **38**: 527–536.

Brown, P., and Gajdusek, D.C., 1991. Survival of scrapie virus after 3 years internment. *The Lancet*, **337**: 269–270.

Chassin, P., Jouany, C., and Quiquampoix, H., 1986. Measurement of the surface free energy of calcium-montmorillonite. *Clay Miner.*, **21**: 899–907.

Douzou, P., and Petsko, G.A., 1984. Proteins at work: "stop-action" pictures at subzero temperatures. *Adv. Protein Chem.*, **36**: 245–361.

Durand, G., 1964. Modifications de l'activité de l'uréase en présence de bentonite. *C.R. Acad. Sci. Paris*, **259**: 3397–3400.

Fletcher, M., 1991. The physiological activity of bacteria attached to solid surfaces. *Adv. Microb. Physiol.*, **32**: 53–85.

Fusi, P., Ristori, G.G., Calamai, L., and Stotzky, G., 1989. Adsorption and binding of protein on "clean" (homoionic) and "dirty" (coated with Fe oxyhydroxides) montmorillonite, illite and kaolinite. *Soil Biol. Biochem.*, **21**: 911–920.

Goldstein, L., Levin, Y., and Katchalski, E., 1964. A water-insoluble polyanionic derivative of trypsin. II. Effect of the polyelectrolyte carrier on the kinetic behavior of the bound trypsin. *Biochemistry*, **3**: 1913–1919.

Gu, B., and Doner, H.E., 1992. The interaction of polysaccharides with Silver Hill illite. *Clays Clay Min.*, **40**: 151–156.

Harter, R.D., and Stotzky, G., 1973. X-ray diffraction, electron microscopy, electrophoretic mobility, and pH of some stable smectite-protein complexes. *Soil Sci. Soc. Am. Proc.*, **37**: 116–123.

Horbett, T.A., and Brash, J.L., 1987. Proteins at interfaces: current issues and future prospects. In Brash, J.L., and Horbett, T.A., eds., *Proteins at Interfaces. Physicochemical and Biochemical Studies.* Washington, DC: ACS Symposium Series 343, pp. 1–33.

Jaynes, W.F., and Boyd, S.A., 1991. Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. *Clays Clay Min.*, **39**: 428–436.

Kondo, A., Oku, S., and Higashitani, K., 1991. Structural changes in protein molecules adsorbed on ultrafine silica particles. *J. Colloid Interface Sci.*, **143**: 214–221.

Larsson, N., and Siffert, B., 1983. Formation of lysozyme-containing crystals of montmorillonite. *J. Colloid Interface Sci.*, **93**: 424–431.

Leprince, F., and Quiquampoix, H., 1996. Extracellular enzyme activity in soil: effect of pH and ionic strength on the interaction with montmorillonite of two acid phosphatases secreted by the ectomycorrhizal fungus. *Hebeloma cylindrosporum. Eur. J. Soil Sci.*, **47**: 511–522.

Loll, M.J., and Bollag, J.-M., 1983. Protein transformation in soil. *Adv. Agron.*, **36**: 351–382.

Mc Laren, A.D., and Estermann, E.F., 1957. Influence of pH on the activity of chymotrypsin at a solid-liquid interface. *Arch. Biochem. Biophys.*, **68**: 157–160.

Mc Laren, A.D., Peterson, G.H., and Barshad, I., 1958. The adsorption and reactions of enzymes and proteins on clay minerals: IV. Kaolinite and montmorillonite. *Soil Sci. Soc. Am. Proc.*, **22**: 239–244.

Noinville, S., Revault, M., Quiquampoix, H., and Baron, M.H., 2004. Structural effects of drying and rehydration for enzymes in soils: a kinetics-FTIR analysis of α-chymotrypsin adsorbed on montmorillonite. *J. Colloid Interface Sci.*, **273**: 414–425.

Norde, W., 1986. Adsorption of proteins from solution at the solid–liquid interface. *Adv. Colloid Interface Sci.*, **25**: 267–340.

Pagel-Wieder, S., Gessier, F., Niemeyer, J., and Schröder, D., 2004. Adsorption of the *Bacillus thuringiensis* toxin (Cry1Ab) on Na-montmorillonite and on the clay fractions of different soils. *J. Plant Nutr. Soil Sci.*, **167**: 184–188.

Quiquampoix, H., 1987a. A stepwise approach to the understanding of extracellular enzyme activity in soil I. Effect of electrostatic interactions on the conformation of a β-D-glucosidase adsorbed on different mineral surfaces. *Biochimie*, **69**: 753–763.

Quiquampoix, H., 1987b. A stepwise approach to the understanding of extracellular enzyme activity in soil II. Competitive effects on the adsorption of a β-D-glucosidase in mixed mineral or organo-mineral systems. *Biochimie*, **69**: 765–771.

Quiquampoix, H., 2000. Mechanisms of protein adsorption on surfaces and consequences for extracellular enzyme activity in soil. In Bollag, J.M., and Stotzky, G., eds., *Soil Biochemistry,* Vol. 10. New York: Marcel Dekker, pp. 171–206.

Quiquampoix, H., and Mousain, D., 2005. Enzymatic hydrolysis of organic phosphorus. In Turner, B.L., Frossard, E., and Baldwin, D., eds., *Organic Phosphorus in the Environment.* Wallingford: CAB International, pp. 89–112.

Quiquampoix, H., and Ratcliffe, R.G., 1992. A 31P NMR study of the adsorption of bovine serum albumin on montmorillonite using phosphate and the paramagnetic cation Mn^{2+}: modification of conformation with pH. *J. Colloid Interface Sci.*, **148**: 343–352.

Quiquampoix, H., Chassin, P., and Ratcliffe, R.G., 1989. Enzyme activity and cation exchange as tools for the study of the conformation of proteins adsorbed on mineral surfaces. *Prog. Colloid Polym. Sci.*, **79**: 59–63.

Quiquampoix, H., Staunton, S., Baron, M.-H., and Ratcliffe, R.G., 1993. Interpretation of the pH dependence of protein adsorption on clay mineral surfaces and its relevance to the understanding of extracellular enzyme activity in soils. *Colloids Surf. A*, **75**: 85–93.

Quiquampoix, H., Servagent-Noinville, S., and Baron, M.H., 2002. Enzyme adsorption on soil mineral surfaces and consequences for the catalytic activity. In Burns, R.G., and Dick, R.P., eds., *Enzymes in the Environment: Activity, Ecology and Applications.* New York: Marcel Dekker, pp. 285–306.

Rao, M.A., Gianfreda, L., Palmiero, F., and Violante, A., 1996. Interactions of acid phosphatase with clay organic molecules and organo-mineral complexes. *Soil Sci.*, **161**: 751–760.

Revault, M., Quiquampoix, H., Baron, M.H., and Noinville, S., 2005. Fate of prions in soil: trapped conformation of full-length ovine prion protein induced by adsorption on clays. *Biochim. Biophys. Acta*, **1724**: 367–374.

Rigou, P., Rezaei, H., Grosclaude, J., Staunton, S., and Quiquampoix, H., 2006. Fate of prions in soil: Adsorption and extraction by electroelution of recombinant ovine prion protein from montmorillonite and natural soils. *Environ. Sci. Technol.*, **40**: 1497–1503.

Rouxhet, P.G., 1990. Immobilization of biocatalysts and interfacial chemistry. In Okada, H., Tanaka, A., and Blanch, H.W., eds., *Annals of the New York Academy of Sciences,* Vol. 613, *Enzyme Engineering 10*. New York: The New York Academy of Sciences, pp. 265–278.

Rouxhet, P.G., and Mozes, N., 1990. The micro-environment of immobilized cells: critical assessment of the influence of surfaces and local concentrations. In de Bont, J.A.M., Visser, J., Mattiasson, B., and Tramper, J., eds., *Physiology of Immobilized Cells*. Amsterdam: Elsevier, pp. 343–354.

Servagent-Noinville, S., Revault, M., Quiquampoix, H., and Baron, M.H., 2000. Conformational changes of bovine serum albumin induced by adsorption on different clay surfaces: FTIR analysis. *J. Colloid Interface Sci.*, **221**: 273–283.

Skipper, N.T., Refson, K., and McConnell, J.D.C., 1989. Computer calculation of water–clay interactions using atomic pair potentials. *Clay Miner.*, **24**: 411–425.

Staunton, S., and Quiquampoix, H., 1994. Adsorption and conformation of bovine serum albumin on montmorillonite: modification of the balance between hydrophobic and electrostatic interactions by protein-methylation and pH variation. *J. Colloid Interface Sci.*, **166**: 89–94.

Tapp, H., and Stotzky, G., 1998. Persistence of the insecticidal toxin from *Bacillus thuringiensis* subsp. *kurstaki* in soil. *Soil Boil. Biochem.*, **30**: 471–476.

Tarasevich, Yu.I., Smirnova, V.A., Manakhova, L.I., Ropot, V.M., and Sivalov, E.G., 1975. Adsorption of albumin on clay minerals. *Kolloidnyi Zhurnal*, **37**: 912–917.

Theng, B.K.G., 1979. *Formation and Properties of Clay–Polymer Complexes.* Amsterdam: Elsevier, pp. 362.

Vasina, E.N., Déjardin, P., Rezaei, H., Grosclaude, J., and Quiquampoix, H., 2005. Fate of prions in soil: Adsorption kinetics of recombinant unglycosylated ovine prion protein onto mica in laminar flow and subsequent desorption. *Biomacromolecules*, **6**: 3425–3432.

Cross-references

Biodegradation
Carbon Cycling and Formation of Soil Organic Matter
Clay Mineral Formation
Clay-Organic Interactions
Fauna
Humic Substances
Hydrophility, Hydrophobicity
Iron Oxides
Microhabitats
Nitrogen Cycle
Phosphorus Cycle
Rhizosphere
Soil Biology
Soil Microbiology
Soil Mineralogy
Sorption Phenomena

EOLIAN

Also Aeolian. Pertaining to wind and applied to materials and deposits in which the movement of air masses has played a formative role. Active in the formation of eolian sands, a common parent material of Arenosols in arid and semi-arid regions; and of loessial silts, parent materials of Phaeozems, Chernozems and other soils of the grassland biome.

Cross-reference

Biomes and their Soils
Wind Erosion

EPIGENOUS

In geology, formed at the surface of the Earth, also known as the epigene or the exogene. Soils may be described as epigenous (or exogenous) deposits, and as components of the epigenetic (or exogenic) cycle.

Cross-reference

Biogeochemical Cycles

EROSION

Derived from the Latin *erodere*, to gnaw away, the term erosion applies to the process involved when the soil or rock formation is loosened and carried away by the agents of wind, water, freeze and thaw or biological activities. It occupies the intermediate slot in the sequence: *weathering – erosion – transportation*. It is sometimes misused in place of “denudation” which is properly applied only to the uncovering or landscape-forming antecedents by the erosive processes. When the transportation is essentially down-slope or gravitational, it is generally covered by the term *mass wasting* (Fairbridge, 1967; Small, 1970; Statham, 1977; Ritter, 1978; Büdel, 1982; Catt, 1986; Paton et al., 1995). Sometimes it is referred to as “mass-erosion”.

Wind erosion

Wind erosion or aeolian action is the process most often associated with climatic aridity that results in the absence or destruction of a vegetative cover. This is the most important hazard resulting from human errors in agronomy, e.g., the “Dust Bowl” effect (but combined with droughts during established climate cycles). On a global basis, there is a lack of natural vegetation in the following geographic areas: the very high latitudes (as in the “dry valleys” of Antarctica); the high-pressure subtropics (Sahara–Arabia–Kalahari, etc.); coastal belts bordered by cold geostrophic currents (Atacama–Namib); rain shadow belts (Patagonia, etc.); and the seasonally dried-out beaches in the intermediate latitudes.

Besides vegetation lack, there is also the question of soil mobility. Deep weathering of a granitic bedrock under a humid climate, may lead to podzolization, in turn leading to the creation of a largely quartz sand with a variety of clays and micas that are most easily carried off as *dust*. Seasonal rivers commonly lead to sand bars in an anastomizing system that are liable to long periods of isolation from the mainstream and are then subject to wind erosion. The great dune fields of the Sahara are partly due to this fluvial source, but also to recycling. Dusts from the Sahara (Figure E10) were already observed far offshore in

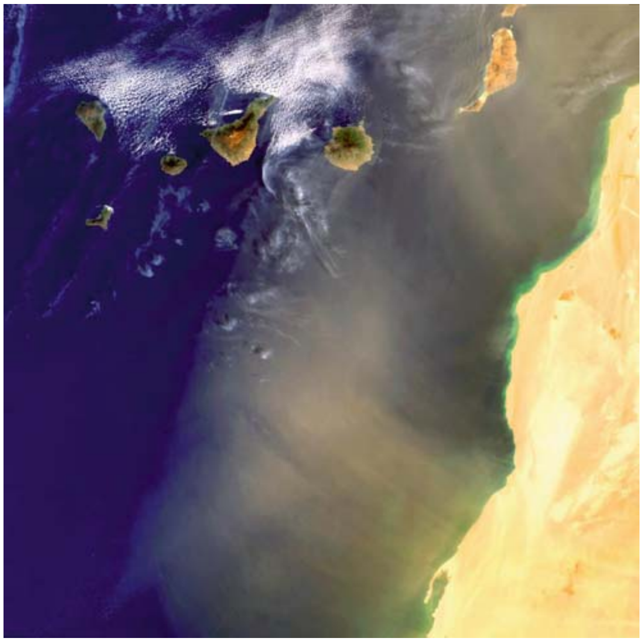


Figure E10 Desert dust blown from the Western Sahara towards the Canary Islands, seen in this 300 meter (medium) resolution imaging spectrometer (MERIS) image, acquired 1 March 2003. The wind can move between 60 and 200 million t of fine dust up from the Sahara each year (courtesy of the European Space Agency).

the Atlantic by Darwin on the voyage of H.M.S. *Beagle*, and seasonally Saharan dusts are collected in Florida and even in South America (Prospero et al., 1981). In fact, dust transport is a global phenomenon (Wasson, 1982; Pye, 1987).

Along the coast, wave action winnows out the fine-grained components of the littoral sediment load and marine currents carry them into deep water. The sands, on the other hand, tend to be washed up into the high-tide swash limits of the waves and in the tide cycles become desiccated and are then picked up by the wind to create longshore beachridges and dunes (Schwartz, 2005). Seasonally, and with stronger wind velocities, there are "blow-outs" that create linear dunes more or less normal to the beach line. In low-relief coastal plains such dunes may move inland by several km.

It is not always appreciated that the world climate of the glacial cycles of the last two million years (at least 20 major fluctuations) was characterized by very widespread aridity. Ocean (sea-surface) temperatures were on average 5 °C colder than today, thus reducing evaporation, and thus rainfall. The westerly circulation, which normally brings rain, was largely replaced by meridional wind systems (Lamb, 1977), which often led to thunderstorms, with violent but brief floods that provided for rapid erosion of the vast glacial outwash deposits, then followed by desiccation and aeolian transportation. In the ice cores of Greenland and Antarctica the beginnings of glacial intervals were marked by abrupt increases of airborne silt and dust by several orders of magnitude, and their terminations equally abrupt (Jouzel et al., 1993).

Besides the high-latitude aeolian material, derived from glacial outwash, there are far greater deposits of *loess*, of the same origin in the temperate latitudes of North America (particularly Nebraska to Maine), northern Europe (from Ireland to Ukraine), Asia (Kazakhstan to northern China), South America (Patagonia), Australia (South Australia, Victoria and New South Wales), and New Zealand (South Island). The loess is commonly calcareous, reflecting the limestone terrain over which the glaciers traveled (Kubiena, 1953; Ruhe, 1986; Pecsi, 1982). On weathering during interglacial warm-wet interludes it tends to change from light yellow or buff, to a dark brown or red, marked by bioturbation ("krotovinas" in Russian papers), caused by the burrowing of worms, rodents and assorted creatures. During the Soviet hegemony, there was a faction that favored a fluviatile origin for loess. Indeed it is true that in places some fluvial reworking is now recognized.

These rich soils determine much of the economic wealth of the mid-latitudes around the world from North America to western Europe, to central Asia, and China, and identify the great wheat and corn producers of the U.S., Canada, eastern Europe and Australia. In Roman times, two millennia ago, much of the Empire's wheat was obtained from the Mediterranean fringe of North Africa and the "Fertile Crescent" from Palestine to Syria and northern Iraq. This differed somewhat from the usual loess and has been identified as the "lee-desert loess", in Israel commonly more reddish and silty (Yaalon, 1997).

During the glaciation stages, reflecting orbital forcing (Cronin, 1999), the subtropical high-pressure belts became significantly expanded, so that the great deserts of today were even more important. In the early part of the 20th century, there was a widespread belief that the last glaciation must have been marked by heavy rains in Africa and South America. Nothing could have been further from the truth. Papers by the writer presented at conferences of the FAO and NATO in the 1950–1970 period were not well received by the "establishment". A chapter in a collective volume of the 1964 NATO conference in Newcastle (U.K.) was entitled "African ice-age aridity" (Fairbridge, 1964) and pointed to the discovery by Belgian scientists that the Kalahari dunes invancing from South Africa were ^{14}C dated in the alluvium of the Congo, where they were met by dunes of the same age heading south from the Sudan, where there were ^{14}C dates on Nile sediments (Fairbridge, 1962). In South America the dunes of Patagonia reached northward into the Mato Grosso of Brazil (Damuth and Fairbridge, 1970). In India the camels from the Indus valley were found, in fossil form, in the Pleistocene of Sri Lanka (made accessible by the low eustatic sea level). In Australia the paleo-dunes, now mostly vegetated, form an almost continuous ring about the continent, reflecting the high-pressure circulation (Figure E11, from McTainsh, 1985).

Water erosion

Water erosion, also commonly referred to as "slope wash" but encompassing more, such as fluvial processes (especially stream bed and river-bank levee accumulation), as well as mudflows and water-mediated aspects of mass-wasting (Emmet, 1970; Small, 1970; Ritter, 1978; Paton et al., 1995).

On the smallest scale, there is the *rain-drop* which according to climate is notoriously variable in size and effect; small drops of a drizzle or steady rain have a greater penetrating effect, but the larger drops associated with thunderstorms and tropical rains impact on the soil surface, almost as explosives, throwing up debris in all directions (Free, 1960). Moreover, on hillslopes such impacts have an amplified down-slope splash effect, greatly accelerating slope wash. The total soil loss has been a question of some research, but is conveniently summarized by Ritter (1978, p. 160–167). The analysis of hillslopes exposed to water erosion under temperate conditions

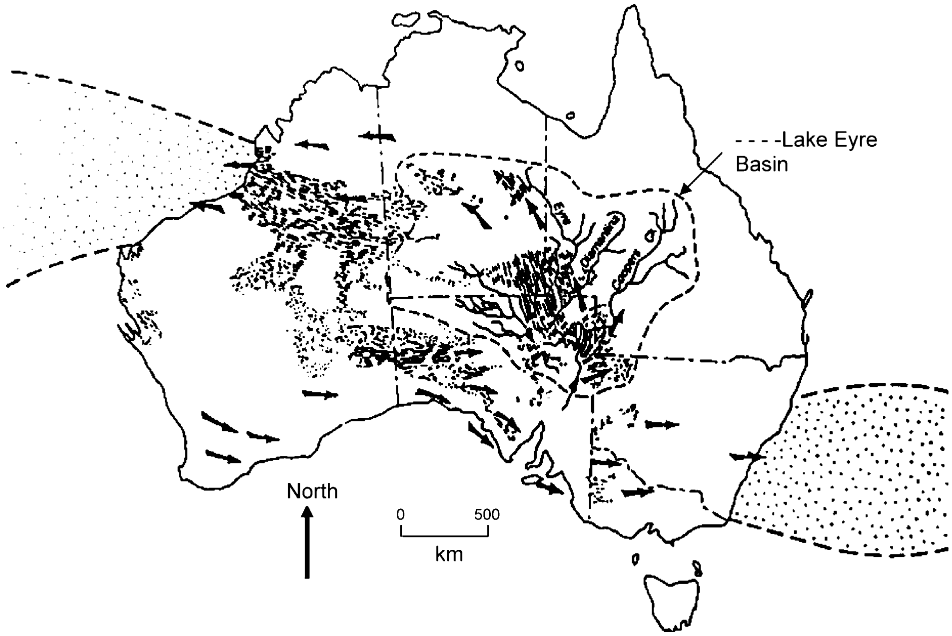


Figure E11 Dust transport encircling the atmospheric high-pressure system of Australia (McTainsh, 1985). Note the plume of fallout to the southeast over the Tasman Sea and to the northwest over the Indian Ocean. Paleodunes are widespread but largely vegetated today. Fluvial drainage in the interior is dominated by the Lake Eyre basin, but numerous smaller endorheic basins also exist. During the glacial stages of the Pleistocene, the anticyclone expanded and shifted northward a few degrees to bring the paleo-dunes far out onto the Rowley Shelf to the NW, and the Sahul Shelf to the north.

has been well reviewed by Young (1972) and by Carson and Kirby (1972). However, in semi-arid regions and in the humid tropics very distinctive environmental settings are involved (Twidale, 1968; Jennings and Mabbutt, 1967), and with the contrasting peneplains (in the temperate belts) and pediplains in the semi-arid to sub-humid tropics (Baulig, 1957).

In strongly seasonal or semi-arid regions, there is a distinctive "piedmont angle", marking the boundary of wash (rill) erosion and the downslope accumulation. At the foot of steep slopes there is even subsurface erosion.

Humid tropics are regions of high temperatures, high humidity and abundant vegetation (they are sometimes referred to as "*selvas*", the Spanish word for jungle). Early explorers in Brazil, India, Malaysia, Indonesia and southern China were struck by the systematic differences from the landscape of the temperate lands. All observers from Darwin and von Humboldt, on down, were impressed by the great depth of weathering, 50–100 m and more. The valleys, unlike the U-shapes of glacial terrain, box-shapes in semi-arid regions, or the sigmoid shapes of the subtropics, tend to sharply defined V-shapes. This V-shapes profile, first studied by the German colonizers in Papua-New Guinea, is closely related to the weathering depth, the uneroded bedrock controlling the thalweg of the streams, into which there is continuous landsliding, which thus controls the slopes (Jennings and Mabbutt, 1967; Wood, 1987). The perennial and heavy precipitation means that the weathered soil is always water-saturated (beside the colloidally hydrated ferallic compounds), but although it is always densely vegetated, it is a highly unstable surface. Significantly, the native footpaths are usually on the ridge crests. In the heavy rainfall areas of Hawaii this almost continuous landsliding keeps the ridgelines sharp, and the process is sometimes called "soil avalanching". The rivers normally carry huge volumes of fine sediment, which also is an inhibitory factor for fringing-reef corals.

Storm and Flood

Storm and flood are known hazards of short-term but sometimes catastrophic dimensions in specific areas. The extremely high winds, reaching more than 200 km h^{-1}, are usually limited to a few minutes or hours in the case of tornados, while the full force of hurricanes can last several days, although the shifting center and highest intensity progress with rates that range from 10 to 100 km h^{-1}. The principal effect on soils is through uprooted trees ("blow-down" or "tree-throw"). On hillslopes blow-down may initiate landslides and mudflows (Sharpe, 1938; Schaetzl and Follmer, 1990).

Anthropogenic effects are at their worst in these events. For example, the dense home building in southern California has several contributory "side-effects". This region, famed for its "perpetual" sunshine, is liable to extremely heavy precipitation in some seasons. The rainfall, instead of being uniformly distributed over the semi-arid landscape, is focused from roofs, cement patios, and "all-weather" surfaces into gutters and drains, thence into flood channels or seasonally "dry washes" which then come down as raging torrents. Results include mudflows and landslides. Home building on escarpments with "spectacular views" is particularly hazardous.

Alluvial plains, as along the Mississippi and Ohio rivers, have been subject to vast engineering works, course "corrections", "flood control" and hydroelectric utilization. (An interesting history of the 1927 flood is told by Barry, 1997.) In the headwater areas general deforestation for grazing lands exposes the soil to gullying and wholesale transport of sediment downstream, eventually blocking the dams and reservoirs. "Fine-tuning" of entire drainage systems, at first may have the appearance of masterpieces in hydraulic planning, but periodically there will be threshold effects when spillways are over-topped, or expected meteorological limits exceeded by the once-in-a-century or once-in-a-millennium condition.

The tropical rivers, like the Orinoco, Amazon, Niger, Congo, Indus, Ganges, Salween, Mekong and so on, are subject to annual flooding, and, when not interrupted by dams, the annual flood generates a welcome "top-dressing" to the soils of the flood plains. All these rivers are called "allogenic"; that is to say, their headwaters rise in regions climatically distinct from their lower reaches, and usually at much higher elevations with much heavier precipitation. The Nile (Said, 1981; Fairbridge, 1962) has not only a polygenetic source (the Blue Nile fed by monsoonal rains in Ethiopia, and the White Nile derived from equatorial rains in Lake Victoria and East Africa), but furthermore has produced a complex history of internal deltas in the Sudd and northern Sudan. Terraced sectors display silty paleosols that are well stratified, pointing to seasonality during low-discharge cycles. High-discharge phases are marked by considerable erosion when the sediment was carried down to the delta or out into the Mediterranean. Although all the tropical rivers (and many others) show evidence of these abrupt climatic oscillations, amounting to 10–20 "events" during the last 10 000 yr, the warm-wet phases tend to be extended, in contrast to the drier interruptions which were generally rather brief. In the seasonally stratified soils of the middle Nile (in Nubia), the gray calcareous silts are marked off by white desiccation layers ($CaCO_3$). High-water levels on some archaeologically dated pharaonic temples are also clearly marked in this way (Wendorf and Schild, 1976).

For long-term planners it might be wise to repeat an old geological axiom: anything that has happened (even in the remote past) can happen in the near future. This axiom applies particularly to volcanic events. Dormant volcanoes that have shown no signs of activity for several centuries may suddenly revive. Where the crater becomes occupied by a lake, as is particularly common in Java and other islands of the Sunda chain, the rising lava may cause the water to boil, which can then overflow in a "lahar". This is a stream of boiling mud that rips down the side of the cone at 50 km h^{-1} or faster, spreading mud over its lower course. After cooling, in a tropical climate this becomes an extremely fertile soil for agriculture, and the settlers, although well aware of the hazard, are apparently lulled by their traditional resignation to the inexplicable will of a supreme being. Nevertheless the Indonesian government has a vigorous and well-trained volcanological service.

In mountain areas, as in the high Andes, the volcanic action may mobilize a large snow field or ice cap. The resultant mudflow is equally catastrophic. In Iceland the same flood is known as a "jökulhlaup", with a brief intervals of flow at up to 100 000 m^3 s^{-1}.

Floods from ice-dammed lakes are a familiar experience today in Switzerland and in the Canadian Arctic. Church (1972) reported a discharge from such a lake in Baffin Island that released 50 million m^3 of water within a 30 hour period. Contemporary flooding there and in Iceland creates a wide fan of sand and silt which is a distinctive feature of the landscape. During the Scandinavian ice retreat during the late phases of the last ice age there (about 10 000–15 000 years ago), these fans, known as "*sandurs*", today cover much of the landscape of northern Denmark.

The largest break-out known to geological science was at Glacial Lake Missoula, sometimes called the "Spokane Flood", the details of which were originally worked out by a single man, J. Harlan Bretz who wrote a series of papers beginning 1923 (most of them reprinted in a review volume by Baker, 1981). His ideas were deemed so outrageous to begin with, that he received violent opposition for nearly half-a-century. Now, universally accepted however, the evidence is of a former glacial lake of large dimensions that reached north from eastern Washington State into Canada. It had numerous breakouts, the last of them close to the end of the last glacial stage about 15 000 yr ago. Maximum flood-water velocity was 2.13 million m^3 s^{-1}, but a constriction downstream caused a discharge of 9.1 million m^3 s^{-1} for about a week. The eroded area is known as the "Channeled Scabland" in the Columbia Plateau of eastern Washington (see Map: Baker, 1981, p. 278). That, by any standards, was a serious flood.

Another inundation, one that has triggered worldwide interest is the early Holocene Black Sea flood. Although more than somewhat controversial, it appears to mark the rising eustatic postglacial level of the world ocean when it overtopped the sill depth in the Bosporus. It seems likely that during the last glacial maximum (peak around 18 000 yr ago) the world cooling, as well as the truncation of the Black Sea fluvial drainage by glacier advances, so reduced the freshwater hydrologic intake, there was the creation of a "Euxine Lake" at some depth in the Black Sea basin. Such a lacustrine haven would probably have supported flourishing human riparian populations, which would have been threatened by the Bosporus flooding (a colorful account by Ryan and Pitman, 1998, compares it with the Biblical "Flood of Noah"). Earlier floods in the same region probably marked a reverse flow when the hydrologic balance of the Black Sea intake rivers was greater than that of the Mediterranean. And still more surprising was a flow from Caspian Sea through the Manych Depression north of the Caucasus. It appears that the rivers like the Volga, feeding the Caspian, are precisely out of phase with those of the Black Sea.

The largest "inter-sea" flooding was in the Messinian stage of the Miocene (about 5–6 million yr ago). At that time the ancestral Mediterranean ("Tethys") became closed by the approach of the African and European tectonic plates, which collided in the region of Gibraltar. The now-isolated basins became a site of evaporating ponds, and thick salt and anhydrite deposits have been found. Around 5.3 Myr ago the world ocean level overtopped a furrow in the Riff area of Morocco, and the waterfall of all time has been visualized ("Gibraltar's Waterfall", chapter 7 in Ryan and Pitman, 1998, p. 73).

Freeze-and-thaw processes

Freeze-and-thaw processes, commonly embraced in the area of "*cryopedology*", are aspects of erosion of great interest to researchers in the U.S. and northern Europe. The "cryosphere" (from the Greek *kryos* for cold) is that part of the Earth's crust that experiences, within any 12 month period, frequent oscillation in mean temperature above and below 0 °C (32 °F). Cryopedology, as a term, was proposed by Kirk Bryan (1946, p. 639), as "the science of intensive frost action and permanently frozen ground", i.e., "permafrost" (although Bryan complained it joined roots of Latin and English). Seasonal melting, however, creates complex disturbances ("cryoturbation"). In German such soils were originally called "Frostboden", also "Strukturboden" or "Brodelboden" (Büdel, 1982).

Frost splitting or "riving" was called by Bryan (op. cit.) "congelifraction" (or for short "gelifraction"). Most French writers prefer “cryoclastic” which has attained rather widespread acceptance. At higher elevations, the term “niveocryogenic” is often appropriate, with “cryonival” (implying the role of snow) at lower levels. When mixed with loess, the term “niveo-eolian” explains cross-bedded layers.

The initial freezing is often observed in the form of “needle ice” or “pipkrake” (a Swedish term) in the winter when groundwater is rising and freezes under surface litter in little columns or pyramids. On melting, there is progressive migration downhill. On a larger scale diapiric action (see illustrations in Fairbridge, 1968, p. 229) is the result of repeated freeze-and-thaw, a process properly called cryoturbation, but also “solifluction” and “gelifluction”. Seen on the horizontal plane, the ground surface, these cryoturbation features create “patterned ground”, “stone nets” and “polygons”, or on slopes “stone stripes” or “hummocks” (illustrations in Ritter, 1978). On major slopes the spring-summer melt season often leads to mudflows and landslides. This “active layer”, following Bryan (1946), may be termed the “mollisol” which in the higher latitudes overlies the “pergelisol” (“tjaele” in Sweden, or “merzlota” in Russia), which is characterized by permafrost. Where there is no groundwater, the latter is underlain by “tabetisol” (or “talik” in Siberia).

During the last ice age (glaciation interval) the belt peripheral to the great ice sheets is known as the periglacial belt. The northern part is still affected by cryoclastic processes and cryoturbation, while the southern part only retains isolated evidence of the formerly frozen ground. For example, spoil pits in northern Virginia (in the neighborhood of Washington, D.C.), while far from the permafrost today, still disclose perfect examples of deep solifluction as an inheritance from the periglacial period.

Frost riving in certain places created a vast quantity of sharp-edged pebbles or bedrock debris, which constitutes a “colluvium” which is gradually, transported downslope (Völkel, 2005). Its popular name in the south of England is “head” and “grèzes litées” in France. In Italy it may be particularly thick, especially around the northern Adriatic, where the bones of Pleistocene mammals were first discovered by geologists of the Austro-Hungarian geological survey in the 1870s.

Biological erosion

Biological Erosion is the last category of these destructive agencies and processes. First and foremost, the bacteria, though microscopic are almost everywhere in vast numbers, playing a primary role in the breakdown of both biological debris and certain minerals. The classic agents are the *earthworms* whose study was pioneered by Charles Darwin, beginning 1837, with his major work in 1881. Their biology is reviewed in detail by Edwards and Lofty (1977) and by Lee (1985). An up-to-date summary is in Paton et al. (1995), who noted that there are 1 800 known earthworm species worldwide, ranging from the permafrost to the tropics. An unusual example from Victoria (Australia) is known to be up to 10 m in length. They are exceeded in numbers by the *ants*, which run to 15 000 species, and range farther, being able to exploit also the semi-arid regions, their subsurface mining reaching in places to considerable depths (Brenner, 1910; Forcella, 1977). Also important in the semi-arid regions are the *termites* (Goudie, 1988; Lee and Wood, 1971), which because of their appetite for wood constitute a serious hazard to man-made structures in many countries. With 2 000 species, they were once labeled the “earthworms of the tropics” by a writer in 1884, but that was before the tropical earthworms were found to be almost universal. The net activity of all these burrowers and mound builders is termed “bioturbation”, which embraces a wide span of both the animal and plant kingdoms.

Mammalian excavators and mound-builders are also universally recognized (Abaturov, 1972; Hole, 1981), notably the rodents of various families, from rabbits, ground hogs and gophers to the meerkats (of South Africa), and the moles and voles of domestic gardens. Even larger creatures, like the badger in Europe or the wombat (*Vumbatus ursinus*) in Australia, play a role in places. The larger mammals, like the cloven-hoofed families (ungulates), oxen, cattle, antelope, deer, etc., all mobilize the soil around water holes and river banks and contribute to the local erosion problems. The largest mammal of all, the elephant (Giardino, 1974) is environmentally friendly as a rule, but if emotionally disturbed is observed to uproot small trees, leaving open craters comparable to blow-down.

Anthropogenic erosion

Anthropogenic Erosion is here left to the end, although it is often the most visible and economically serious form of erosional triggering. In Europe, the earliest evidence of widespread anthropic interference is seen on the Chalk downs and plateaus of southern England and northern France, where forest clearing was needed to permit Bronze Age sheep and goat pasturage. Tree-felling was a first step in the preparation of charcoal essential for the smelting of copper, and later, iron ores, the latter being a precursor to the Roman Empire with its organized government, economy and highway system which spanned much of Europe and even North Africa and the Middle East. The erosional effect was especially evident in the Mediterranean belt with its strongly seasonal wet and dry seasons (Vita-Finzi, 1969).

Overgrazing in both the Sahara’s northern and southern edges (the “Sahel”) has always been a problem during drought cycles, but are now exacerbated by many factors: *(a)* over-population (growth of hospitals means reduction of natural culling by disease), *(b)* ignorance (engenders lack of birth control), *(c)* politics (prevention of migration), *(d)* poverty (lack of food reserves; deforestation and dung-burning for fuel). It has been said that “the nomad is not so much the son of the desert as the father”, but he is hardly the one to blame. Removal of scrub vegetation and forest leads to increased aeolian mobilization, and once the dunes are on the march, there is little to stop them. Even after the rains return, if the formerly fertile soils are buried by dune sands, shallow-rooted plants cannot survive, although protected plantations of deep-rooted eucalypts will reduce wind erosion.

Water erosion is best evidenced by rill development and gullies. As remarked by Twidale (1968), individual areas of gullies in South Australia can often be linked to a discrete downpour. In Assam, India, the average monsoonal rainfall at Cherrapunji is about 425 inches (over 10 m) to which the landscape is adjusted, but it may be doubled in a bad year, when streams, roadways, drains and so on are overwhelmed and widespread flooding ensues, leading to disastrous soil erosion. In the case of the Brahmaputra, man-made deforestation has taken place in the Himalayan foothills, but the flooding downstream may engulf 90% of the entire country of Bangladesh.

Everywhere, the twin hazards are ignorance and poverty. Every case appears ultimately to be traceable back to one or other of these twin evils. For the future, each can be tackled by international programs, but unfortunately at the present time and foreseeable future there is

Rhodes W. Fairbridge

Bibliography

Abaturov, B.D., 1972. The role of burrowing animals in the transport of mineral substances in the soil. *Pedobiologia*, **12**: 261–266.

Baker, V.R., 1981. *Catastrophic Flooding. The Origin of the Channeled Scabland.* Benchmark Papers in Geology, Vol. 55.Stroudsburg: Dowden, Hutchinson & Ross, 360 pp.

Branner, J.C., 1910. Geological work of ants in tropical America. *Geol. Soc. Am. Bull.*, **21**: 449–496.

Bridges, E.M., 1978. *World Soils*, 2nd edn. Cambridge: Cambridge University Press, 125 pp.

Bryan, K., 1946. Cryopedology, the study of frozen round and intensive frost-action. *Am. J. Sci.*, **29**: 473–475.

Büdel, J., 1982. *Climatic Geomorphology* (transl. from German of 1977). Princeton, NJ: Princeton University Press, 443 pp.

Butler, B.E., 1956. Parna an aeolian clay. *Aust. J. Sci.*, **18**: 145–151.

Carson, M.A., and Kirby, M., 1972. *Hillslope Form and Process.* London: Cambridge University Press. 475 pp.

Catt, J.A., 1986. *Soils and Quaternary Geology.* Oxford: Oxford University Press. 267 pp.

Church, M., 1972. Baffin Island sandurs. *Can. Geol. Surv. Bull.*, 216.

Cronin, T.J., 1999. *Principles of Paleoclimatology.* New York: Columbia University Press, 560 pp.

Damuth, A.E., and Fairbridge, R.W., 1970. Equatorial Atlantic deep-sea arkosic sands and ice-age aridity in tropical South America. *Bull. Geol. Soc. Am.*, **81**: 189–206.

Darwin, C., 1881. *The Formation of Vegetable Mould Through the Action of Worms, with Observations on Their Habits.* London: John Murray. 328 pp.

Edwards, C.A., and Lofty, J.R., 1977. *Biology of Earthworms.* London: Chapman & Hall. 333 pp.

Emmett, W.W., 1970. *The Hydraulics of Overland Flow on Hillslopes.* USGS Professional Paper 662A. 68 pp.

Fairbridge, R.W., 1962. New radiocarbon dates of Nile sediments. *Nature*, **196**: 108–110.

Fairbridge, R.W., 1964. The importance of limestone and its Ca/Mg content to paleoclimatology. In Nairn, A.E.M., ed., *Problems in Paleoclimatology.* New York: Wiley, pp. 431–530.

Fairbridge, R.W., 1967. Geological and cosmic cycles. *NY Acad. Sci. Ann.*, **138**(2): 433–439.

Fairbridge, R.W., ed., 1968. *The Encyclopedia of Geochemistry and Environmental Sciences.* New York: Van Nostrand Reinhold, 1321 pp.

Forcella, F., 1977. Ants on a Holocene mudflow in the Coast Range of Oregon. *Soil Survey Horizons*, **18**: 3–8.

Free, G.R., 1960. Erosion characteristics of rainfall. *Agric. Eng.*, **41**: 447–449.

Giardino, J.R., 1974. When elephants destroy a valley. *Geogr. Mag*, **47**: 175–181.

Goudie, A.S., 1988. The geomorphological role of termites and earthworms in the tropics. In Viles, H.A., ed., *Biogeomorphology.* Oxford: Basil Blackwell, pp. 166–192.

Hole, F.D., 1981. Effects of animals on soils. *Geoderma*, **25**: 75–112.

Jennings, and J.N., Mabbutt, 1967. *Landform Studies from Australia and New Guinea.* Canberra: The Australian National University Press. 434 pp.

Jouzel, J. et al., 1993. Extending the Vostok ice-core record of paleoclimate to the penultimate glacial period. *Nature*, **364**: 407–411.

Kubiena, W.L., 1953. *The Soils of Europe.* London: Allen & Unwin (Thomas Murby). 318 pp.

Lamb, H.H., 1977. *Climate History and the Future.* London: Methuen (and Princeton University Press), 835 pp.

Lee, K.E., 1985. *Earthworms: Their Ecology and Relationships with Soils and Land Use.* Sydney: Academic Press. 411 pp.

Lee, K.E., and Wood, T.D., 1971. *Termites and Soils.* London: Academic Press. 251 pp.

McTainsh, G., 1985. Dust processes in Australia and West Africa: a comparison. *Search*, **16**: 104–106.

Paton, T.R., Humphreys, G.S., and Mitchell, P.B., 1995. *Soils: A New Global View.* New Haven: Yale Univ. Press, 213 pp.

Pecsi, M., ed., 1982. *Quaternary Studies in Hungary.* Budapest: Geographical Institute of Hungarian Academy of Sciences. 313 pp.

Prospero, J.M., Glaccum, R.A., and Nees, R.T., 1981. Atmospheric transport of soil dust from Africa to South America. *Nature*, **289**: 570–572.

Pye, K., 1987. *Aeolian Dust and Dust Deposits.* London: Academic Press. 334 pp.

Ritter, D.F., 1978. *Process Geomorphology.* Dubuque, IA: W.C. Brown, 603 pp.

Ruhe, 1984. Loess-derived soils, Mississippi Valley region, I: soil sedimentation system. *Soil Sci. Soc. Am. J.*, **48**: 859–863.

Ruxton, B.P., 1958. Weathering and subsurface erosion in granite at the piedmont angle, Balas, Sudan, *Geol. Mag.*, **95**: 353–377.

Ryan, W., and Pitman, W., 1998. *Noah's Flood.* New York: Simon and Schuster (Touchstone), 319 pp.

Said, R., 1981. *The Geological Evolution of the River Nile.* New York: Springer, 151 pp.

Schaetzl, R.J., and Follmer, L.R., 1990. Longevity of treethrow microtopography: implications for mass wasting. *Geomorphology*, **3**: 113–123.

Schwartz, M.L., 2005. *Encyclopedia of Coastal Science.* Dordrecht: Springer, 1211 pp.

Sharpe, C.F.S., 1938. *Landslides and Related Phenomena.* New York: Columbia University Press. 137 pp.

Small, K.J., 1970. *The Study of Landforms.* Cambridge: Cambridge University Press. 486 pp.

Statham, J., 1977. *Earth Surface Seiment Transport.* Oxford: Oxford University Press. 184 pp.

Twidale, C.R., 1968. *Geomorphology.* Melbourne: Nelson, 406 pp.

Vita-Finzi, C., 1969. *The Mediterranean Valleys.* Cambridge: Cambridge University Press, 131 pp.

Völkel, J. ed., 2005. Colluvial Sediments, Flood Loams and Peat Bogs. *Zeitschrift Geomorphologie, N.F., Suppl.*, **139**.

Wasson, R.J. 1982. *Quaternary dust mantles of China, New Zealand and Australia.* Canberra: Australian National University. 253 pp.

Wood, A.W., 1987. The humic brown soils of the Papua New Guinea highlands: a reinterpretation. *Mt Res. Dev.*, **7**: 145–156.

Yaalon, D.H., 1997. Soils in the Mediterranean region: what makes them different? *Catena*, **28**: 157–169.

Young, A., 1972. *Slopes.* Edinburgh: Oliver and Boyd, 288 pp.

Young, A., 1976. *Tropical Soils and Soil Survey.* Cambridge: Cambridge University Press. 468 pp.

Cross-references

Ice Erosion
Water Erosion
Wind Erosion

ERRATIC

Extraneous boulders or other masses of rock transported from their original site and deposited in a new locality by glacial action.

Cross-reference

Ice Erosion

ESCARPMENT

A cliff or abrupt face of a hill or ridge such as the Niagara escarpment (which is a special type called a cuesta). Escarpments support the least disturbed and oldest forest ecosystems in North America, at least in part because of the inaccessibility of their steep faces to anthropic disturbance.

Bibliography

Larson, D.W., Matthes-Sears, U., and Kelly, P.E., 1999. The Niagara Escarpment Cliff Ecosystem. *Savanna, Barrens and Rock Outcrop Plant Communities of North America*. Anderson, R., Fralish, J., and Baskin, J., eds., Cambridge, U.K.: Cambridge University Press. pp. 362–374.

ESKER

The name given to elongated deposits of gravel left originally by meltwaters running under ice sheets. When the ice melts, the deposits are left as serpentine, generally flat-topped ridges on the post-glacial landscape.

Cross-reference

Ice Erosion

EUTROPHICATION

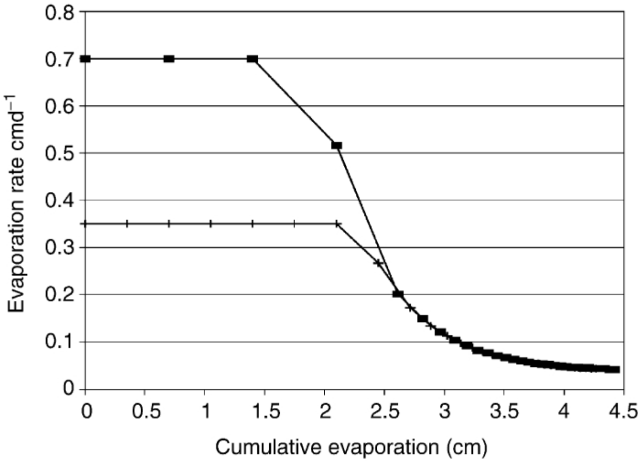
The depletion of oxygen as a result of the proliferation of organisms, especially algae (see Figure E12), as a result of a high nutrient content in a body of water such as a sea, river, lake or swamp.

EVAPORATION

Water returns from the soil directly into the atmosphere by the *evaporation process* (*Es*). Associated with soil evaporation is the *transpiration process* (*T*) by which water is taken up by plant roots, moved through the plant system, and vaporized at the plant leaf surface. These two processes are often combined in the *evapotranspiration process* (*ET*) because they are closely related and difficult to differentiate in the field.

The amount of water returned to the atmosphere depends on many factors such as amount and frequency of precipitation (or irrigation), soil type, plant cover, and presence of mulch. Under dryland agriculture where *summer fallow* (the practice of leaving the soil undisturbed on alternate years) is practiced, *Es* may be as much as 60% of precipitation. In contrast, in regions where complete plant cover occurs all year, *Es* may be as low as 5%.

Evaporation from a soil that has been previously wetted, involves two stages, a climate-controlled stage and a soil-controlled stage. During the climate-controlled stage, the amount of *Es* is controlled by the energy available for vaporization of the liquid water in the soil. At this time *Es* is essentially the same as free water evaporation and is often called potential soil water evaporation, *Esp*. The energy required to evaporate water, the latent heat of vaporization, is about 585 cal g^{-1} (28.3 Watts m^{-2} mm^{-1} d^{-1}). This energy comes mostly from solar radiation but can also come from energy extracted from the air or energy stored in the soil. Figure E13 shows *Es* for two different *Esp* rates. When *Es* is constant the ratio of Es/Esp is one. The amount of energy adsorbed by the soil surface, *net radiation*, is dependent on shading by plants or mulches that will modify the value *Esp*. On a clear summer day *Es* from a bare soil may be 6 mm of water if soil water content is high so $Es = Esp$. Evaporation will cause the water content near the soil surface to decrease rapidly so the climate-controlled stage will last for only a day or two. As the soil dries there comes a time when water cannot be transported to the soil surface fast enough to supply the climatic demand and the soil-controlled phase starts. The soil-controlled phase lasts much longer than the climate-controlled phase because the water lost to soil evaporation comes from the soil surface zone of about 20 cm (Jackson et al., 1973).



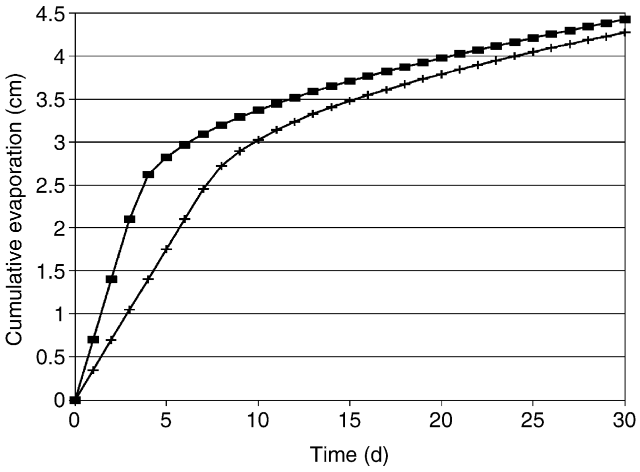


Figure E14 Cumulative evaporation with time for the two conditions shown in Figure E13.

Figure E14 shows that cumulative Es, for the two different Esp rates of Figure E13 is equal after several days even though the high rate (for bare soil) is twice as high as the low rate (like a mulch). The potential rate lasted 2 d for 0.7 cm d^{-1} and 6 d for 3.5 cm d^{-1} rate. After 8 days Es for both conditions was the same. This has practical consequences for water conservation because if the length of time between rains is 8 days or longer, for the silt loam soil data shown, there will be little water saved by a mulch. If the climatic environment were less severe then the time discussed above would be longer.

Evaporation falls off rapidly as the soil dries as shown in Figure E14. The first 2 cm of evaporation occurred in 3 days (0.7 cm d^{-1}) or 6 days (0.35 cm d^{-1}) but the next 2 cm of water was not lost until about 23 days. At 30 days Es was about 0.05 cm d^{-1} or about 7% of Esp.

Thus the total amount of water lost as Es depends on rainfall (or irrigation) frequency. In one experiment where 0.25 cm water was added to a soil each day for 30 days, 96% evaporated, whereas only 44% evaporated when the same amount of water was added at one time. This result is partially explained by the influence of depth of wetting on Es. If water applied is sufficient to wet the soil below about 20 cm, additional wetting will not result in additional evaporation.

In many areas of the world where water limits plant growth, many practices have been proposed that will limit Es and thus increase water available for transpiration. Many of these efforts have not proved to be economical. Common practices are fallowing and the use of straw, plastic, or (rarely) rock mulch. Fallow every other year is still practiced in spite of the saving of less than one-third of the rainfall during the fallow period. Straw mulches are often a problem because production of straw in these areas is not enough to produce a measurable effect. Use of plastic mulch is widespread for use with high-income crops to increase soil temperature, decrease weed growth and decrease Es (see *Mulch*). Rock mulch is only common in indigenous cultures (the Hopi for example), or in some semi-arid volcanic areas such as the Canary Islands.

A problem associated with Es where water tables are close to the surface is that of salt accumulation. In many areas of the world, especially those that are irrigated, a water table may be sufficiently close to the surface that water flow from the water table replaces that lost by Es. If the soil solution of the water table contains salts they will be transported to the surface by liquid flow and deposited there where the liquid water is vaporized. This results in high salt concentrations at or very near the soil surface, which may inhibit plant growth as well as having negative effects on soil properties (Bradford et al., 1991; Cardon and Letey, 1992).

Many models of soil water flow in response to evaporation and transpiration demands have been published (Hanks, 1991). A specific need of these models is information about Esp as a function of time under different crops. Figure E15 shows such a relation measured for corn (maize) at Logan, UT in 1990. The ratio of $Esp/Epan$ is equal and constant until significant plant growth occurs after which it decreases to a low value at full plant cover. We define $Epan$ to be the amount of water evaporated from a wet soil with no limitations on soil water for Es or T ($Epan = Es + T\mathrm{p}$ where $T\mathrm{p}$ is potential T). Figure E15 also shows Es with time with many periods where $Es < Esp$ even though transpiration was never limited by low soil water.

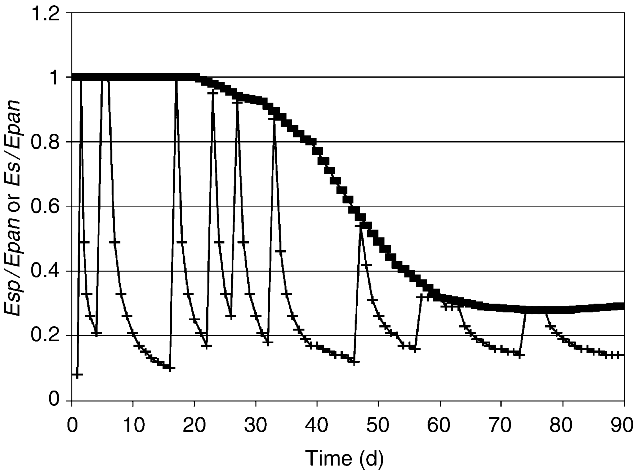


Figure E15 Illustration of changes in $Esp/Epan$ (*top*) and Esp (*bottom*) for a corn crop from planting to harvest.

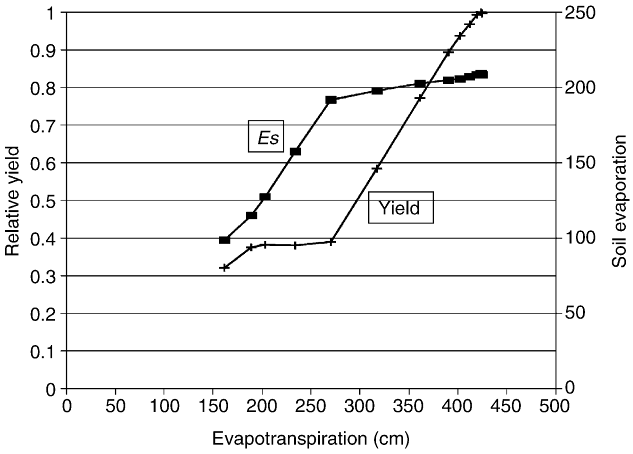


Figure E16 Relative yield and Es as related to ET for a study where irrigation was varied from zero to excess.

This illustrates the large differences of soil water conditions on *Es* and *T*.

These relations are further illustrated by Figure E16, which shows relative; yield simulations for corn (maize) at Logan, UT for 1990. In this experiment variable amounts of irrigation were applied from zero to excess. This resulted in a wide range of yields and *ET*. Irrigation was applied on all plots at the same time but in different amounts. As *ET* decreased from maximum to about 260 cm, yield decreased linearly. For the same range of *ET*, *Es* was nearly constant at about 200 cm. If the linear portion of the curve is extrapolated to zero relative yield *ET* would be 200 cm indicating that all of *ET* is *Es*. A linear relation of *ET* to relative yield has been widely reported in many field studies (Hanks, 1983). The linear change in yield with *ET* is caused by any changes in *T* not *Es*. Hanks (1983) has discussed the high correlation of yield and transpiration. At low values of *ET* the relation departs from linearity because water applied is insufficient to wet the top layer so *Es* decreases as both water applied and *ET* decreases.

R. J. Hanks and G. E. Cardon

Bibliography

Bradford, S., Letey, J., and Cardon, G.E., 1991. Simulated crop production under saline high water table conditions. *Irrig. Sci.*, **12**: 73–77.

Cardon, G.E., and Letey, J., 1992. Soil based irrigation and salinity management model: II Water and solute movement calculations. *Soil Sci. Soc. Am. J.*, **56**: *Biochem; Biophys. Acta*, **1724**: 367–374.

Hanks, R.J., 1983. Yield and water use relationships: an overview, Ch.9. In Taylor, H.M., et al., *Limitations of Efficient Water Use in Crop Production*. Madison, WI: ASA, CSSA, and SSSA.

Hanks, R.J., 1991. Soil evaporation and transpiration, Ch.11. In *Modeling Plant and Soil Systems*. Agronomy Monograph 31. Madison, WI: American Society of Agronomy.

Hanks, R.J., 1992. *Applied Soil Physics – Soil Water and Temperature Applications*. New York: Springer.

Jackson, R.D., Kimball, B.A., Reginato, R.J., and Nakayama, F.S., 1973. Diurnal soil water evaporation: time–depth–flux patterns. *Soil Sci. Soc. Am. Proc.*, **37**: 509–513.

Cross-references

Water Budget in Soil
Water Content and Retention

EVAPOTRANSPIRATION

The combination of evaporation of water from the soil with water lost by transpiring plants growing on and within the soil.

EVOLUTION

Literally “an unrolling” now usually concerned with modification of organisms and the development of new species from earlier forms, as a consequence of natural selection (also referred to as the struggle for survival). Specifically, natural selection this is the Darwin-Wallace mechanism by which evolution is achieved. The term may be applied to soil in two senses: (a) the broad scale changes that have taken place in global soils throughout geological time, and that are revealed by the study of paleosols (Retallack, 2001); and (b) the development of a specific soil throughout its life history as a consequence of progressive acidification, alkalinization or reduction, or any combination of these (Martini and Chesworth, 1992, chapter 2).

Bibliography

Martini, I.P., and Chesworth, W., eds., 1992. Weathering, soils & paleosols. Amsterdam; New York: Elsevier. 618 pp.

Retallack, Greg J., 2001. Soils of the past: an introduction to paleopedology. 2nd ed. Oxford; Malden, MA: Blackwell Science. 404 pp.

Cross-reference

Soil

EXCHANGE COMPLEX

The combination of mineral and organic surfaces that is capable of holding cations in a temporary and easily exchangeable way.

Cross-references

Activity Ratios
Base Saturation
Exchange Phenomena
Solute Sorption-Desorption Kinetics
Sorption Phenomena

EXCHANGE PHENOMENA

Soil colloids have two basic properties that make them chemically active: a large surface area and a surface electric charge. Due to the requirement of electroneutrality, this surface electric charge must be balanced by an equal quantity of oppositively charged counterions. The general term, *exchange phenomena*, or more specifically *ion exchange in soils*, refers to the exchange between the counterions balancing the surface charge on the soil colloid and the ions in the soil solution (McBride, 1994, Muraviev, 2000).

Constant charge surfaces

The charge on soil colloids may result from either structural imperfections in the interior of the crystal structure or preferential adsorption of certain ions on particle surfaces (Giese, 2002). Structural imperfections due to ion substitutions or site vacancies frequently result in a permanent charge on soil colloidal particles. This type of colloid is considered to have a constant charge, variable potential surface. Such colloids are typified by clay minerals with a 2 : 1 sheet structure such as illites or smectites, where the charge results from isomorphous substitution of octahedrally or tetrahedrally coordinated cations within the structure. The charge resulting from a given ion substitution may theoretically be either positive or negative, but in the case of the 2 : 1 type clay minerals, which consist largely of Si^{4+} or Al^{3+} in tetrahedral coordination and Fe^{3+}, Fe^{2+}, Al^{3+}, and Mg^{2+} in octahedral coordination, ion size limitations generally result in a substitution of cations of lower valence for those of higher valence resulting in a net negative charge on the clay structure (Pauling, 1 930, Meunier, 2005).

On the basis of known ion size limitations, coordination numbers, and a knowledge of the chemical composition for a given 2 : 1 type clay mineral, it is possible to calculate the chemical formula, assign atoms to the structural planes, and calculate unit cell dimensions, surface area, charge deficit per unit cell, surface charge density, and a theoretical cation exchange capacity (van Olphen, 1963). However, because such calculations apply only to homogeneous samples of a given clay mineral, they cannot be generally applied to the complex mixture of clay minerals found in most soils. As a result, it is necessary to measure the extent of the surface charge experimentally by determining the quantity of counterions (cations) compensating the negative charge. The charge determined in this manner is commonly referred to as the *cation exchange capacity* (CEC) and if appropriate precautions are taken, is a measure of the negative charge balanced by cations available for exchange by the saturating cations.

Cation exchange capacity measurements (Sparks, 1996), generally involve washing the soil sample with a given salt solution until the negative charge is compensated by only the added cation species. The quantity of compensating cations, and hence the net negative charge or CEC, can then be determined by either extracting with an excess of a second salt solution and determining the quantity of counterions present or by labeling the saturating cation with an appropriate radioisotope and counting it directly without extraction from the soil). In either case, it is common to wash out the excess salt before extraction or counting. Other than the possible retention of excess salt and loss of sample by dispersion hydrolysis of the saturating cation during the washing procedure constitutes the most likely discrepancy between the net negative charge and the measured CEC.

The charge or CEC measured in this manner is the charge neutralized by cations that are available for exchange with those in the saturating solution. Therefore, it is important to use a cation that is preferred or held more tightly by the surface than the cations being replaced. For this reason, Cs^+, Ca^2, Mg^{2+}, or Sr^{2+} are commonly used. Even when an excess of a highly preferred cation is used, part of the net negative charge on the surface may be blocked in such a manner that the compensating cations are not replaced by those in the saturating solution. This is frequently the case in micas and illites where the K^+ is "fixed" against normal exchange processes. In these cases the measured CEC is significantly less than the net charge deficit on the mineral structure.

pH charge dependent surfaces

In contrast to ions in the flat surfaces of clay minerals that are fully coordinated, the surfaces of oxide and hydrous-oxide minerals contain ions that are not fully coordinated and hence are electrically charged (Parks, 1967). When placed in an aqueous environment such as exists in soils, the net charge on such surfaces is balanced by the adsorption of H^+ or OH^- ions resulting in a hydroxylated surface. Charge can develop on these hydroxylated surfaces either through amphoteric dissociation of the surface hydroxyl groups or by adsorption of H^+ or OH^- ions. Following Parks (1967), these reactions can be written as follows, where italicized symbols refer to species forming part of the surface.

$$\textit{M}\ \mathrm{OH} \rightleftharpoons \textit{M}\ \mathrm{O}^- + \mathrm{H}^+(\mathrm{aq}) \tag{1}$$

$$\textit{M}\ \mathrm{OH} \rightleftharpoons \textit{M}^+ + \mathrm{OH}^-(\mathrm{aq}) \tag{2}$$

$$\textit{M}^+\ \mathrm{H_2O} \rightleftharpoons \textit{M}\ \mathrm{OH}_2^+ \tag{3}$$

Since the probability of bare M^+ existing at the surface is small, the basic dissociation or formation of a positively charged site probably occurs through a combination of the reactions shown in Equations (2) and (3) (Mott, 1970).

$$\textit{M}\ \mathrm{OH} + \mathrm{H_2O} \rightleftharpoons \textit{M}\ \mathrm{OH}_2^+ + (\mathrm{OH}^-)_{\mathrm{aq}} \tag{4}$$

In both the preceding mechanisms, the H^+ and OH^- ions that establish the surface charge are referred to as *potential determining ions* (PDI). Concentrations of the PDI and the net surface charge are obviously pH dependent, and there will be a pH value at which the net surface charge is zero; i.e., the density of positive and negative charge is equal. This pH is referred to as the *isolectric point* (IEP) or zero point of charge (ZPC) of the solid. Since the net charge on such surfaces depends on the H^+ or OH^- concentration in the equilibrium soil solution, it can be made positive or negative by raising or lowering the pH and is referred to as pH dependent charge.

Soils in the temperate regions tend to be dominated by the crystalline or constant charge-clay minerals while the high oxide content of many extensively weathered tropical soils results in a dominance of oxides that have pH dependent charge surfaces. All soils will, however, contain a mixture of both types of surfaces even though one type might tend to dominate the other. These mixtures may result from any one or all of the following:

- Edge effects on crystalline clay minerals
- Isomorphous substitution or site vacancies in Si-Al cogels
- Oxide coatings or interlayers on crystalline clay minerals

Edges of crystalline clay minerals contain ions not fully coordinated, much the same as oxide surfaces. These edges also adsorb H^+ and OH^- to form hydroxylated surfaces, which in turn develop an electrical charge through amphoteric association or dissociation. Since all clay minerals have such edges, they all must have a mixture of constant and pH dependent charged surfaces. However, in the case of the 2 : 1 type clay minerals, the edges constitute about only 1% of the total available surface area (Dyal and Hendricks, 1950). Consequently, the pH dependent charge on these minerals has limited effect on their overall behavior.

The 1 : 1 or kandite type clay minerals, however, tend to be aggregated into much larger particles through stacking in the *c* axis direction. Since the internal surfaces do not tend to separate except through rather specific intercalation reactions, they are not available for surface reactions. Consequently, these minerals have relatively low exchange capacities (Grim, 1969); and while much of the surface charge can be attributed to the amphoteric dissociation on the particle edges, it is difficult to rule out the possibility of a negative charge resulting from some isomorphous substitution (Schofield and Samson, 1953).

Anion exchange

In contrast to the fixed-charge clay minerals, the charge on oxide surfaces and the edges of clay minerals may either be negative, resulting in a cation exchange capacity (CEC), or positive, resulting in an anion exchange capacity (AEC), depending on the pH (Wingrave, 2001). Anion exchange capacities exist at low pHs where there is adsorption of H^+ ions resulting in a positive charge on the mineral surface. This positive charge must be balanced by an equal amount of anions such as Cl^-, NO_3^-, and SO_4^{2-}. As a result, soils in which these types of surfaces predominate will retain anions at low pH and potentially alter their behavior in terms of leaching and availability for plant uptake. In contrast, soils in which negatively charged clay minerals predominate do not retain anions, and hence they are readily available for leaching and plant uptake. At high pH, oxide surfaces will be negatively charged due to OH^- adsorption (or H^+ dissociation) and have a CEC that must be balanced by an equal amount of cations such as K^+, Na^+, Ca^{2+}, or Mg^{2+}.

Ion exchange process

Ion exchange refers to the exchange between the electrostatically held counterions balancing the surface charge on the soil particles and other ions in the soil solution and has the following general characteristics (Helfferich, 1962):

- It is reversible.
- It is diffusion controlled; i.e., the rate-limiting step is the diffusion of one counterion against another.
- It is stoichiometric.
- In most cases there is some selectivity or preference for one ion over the other by the surface.

All these characteristics can be readily demonstrated in the case of a pure montmorillonite clay suspension where the quantity of counterions equals the charge deficit on the crystal structure, one counterion species can be stoichiometrically exchanged for another, and the exchange of one ion for another occurs within the time limits of detection if the suspension is rapidly stirred to eliminate concentration gradients.

While these general processes also apply to soil systems, they are often more complex and less obvious as in the case of "fixed" K^+ on mica surfaces. This K^+ can be considered a counterion because it does balance the fixed charge on the mica structure resulting from isomorphous substitution, and it can be removed without altering the mineral structure itself. The exchange of another cation species for the interlayer K^+ is stoichiometric, and the exchange rate is controlled by the diffusion rate in the interlayer region of the clay particles. This exchange process is therefore reversible, stoichiometric, and diffusion controlled. Since the interparticle-diffusion rates are very slow (Jacobs, 1963) and since the K^+ is so highly preferred over other cations most commonly found in soils, ion exchange on mica-like surfaces is generally considered separately from ion exchange on the "more available" colloidal surfaces.

The total diffusion process, which involves movement of both solution and counterions against a concentration gradient, has been demonstrated to play a significant role in the movement of nutrient ions to plant root surfaces (Barber, Walker, and Vasey, 1963). The extent that "ion exchange" diffusion, or stoichiometric exchange of one counterion for another during movement along the colloid surface, contributes to the total movement or flux of ions through the soil, however, depends on the relative quantities of ions in the soil solution versus those balancing the surface charge. Solution diffusion is in general a much faster process than "ion exchange" diffusion.

Ion exchange selectivity, or the preference of one ion over another, has been the subject of a great deal of study. If these ions could be treated as point charges, then there would be no preference between ions of equal valence; ions do, however, have significantly different crystalline and hydrated sizes. Since electrostatic forces are involved in the retention of counterions, it can be predicted from *Coulomb's law* (Pauley, 1953) that the ion having the smallest effective radius and highest valence will be preferred. It has been frequently demonstrated that there is a definite relationship between ion size and ion selectivity (Gast, 1969; Meunier, 2005). Since cations present in soils are hydrated, ions with the smaller hydrated size or the larger crystalline size are preferred over other ions having the same valence. This is reflected in the so-called *lyotropic series*, which shows the following order of monovalent cation preference by soil colloids: $Cs > Rb > K > Na > Li$. Close relationships have been demonstrated between selectivity and various ion size parameters including polarizability, Debye Huckle parameters of closest approach, and hydrated radii.

Ion exchange reactions in soils have been intensively studied for well over 100 years and very justifiably so. It is the mechanisms by which many nutrient ions are retained by soils against leaching losses and at the same time made generally available for meeting the nutrient requirements of plants.

Robert G. Gast

Bibliography

Barber, S.A., Walker, J.M., and Vasey, E.H., 1963. Mechanisms for the movement of plant nutrients from the soil and fertilizer to the plant root. *Agric. Food Chem.*, **11**: 204–207.

Dyal, R.S., and Hendricks, S.B., 1950. Total surface of clays in polar liquids as a characteristic index. *Soil Sci.*, **69**: 421–432.

Gast, R.G., 1969. Standard free energies of exchange for alkali metal cations on Wyoming bentonite. *Soil Sci. Soc. Am. Proc.*, **33**: 37–41.

Giese, R.F., and van Oss, C.J., 2002. *Colloid and Surface Properties of Clays and Related Minerals.* New York: Marcel Dekker, 295 pp.

Grim, R.E., 1968. *Clay Mineralogy.* New York: McGraw-Hill, 396 pp.

Helfferich, F., 1962. *Ion Exchange.* New York: McGraw-Hill, 624 pp.

Jacobs, D.G., 1963. The effect of collapse-inducing cations on the cesium sorption properties of hydrobiotite. *Int. Clay Conf. (Stockholm)*, **1**: 239–248.

McBride, M.B., 1994. *Environmental Chemistry of Soils.* New York: Oxford University Press, 406 pp.

Meunier, A., 2005. *Clays.* New York: Springer, 472 pp.

Mott, C.J.B., 1970. Sorption of anions by soils. Sorption and transport processes in soils. *Soc. Chem. Ind. Mon.*, **37**: 40–53.

Muraviev, D., Gorshkov, V., and Warshawsky, A., 2000. *Ion Exchange.* New York: Marcel Dekker, 905 pp.

Parks, G.A., 1967. Aqueous surface chemistry of oxides and complex oxide minerals. In Gould, R.F., ed., Isoelectric point and zero point of charge. Adv. Chem. Series, **67**: 121–160.

Pauley, J.L., 1953. Prediction of cation exchange equilibria. *J. Am. Chem. Soc.*, **76**: 1422–1425.

Pauling, L., 1930. The structure of micas and related minerals. *Proc. Natl Acad. Sci. USA*, **16**: 123–129.

Schofield, R.K., and Samson, H.R., 1953. The declaration of kaolinite suspensions and the accompanying change-over from positive to negative chloride adsorption. *Clay Mineral Bull.*, **2**: 45–51.

Sparks, D.L., ed., 1996. *Methods of Soil Analysis. Part 3, Chemical Methods.* Madison, WI: Soil Science Society of America, American Society of Agronomy, 1390 pp.

Wingrave, J.A., 2001. *Oxide Surfaces.* New York: Marcel Dekker, 524 pp.

Cross-references

Acids, Alkalis, Bases and pH

Clay Mineral Formation
Clay-Organic Interactions
Humic Substances
Hydrophility, Hydrophobicity
Sorption Phenomena

EXFOLIATION

To split off into layers or scales seen especially in an outcrop where the rock has been relieved of its original tectonic load. More generally applied to any process of delamination at any scale including that of individual mineral grains e.g., the separation of mica into flakes along cleavage planes.

EXOGENE

Also epigene. The outer part of the lithosphere where low temperature-low pressure processes occur. In geomorphology, one may distinguish structural land forms (endogenic) from denudational land forms (exogenic).

Cross-reference

Biogeochemical Cycles

EXTRACT

In soil science, a sample of the aqueous solution drawn or taken out of the soil for analytic or diagnostic purposes. The solution may be intrinsic, or may be the result of addition, in which case the fluid added may or may not be aqueous, and is referred to as an extractant.

F

F HORIZON

See *Horizon, Profile, Horizon Designations.*

Cross-reference

Micromorphology

FABRIC

The arrangement of soil constituents and soil pores into a basic three-dimensional structure.

Cross-reference

Micromorphology

FACTORS OF SOIL FORMATION

These may be defined as "the interrelated natural agencies responsible for the formation of soil" (Gregorich, 2001). Dokuchaev introduced the "factorial" approach to soil genesis and considered the important factors to be living and dead organisms, parent rock, climate and relief (Strzemski, 1975). In North America, the idea was taken up by the U.S. Department of Agriculture, and a clear statement along these lines may be found in "Soils and Men" (USDA, 1938):

"True soil is the product of the action of climate and living organisms upon the parent material, as conditioned by the local relief. The length of time during which these forces are operative is of great importance in determining the character of the ultimate product. Drainage conditions are also important and are controlled by local relief, by the nature of the parent material or underlying rock strata, or by the amount of precipitation in relation to rate of percolation and run-off water. There are therefore, five principal factors of soil formation: (1) Parent material; (2) climate; (3) biological activity (living organisms; (4) relief; and (5) time. These soil-forming factors are interdependent, each modifying the effectiveness of the others" (Byers et al., 1938).

The next significant advance came with Jenny (1941) who expressed the relationship in implicit form:

$$\text{Soil (or } s) = f(cl, o, r, p, t \ldots)$$

Where *cl* is the climatic factor, *o* the biotic factor, *r* the topographic factor, *p* the parent material and *t* the time factor. The dots provide the flexibility of introducing additional factors if necessary or advisable. More controversially, Jenny introduced an explicit form of this relationship:

$$ds = \left(\frac{\delta s}{\delta cl}\right)_{o,r,p,t}^{dcl} + \left(\frac{\delta s}{\delta o}\right)_{cl,r,p,t}^{do} + \left(\frac{\delta s}{\delta r}\right)_{cl,o,p,t}^{dr} + \left(\frac{\delta s}{\delta p}\right)_{cl,o,r,t}^{dp} + \left(\frac{\delta s}{\delta t}\right)_{cl,o,r,p}^{dt}$$

which can only hold if all the soil-forming factors are independent variables. However, although this is clearly not the case, and is well recognized in the extended quotation above, there are field situations in which one of the factors may be of such a dominant influence in controlling soil formation that it may be considered alone, with the assumption that all other factors are essentially constant. In such a case, if climate were the sole variable to be considered, the soils in question are collectively called a climosequence. Other single variable soil populations are similarly denoted i.e., biosequence, toposequence, lithosequence and chronosequence, the respective variables of significance being *o*, *r*, *p* and *t*.

The following brief description of the classical factors of Jenny, follows Birkeland (1999, p. 143).

Climatic factor. Climate is usually considered in terms of temperature and precipitation, whether on local, regional or global scales. Yearly averages of these parameters are the data commonly

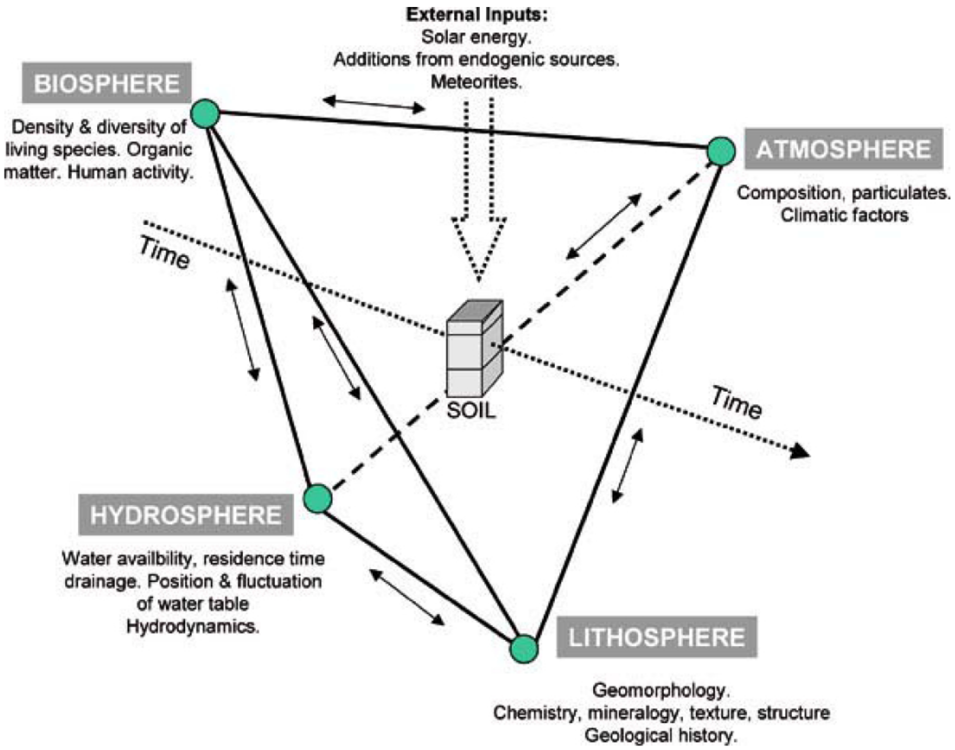


Figure F1 Atmospheric, hydrospheric, lithospheric and biospheric factors affecting the formation of soil. Time, which may be the only independent factor (see Chesworth, 1973, and Birkeland, 1999, p. 144) is depicted as a trajectory along which the tetrahedral frame is traveling and changing.

taken as a basis for interpretations of soil formation. Since losses of soil components by leaching are one of the major elements of change in an evolving soil system, Yaalon (1975) derived a factor *L*, defined as water available for leaching, from the raw precipitation data. *L* is the water left over after evapotranspiration losses, and after the water-holding capacity has been taken into account.

Biotic factor. Since climate is the primary variable that determines the geographic distribution of organisms (plant life especially) at a global level, a map of vegetation zones follows closely the contours of a map of climate. In effect, the climatic and biotic factors are so interrelated that it is not uncommon for them to be considered a single, linked factor.

Topography. The fundamental aspects of topography in soil formation are the shape and slope of a landscape. Essentially, these determine the stability of loose materials (such as soil) on a landscape feature, and therefore tend to limit the length of time that a soil may stay in place. Steep slopes for example, being conducive to mass movement, will tend to have younger soils than flatter features such as plains and plateaus.

Parent material. The parent material can be considered to be the soil system at time zero – in other words, the initial state of the system. It may be igneous, sedimentary or metamorphic rock, or unconsolidated sediment, or indeed, a pre-existing soil.

Time factor. This refers to the elapsed time over which a specific episode of soil formation began. For a current episode it requires an estimate of the starting time of the process. Except in relative terms this may be difficult if not impossible to determine.

A way to integrate the soil forming factors in an overall scheme is shown in Figure F1. Here the conventional factors are augmented by additional ones, in groupings that are related to the four major reservoirs at the surface of the Earth that interact to produce soil. A diagram of this type clearly emphasizes the lack of independence of the various factors, and the importance of feedback between them.

Carlota Garcia Paz and Teresa Taboada Rodríguez

Bibliography

Birkeland, P., 1999. *Soils and Geomorphology*, 3rd edn., New York [etc]: Oxford University Press, 430 pp.
Byers, H.G., Kellog, C.E., Anderson, M.S., and Thorp, J., 1938. *Formation of soil*. USDA, pp. 948–978.
Chesworth, W., 1973. The parent rock effect in the genesis of soil. *Geoderma*, **10**: 215–225.
Gregorich, E.G., Turchenek, L.W., Carter, M.R., and Angers, D.A., 2001. *Soil and Environmental Science Dictionary*. Boca Raton, FL: CRC Press, 577 pp.
Jenny, H., 1941. *Factors of Soil Formation: A System of Quantitative Pedology*. New York/London: McGraw-Hill, 281 pp.
Strzemski, M., 1975. *Ideas Underlying Soil Systematics*. Washington, DC: U.S. Department of Commerce, National Technical Information Service, 542 pp.
USDA, 1938. *Soils and Men*. Washington, DC: Government Printing Office, 1232 pp.
Yaalon, D., 1975. Conceptual models in pedogenesis. Can soil-forming functions be solved? *Geoderma*, **14**: 189–205.

Cross-references

Biomes and their Soils
Climate

FALLOUT

Fallout is the process by which particles carried into the atmosphere fall back to the surface. As a noun it is the accumulated particles, usually contaminated (with radioactive nuclides for example), formed in this way. Caesium-137, is present in modern soils as a result of fallout from nuclear testing. With a half life of 30.23 years, it has proven useful in quantifying rates of soil erosion (Porto et al., 2003).

Bibliography

Porto, P., Walling, D.E., Tamburino, V., and Callegari, G., 2003. Relating caesium-137 and soil loss from cultivated land. *Catena*, **53**: 303–326.

Cross-reference

Erosion

FALLOW

Land that is ploughed and harrowed but left uncropped for a year or more. If the ploughing takes place in the summer (with the objective of controlling weeds, the proper term is summer fallow). A season's fallow was a common feature of agriculture up to the end of the second world war. It was meant to allow soil to recover some of the fertility diminished by two or three years of cropping. Post WWII, fallowing became less common (at least in the developed economies) with fertility more likely to be maintained by the use of chemically manufactured fertilizers.

FAMILY

A grouping of soils related principally in terms of physical and/or chemical properties. It is one of six categories of classification in Soil Taxonomy.

Cross-reference

Classification of Soils: Soil Taxonomy

FAN

A fan-shaped or flat cone of alluvial deposits formed by a stream or river where it enters a lake or becomes confluent with another river, or reaches the edge of a plain. As a consequence it becomes less steep, and deposits part of its sedimentary load. A common environment for Fluvisols.

FAUNA

The soil fauna includes those animals that pass one or more active stages in soil or litter; some may be temporary occupants of this habitat, most are permanent (Wallwork, 1970; Coleman et al., 2004). Animals live in either the air spaces or in water in soil, though certain species can function in both media (Walter et al., 1991). Soil animals participate in the genesis of the habitat in which they live. They are found in all soil types, in Arctic and Antarctic fell-field and tundra, at edges of glaciers, in deserts, in caves, in cultivated soils, and in soil analogs, such as accumulations of organic matter in tree-holes, bromeliads and other canopy habitats. Only the species composition, diversity, quantity and function of soil animals varies with changing soil types, the main groups represented, remain the same.

Evolution and development

Since the Devonian era when soil developed around the first terrestrial plants, animals have been closely associated with this habitat. Fossilized fecal pellets of soil arthropods are known from the Silurian (Sherwood-Pike and Gray, 1985), and Carboniferous (Labandeira et al., 1997) and fossil mites and collembola from the Devonian (Shear et al., 1984; Kevan et al., 1975). Despite their long relationship with soil, knowledge of this fauna was minimal and restricted to a few conspicuous species until Müller (1879) noted that humus types were biological as well as physico-chemical systems, and Darwin (1881) highlighted the role of earthworms in "the formation of vegetable mould". The Berlese and Tullgren funnels, which revolutionized research on soil arthropods, were only invented in the early 20th century (Berlese, 1905; Tullgren, 1917). Following the Second World War, a series of publications on aspects of soil fauna established the discipline and led to the first international colloquium on soil fauna in 1955 (Franz, 1950; Kühnelt, 1961; Kevan, 1955). Subsequent texts emphasizing soil fauna include Kevan (1968), Wallwork (1970, 1976), Coineau (1974), Dindal (1990), Lavelle and Spain (2002), and Adl (2003). Scientific journals largely devoted to research on soil fauna include *Pedobiologia*, and *European Journal of Soil Biology,* and *Soil Biology and Fertility*, *Agriculture Ecosystems and Environment*, and *Biology and Fertility of Soils* often contain articles on these organisms and their relationships to decomposition and ecosystem function. Kevan (1986) provided an elegant review of the history of the discipline of soil zoology.

Much of the dynamic evolution of soil zoology in the last 25 years can be attributed to the stimulation of the International Biological Program (IBP), (Phillipson, 1971; Persson and Lohm, 1977), soil ecological studies at Long Term Ecological Research sites in the USA (http://www.lternet.edu/), the Soil Biodiversity Programme in the UK (http://soilbio.nerc.ac.uk/), and the Tropical Soil Biology and Fertility Institute of the International Center for Tropical Agriculture (http://www.ciat.cgiar.org/tsbf_institute/index_tsbf.htm). The importance of soil biology in general is a focus of the Soil Biodiversity Portal of FAO (http://www.fao.org/AG/AGL/agll/soilbiod/default.stm). In addition, emphasis on ecological agriculture, environmental destruction, sustainable development and landscape ecology and restoration has developed interest in using natural processes in soil, including soil animals, to optimize nutrient cycling (e.g., Edwards et al., 1988; Crossley et al., 1991; Paoletti and Pimental, 1992).

Table F1 Biodiversity of soil fauna

Taxon	Common name	Size	Quantity	Feeding	Selected references
Protozoa	Flagellates, naked amoebae, testacea, ciliates	<100 µm	1–20 million/m^2 10^3–10^6/g wet soil	Main consumers of bacteria; also fungi, yeasts, algae, detritus	Lousier and Bamforth 1990; Adl 2003
Rotifera	Rotifers	<120 µm	10^4–10^5/m^2 wet soil	Algae	Wallwork 1976
Gastropoda	Snails, slugs	2–100 mm	5–150/m^2	Mainly herbivorous; some fungivores, predators	Burch and Pearce 1990
Annelida Lumbricidae Megascolecidae Enchytraeidae	Earthworms Pot-worms	10–400 mm 5–50 mm	0.5–524/m^2–120 g/m^2 200–2 90 000/m^2	Earthworms: organic material, mineral soil; pot-worms: organic material, silica, fungi, algae, bacteria	Edwards and Lofty 1977; Dash 1990; Schwert 1990; Hendrix 2000
Nematoda	Nematodes, todes	100–4 500 µm	1–30 × 10^6/m^2	Herbivores, microbivores, fungivores, omnivores, predators, detritivores, parasites	Freckman 1982; Freckman and Baldwin 1990
Tardigrada	Tardigrades	50–1 200 µm	50–2 000/10 cm^2	Algae, plants, bacteria, detritus, predators	Nelson and Higgins 1990
Arthropoda					
Isopoda	Woodlice	2–30 mm	–500/m^2	Decaying plant material, omnivores	Muchmore 1990
Myriapoda	Millipedes,	1–25 cm	–300/m^2	Dead plant material;	Hoffmann 1990; Edwards 1990
	Centipedes,	1–25 cm	–19 000/m^2	Predators;	
	Pauropods,	0.5–1 mm		Dead plant material, fungi;	
	Symphylans	2–10 mm		Phytophages, saprophages	
Araneae	Spiders	1–10 mm	180–840/m^2	Predators	Dondale 1990
Acari	Mites	100–5 000 µm	–1 × 106/m^2	Predators, microbivores, fungivores, saprophages, phytophages, detrivores, omnivores, parasites	Krantz and Ainscough 1990; Norton 1986; Kethley 1990; Walter and Proctor 1999
Collembola	Collemboles, springtails	150–5 000 µm	–40 000/m^2	Microbivores, fungivores, saprophages, phytophages, omnivores	Christiansen 1990
Insecta	Insects including: flies, beetles, ants, termites	0.5–30 mm	–1 000/m^2 for each group	Microbivores, fungivores, saprophages, phytophages, omnivores, predators, parasites	Wallwork 1970; Dindal 1990; Kosztarab and Schaefer 1990
Vertebrata	Including: amphibians, reptiles, mammals	>40 mm		Predators; phytophages	Wallwork 1970

Biodiversity of soil animals

Representatives of every phylum are found in soil, other than those that are strictly marine (Table F1). Free-living protozoa are most commonly associated with the surface layer of soil and litter, particularly with decomposing plant material in terrestrial ecosystems. Because they are able to live in the very thin water films that surround soil particles they are found most frequently in the smaller pores where moisture usually persists. Terrestrial snails and slugs are common in moist habitats with an abundant food supply and (for snails) with neutral to alkaline soils. Although representatives of 140 genera of these mollusks occur in North America, this group often is ignored by soil zoologists because of their comparative rarity within the soil and because many feed on the vegetative layer above the soil.

Most of the dominant earthworm species in North America, excluding the southern States, are Lumbricidae, which include species of greatest agricultural and economic importance. Many of these Lumbricidae are found worldwide as a result of distribution by humans (Hendrix and Bohlen, 2002). Lumbricidae occur in a wide variety of habitats, but all share a requirement for adequate moisture, and thus rarely occur in dry or desert regions. In North America, the other main family of earthworms, the Megascolecidae, is largely restricted to regions south of the limit of the Wisconsinan glaciation. The smaller relatives of Lumbricidae, the Enchytraeidae, are very sensitive to drought and are most abundant in acid soils with high organic matter content, such as boreal and taiga soils.

Other than Protozoa, nematodes are the most abundant animals in soil and are among the most diverse; about half of known nematode species are found in soil. Most of these are free-living soil inhabitants, but some are the free-living stages of vertebrate and invertebrate parasites (Yeates et al., 1993). All terrestrial nematodes require a small film of water around a soil particle in which to move and reproduce. Various other groups of "worms", e.g., Turbellaria, or flatworms, and Gastrotricha are also found in soil, but are not found in abundance and little is known of their biology. Predaceous species of the land leech family Haemadipsidae are burrowers in soil where they feed on earthworms. They are common and diverse in South America, and two species occur in the southeastern United States.

Most species of the microscopic group, tardigrades, are found associated with moss and lichen, but some species are found in soil. Tardigrades have been placed in various systematic categories and at present are considered a Phylum closely related to either Arthropoda or the aschelminth complex. The ability of tardigrades and nematodes to revive after extended periods of dehydration (anhydrobiosis) may contribute to their distribution throughout the world and to the broad geographic distribution of many cosmopolitan species.

The most species rich category of recorded living organisms is insects, and arthropods other than insects are second only to plants in number of described species. It is difficult to define "soil arthropods", because with few exceptions all arthropod groups have some members in soil. Based on recent syntheses of data about 50 000 species of arthropods are expected to be represented in the soils of North America, of which a little more than half have been described (Kosztarab and Schaefer, 1990; Behan-Pelletier and Bissett, 1992). The groups that contribute most to this species richness in soils of North America are (in order of species richness): Acari (mites), Diptera (fly larvae), Coleoptera (beetles and their larvae), Araneae (spiders), Myriapoda (centipedes and millipedes), Collembola (springtails) and Formicidae (ants). Other common groups of importance in soil include Isoptera (termites), Isopoda (woodlice), Lepidoptera (caterpillars), root feeding bugs such as immature cicadas, aphids and scale insects (Hemiptera), and burrowing crickets (Orthoptera). Mites and collembola are numerically the dominant groups of arthropods in most soils. Mites of the suborder Oribatida (Cryptostigmata) and Collembola, the majority of which are saprophagous and mycophagous, are of particular interest from the standpoint of development and maintenance of soil structure and fertility, because they are so numerous in soil and, as particulate feeders, they produce fecal pellets that contribute to soil microstructure.

A number of mammal species, particularly rodents (e.g., voles (*Microtus*), the gophers (*Geomys* and *Thomomys*), kangaroo-rats (*Dipodomys*)) of North America, ground squirrels (*Citellus*) and rats (*Neotoma*) and the insectivores (e.g., moles (*Talpa*, *Scapanus*)) have burrow systems that may be locally important in soil formation (Wallwork, 1970). Certain lizards have evolved special adaptations for living in soil; for example, some Scincomorpha (skinks) and Anguidae (slow worms) have reduced limbs or are limbless and move in a snake-like manner. The lizard family Amphisbaenidae is permanent soil dwellers as are *Typhlops* snakes.

The diversity of animals that inhabit soils can hamper those without the taxonomic skills to identify the species. Development of interactive, image-based, computerized identification guides to the fauna, such as that of Hunt et al. (1998) for Australian Oribatida, and Walter and Proctor (2004) on Soil Arthropods (http://www.lucidcentral.com/keys/cpitt/public/Mites/Microarthropods/Index.htm) will be used more widely in the future.

Feeding

Animals in soil include detritus feeders, herbivores, phytophages, saprophages, microbivores, bacteriophages, predators on protozoa and nematodes and predators on arthropods (Table F1). Many soil animals feed at more than one trophic level, and many are opportunistic feeders or generalists (Walter et al., 1991). The nature of soil prevents easy access to information on feeding, and the soil fauna is very diverse, thus only a few food webs have been studied in any detail, but they show that food webs in soil are similar in diversity and complexity to those in above ground habitats and in aquatic systems (Moore and De Ruiter, 1991; Scheu and Falca, 2000). Detailed feeding studies, molecular techniques and use of stable isotopes, are making feeding habits of individual species, and the soil fauna in general, more easily measurable (Scheu and Falca, 2000; Meier et al., 2002; Scheu, 2002).

Techniques

Animals that inhabit soils are extremely diverse in size and form, can occur in extremely large numbers and often have an aggregated distribution. Animals are integrated with the complex soil structure, they generally are cryptic in habit, and sampling them is analogous to sampling the total fauna of a tropical forest or a coral reef. Most live at or near the soil surface, but an interesting and diverse soil fauna exists to a depth of 100 cm in certain soils (Kethley, 1990). Techniques for sampling and extracting soil animals vary depending on the group being sampled, their depth in soil, and their association with air or water in soil (Crossley et al., 1991; Coleman et al., 2004). For larger soil animals (macrofauna), such as earthworms, gastropods, myriapods and larger insects, sifting of a known area or volume of soil and handsorting the animals can the simplest and most effective method, but may not collect deep burrowing species (Hendrix, 2000). Pitfall traps and baited modifications of these are used for groups often active on the soil surface, such as spiders, myriapods and adult insects. Smaller soil animals, or mesofauna (200–10 000 μm) and microfauna (less than 200 μm), are not readily visible to the naked eye. They are removed from soil either physically, by flotation, elutriation, or centrifuging, or dynamically in which a chemical or environmental stimulus, such as heat, drives the invertebrates from the soil using a dry-funnel (Berlese, Tullgren, Macfadyen High Gradient, Merchant-Crossley) or wet-funnel (Baermann, O'Connor) (Edwards, 1991; Coleman et al., 2004). As dry funnel methods depend on an active response to a humidity gradient for extraction, they are not efficient in arid soils, for dry-adapted species, or for quiescent individuals, and soil washing and flotation methods are more effective (Walter et al., 1987). Methods for observing soil animals in situ including rhizotrons, minirhizotrons and soil biotrons, linked to microscopes, video cameras and computer image analysis, allow the recording of the interactions of organisms in soil or in culture at a minute spatiotemporal scale (Lussenhop et al., 1991; Coleman et al., 2004).

Soil environment

The association of animals in any particular soil is determined by the physicochemical and biological aspects of the soil environment (Coleman et al., 2004). Soil structure (the arrangement of particles) and texture (relative proportion of particles of different sizes) can be considered the architecture of the soil, and are critical factors for soil animals, both those that burrow, such as earthworms, millipedes, amphibians and mammals, and non-burrowing species. For non-burrowing animals, a critical additional factor is size of pore spaces, which determines the dimensions of animals in any particular soil. In addition, animals are intimately associated with the creation of soil structure, and their activities in turn are governed and limited by this structure (Elliott and Coleman, 1988; Zwart and Brussaard, 1991).

Moisture content is of vital importance to the soil fauna, most needing 95–100% relative humidity to reproduce. However, among populations of microarthropods species with widespread distribution, specimens are found with a range of moisture tolerance from low to high. Collembola, nematodes and tardigrades can enter a desiccated, inactive form as humidity drops, in a process known as anhydrobiosis (Crowe and Madin, 1975).

Soil and litter function as insulators and protect soil fauna from dramatic shifts in temperature. Many soil animals exposed to long periods of cold (for example in arctic, boreal and Antarctic soils) can supercool (Block, 1990), or continue metabolizing at temperatures close to freezing. Testate amoebae, for example, are active and reproduce during the long and cold (–5 to –20 °C) winters in western Canada (Parkinson, 1988). The composition of fauna in any soil also is affected by pH and litter depth (Hågvar, 1990; Ponge, 1991). Biotic factors, such as variation in organic matter content, amount and composition of living and dead roots, fungi and bacteria, fungal, bacterial and root secretions, and the composition of surface vegetation, all have direct and indirect effects on soil animals (Coleman et al., 2004). In addition, the physical environment of the soil affects each of these.

Function of animals in soil

The importance of animals to the soil environment is usually considered to be in the following four areas, (1) soil formation and maintenance of soil structure; (2) decomposition and nutrient release; (3) biological control; and (4) as pests.

Soil formation and maintenance of structure. Soil animals directly and indirectly affect the transport of organic and inorganic materials within and between soil systems. Feeding and burrowing activities of larger soil invertebrates, such as earthworms and termites, substantially mix organic matter and mineral particles and modify the physical properties of soil, which in turn affects water balance in soil, water infiltration rates, and the production of water-stable aggregates (Anderson, 1988; Lal, 1988; Lavelle, 1997). Earthworms have been introduced into soils for their beneficial effects on soil structure. For example, in the Netherlands they were introduced into reclaimed polder to ameliorate growing conditions, and in New Zealand they were introduced into grassland to improve its productivity (Paoletti et al., 1991).

Insect larvae, collembola, millipedes, and oribatid mites feed directly on decomposing leafy or woody vegetation, shred the plant fragments and reorganize humic and fine mineral material into discrete faecel pellets, which help develop microstructure in soil (Pawluk, 1986; Rusek, 1986).

Decomposition and nutrient cycling. The importance of soil fauna in decomposition and nutrient cycling has been the subject of extensive research, and has been reviewed by Seastedt (1984), Lavelle et al. (1997), Mikola et al. (2002) and Wardle and van der Putten (2002). Ecosystem studies demonstrate that 40 to 90% of net primary productivity is metabolized by decomposers. In grasslands, the soil fauna alone can contribute up to 40% of nitrogen mineralization (Elliott et al., 1988). Soil animals directly affect the decomposition process through shredding plant remains, but their main effect is indirect and catalytic, through their interactions with soil microorganisms. By feeding on bacteria, protozoa and nematodes enhance nitrogen and phosphorus mineralization within the soil. Other small soil animals, particularly mites and collembola, stimulate and control fungal growth, distribution and abundance through selective grazing of fungi and dispersal of fungal inoculum (reviewed by Lussenhop, 1992). In addition, they stimulate microbial activity by supplying nutrients in their feces and urine and by reducing competitive stasis among fungi (Moore et al., 1988; Lussenhop, 1992). These effects on microbial growth affect the rate of decomposition and thus nutrient content in soil, which will, in turn, have a positive effect on plant growth.

Unfortunately, measurements of numbers and biomass underestimate the importance of this indirect and catalytic role of soil animals. A clearer picture is presented through microcosm studies in which mass loss, respiration and changes in mineral content can be measured (Huhta et al., 1991; De Deyn et al., 2003). Other techniques include experiments in which known soil animals are added to sterilized soil (Bradford et al., 2002), and exclusion experiments in which specific segments of the soil fauna are either physically excluded or reduced using biocides. Litter bags are the most widely used technique for measuring nutrient dynamics and release during decomposition and its mediation by soil fauna (Coleman et al., 2004).

Biocontrol and beneficial effects. The beneficial effects of soil animals are multiple, but few have been quantified, although more than 90% of pest insects have a stage in soil, potentially the object of biocontrol. The protozoan *Nosema locustae* Canning is used commercially for biocontrol (of grasshoppers in western U.S.) (Klein, 1988). Entomopathogenic nematodes are used as alternatives to chemicals for suppression of soil inhabiting insects with spectacular results (Gaugler, 1988). Mites and collembola that feed on bacteria and fungi carry beneficial fungal and bacterial inoculum to roots, and they can do this through sterile soil (reviewed in Curl and Harper, 1990; Lussenhop, 1992). Mites and collembola by carrying fungal pathogens to roots may also spread disease. However, some pathogenic fungi apparently lack defenses against grazers, and are preferentially grazed by collembola and nematodes, which thus effectively act as biocontrol agents (Curl et al., 1988). Many soil arthropods are nematophagous and are potential biocontrol agents for plant parasitic nematodes (Walter, 1988; Walter and Proctor, 1999). In the future it should be feasible to manipulate nonphytophagous soil fauna and fungal biocontrol agents for optimum protection of plants from root pests, including nematodes and insects.

Through their interactions with microorganisms, soil animals have a positive impact on plant productivity. For example, they considerably increased biomass production and nitrogen content of birch tree seedlings (Huhta et al., 1991). They also can alter plant community structure (Klironomos, 2002; DeDeyn et al., 2003).

Pests. Soil animals can have detrimental effects on the soil system in the following ways. *(a)* Feeding. Some microbivores feed on beneficial fungi, and microbivorous nematodes and some collembola have been shown to affect growth of cultures of ectomycorrhizal fungi (Rabatin and Stinner, 1988; Klironomos, 2002). When their preferred microbial food supply is unavailable Collembola may injure germinating seeds and seedling roots of crops (Curl et al., 1988). However, this can be remedied easily by amending the soil with organic matter, which stimulates the growth of saprophagous fungi. *(b)* Vectoring parasites of vertebrates. Certain genera of oribatid mites, particularly *Scheloribates*, *Oribatula* and *Galumna*, are vectors of anoplocepheline tapeworms, debilitating parasites of sheep and other vertebrates (Denegri, 1993). These mites move up onto the grass stems and are eaten by the sheep as they graze. *(c)* Plant parasites. Many of the nematodes in soil are plant parasites, feeding on roots and also vectoring plant-pathogenic bacteria, viruses, and fungi (Yeates et al., 1997).

Impact of human activities on soil fauna. Human activities, such as pesticide use, monoculture, clear-cutting of forests, peatland drainage, large-scale pollution and urbanization, have had a negative impact on diversity and activity of soil fauna. Tropical soils in particular, are vulnerable to compaction, structural collapse and accelerated erosion (Lal, 1988; Chauvel et al., 1999). Heavy metals can have a lethal effect on soil biota (Paoletti et al., 1991). In contrast, low-till agriculture, return of organic matter to soil, and diversified cropping systems can have a positive effect on diversity. For example, organic manure application and liming reduces soil compaction and increases diversity of decomposer animals such as mites and collembola (reviewed in Potter and Meyer, 1990). In general, any soil management practice that modifies the physicochemical or biological parameters in soil will affect the soil animals (Potter and Meyer, 1990).

Human induced global change has the potential to alter the capacity of soil biota to contribute to ecosystem services (Wolters et al., 2000). Higher levels of CO_2 and N can positively affect components of the soil fauna by increasing net primary productivity. Where global change induces cooling, the soil fauna can be negatively affected, such as nematode populations in the Antarctic (Doran et al., 2002). In contrast, increase in enchytraeid biomass in northern soils associated with increased atmospheric temperatures, could result in a significant increase in soil CO_2 release (Briones et al., 2004).

The sensitivity of many soil animals to environmental pollutants and pesticides facilitates their use as bioindicators of heavy metals and pesticide residues in soil (reviewed by Paoletti et al., 1991). Soil animals are a component of ‘non-target organisms’ and thus can be used effectively to analyze the impact of human perturbation in agriculture, forestry and urban areas (Coleman et al., 2004).

Future developments. The interactions between soil inhabiting invertebrates and microorganisms and their mutual response to changes in the soil environment is, and must continue to be, the focus of soil ecology. These two groups comprise the majority of soil-dwelling biota and they play a critical role in carbon cycling, are the principal agents for the decomposition of organic matter and natural maintenance of soil fertility. Planning and managing land use requires reliable diagnostic parameters for predicting effects such as productivity, stability, and resistance to erosion. Changes in diversity of soil animals are powerful predictive tools that can be used as bioindicators of these effects. Changes in populations and diversity of soil fauna can also indicate environmental disturbance and recovery. Managing soil to optimize productivity in agriculture and forestry without the use of chemicals, to minimize environmental degradation, or to restore degraded soils, will require the use and manipulation of soil animals as natural biocontrol agents and as catalysts in decomposition and nutrient cycling. The core of this management concept is letting “the soil work for us” (Elliott and Coleman, 1988). The working principles are: keeping the soil covered with plants or mulches, avoiding the application of toxic substances, and thus providing ideal working conditions for soil fauna and microorganisms.

Valerie M. Behan-Pelletier and Stuart B. Hill

Bibliography

Adl, S.M., 2003. *The Ecology of Soil Decomposition*, Wallingford, UK: CABI Publishing.

Anderson, J.M., 1988. Invertebrate-mediated transport processes in soil. *Agric. Ecosyst. Environ.*, **23**: 5–21.

Behan-Pelletier, V.M., and Bissett, B., 1992. Biodiversity of Nearctic soil arthropods. *Can. Biodiversity*, **2**: 5–14.

Berlese, A., 1905. Apparachio per raccoglieri presto ed in gran numero piccoli artropodi. *Redia*, **2**: 85–89.

Block, W., 1990. Cold tolerance of insects aand other arthropods. *Phil. Trans. R. Soc. Lond. (B)*, **326**: 613–633.

Bradford, M.A., Jones, T.H., Bardgett, R.D., Black, H., Boag, B., Bonkowski, M., Cook, R., Eggers, T., Gange, A.C., Grayson, S.J., Kandeler, E., McCaig, A.E., Newington, J.E., Setala, H., Staddon, P.L., Tordoff, G.M., Tshcerko, D., and Lawton, J.H., 2002. Impacts of soil faunal community composition on model grassland ecosystems. *Science*, **298**: 615–618.

Briones, M.J.I., Poskitt, J., and Ostle, N., 2004. Influence of warming and enchytraeid activities on soil CO_2 and CH_4 fluxes. *Soil Biol. Biochem.*, **36**: 1851–1859.

Burch, J.B., and Pearce, T.A., 1990. Terrestrial gastropoda. In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 201–310.

Chauvel, A., Grimaldi, M., Barros, E., Blanchart, E., Sarrazin, M., and Lavelle, P., 1999. Pasture degradation by an Amazonian earthworm. *Nature*, **389**: 32–33.

Christiansen, K.A., 1990. Insecta: collembola. In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 965–996.

Coleman, D.C., Crossley, D.A., and Hendrix, P.F., 2004. *Fundamentals of Soil Ecology.* Amsterdam: Elsevier.

Coineau, Y., 1974. Introduction a l'étude des microarthropodes du sol et ses annexes. *Documents pour l'enseignement pratique de l'Ecologie (1).* Paris: Doin, p. 118.

Crossley, D.A., Jr., Coleman, D.C., Hendrix, P.F., Cheng, W., Wright, D.H., Beare, M.H., and Edwards, C.A., eds., 1991. *Modern Techniques in Soil Ecology. Proc. Int. Workshop, University of Georgia, Athens, September 1989.* New York: Elsevier, p. 510.

Crowe, J.H., and Madin, K.A.C., 1975. Anhydrobiosis in nematodes: evaporative water loss and survival. *J. Exp. Zool.*, **193**: 323–334.

Curl, E.A., and Harper, J.D., 1990. Fauna–microflora interactions. In Lynch, J.M., ed., *The Rhizosphere.* New York: John Wiley & Sons, pp. 369–388.

Curl, E.A., Lartey, R., and Peterson, C.M., 1988. Interactions between root pathogens and soil microarthropods. *Agric. Ecosyst. Environ.*, **24**: 249–261.

Darwin, C.R., 1881. *The Formation of Vegetable Mould Through the Action of Worms, with Observations on Their Habits.* London: J. Murray, p. 326. (Numerous subsequent editions.)

Dash, M.C., 1990. Oligochaeta: Enchytraeidae. In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 311–340.

De Deyn, G.B., Raaljmakers, C.E., Zoomer, H.R., Berg, M.P., de Ruiter, P.C., Verhoef, H.A., Bezemer, T.M., and van der Putten, W.H., 2003. Soil invertebrate fauna enhances grassland succession and diversity. *Nature*, **422**: 711–713.

Denegri, G.M., 1993. Review of oribatid mites as intermediate hosts of the Anoplocephalidae. *Exp. Appl. Acarol.*, **17**: 567–580.

Dindal, D., ed., 1990. *Soil Biology Guide.* New York: John Wiley & Sons, p. 1349.

Dondale, C.D., 1990. Litter Araneae (Araneida). In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 477–502.

Doran, P.T., Priscu, J.C., Lyons, W.B., Walsh, J.E., Fountaink, A.G., McKnight, D.M., Moorhead, D.L., Virginia, R.A., Wall, D.H., Clow, G.D., Fritsen, C.H., McKay, C.P., and Parsons, A.N., 2002. Antarctic climate cooling and terrestrial ecosystem response. *Nature*, **415**: 517–520.

Edwards, C.A., 1990. Symphyla. In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 891–910.

Edwards, C.A., 1991. The assessment of populations of soil-inhabiting invertebrates. *Agric. Ecosyst. Environ.*, **34**: 145–176.

Edwards, C.A., and Lofty, J.R., 1977. *Biology of Earthworms.* London: Chapman & Hall Ltd, p. 283.

Edwards, C.A., Stinner, B.R., Stinner D., and Rabatin, S., eds., 1988. *Biological Interactions in Soil.* Amsterdam: Elsevier, p. 380.

Elliott, E.T., and Coleman, D.C., 1988. Let the soil work for us. *Ecol. Bull.*, **39**: 23–32.

Elliott, E.T., Hunt, H.W., and Walter, D.E., 1988. Detrital foodweb interactions in North American grassland ecosystems. *Agric. Ecosyst. Environ.*, **24**: 41–56.

Franz, H., 1950. *Bodenzoologie alz Grundlage der Bodenpflege.* Berlin: Akademie-Verlag, p. 316.

Freckman, D.W., ed., 1982. *Nematodes in Soil Ecosystems.* Austin: University of Texas Press, p. 206.

Freckman, D.W., and Baldwin, J.G., 1990. Nematoda. In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 155–200.

Gaugler, R., 1988. Ecological considerations in the biological control of soil-inhabiting insects with entomopathogenic nematodes. *Agric. Ecosyst. Environ.*, **24**: 351–359.

Hågvar, S., 1990. Reactions to soil acidification in microarthropods: is competition a key factor? *Biol. Fertil. Soils*, **9**: 178–181.

Hendrix, P.F., 2000. Earthworms. In Sumner, M.E., ed., *Handbook of Soil Science.* Boca Raton, FL: CRC Press, pp. C77–C85.

Hendrix, P.F., and Bohlen, P.J., 2002. Exotic earthworm invasions in North America: ecological and policy implications. *Bioscience*, **52**: 801–811.

Hill, S.B., 1985. Soil fauna and agriculture: past findings and future priorities. *Quaest. Ent.*, **21**: 637–644.

Hoffman, R.L., 1990. Diplopoda. In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 835–860.

Huhta, V., Haimi, J., and Setälä, H., 1991. Role of fauna in soil processes: techniques using simulated forest floor. *Agric. Ecosyst. Environ.*, **34**: 223–230.

Hunt, G.S., Colloff, M.J., Dallwitz, M.J., and Walter, D.E., 1998. *An Interactive Key to the Oribatid Mites of Australia.* East Melbourne: CSIRO Publications (CDROM and booklet).

Kethley, J., 1990. Acarina: Prostigmata (Actinedida). In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 667–756.

Kevan, D.K. McE., ed., 1955. *Soil zoology: Proceedings of the University of Nottingham Second Easter School in Agricultural Science.* London: Butterworths, p. 512.

Kevan, D.K. McE., 1968. *Soil Animals.* London: H.F. & G. Witherby Ltd, p. 244.

Kevan, D.K. McE., 1986. Soil zoology, then and now – mostly then. *Quaest. Ent.*, **21**: 371.7–472.

Kevan, P.G., Chaloner, W.G., and Savile, D.B.O., 1975. Interrelationships of early terrestrial arthropods and plants. *Palaeontology*, **18**: 391–417.

Klein, M.G., 1988. Pest management of soil-inhabiting insects with microorganisms. *Agric. Ecosyst. Environ.*, **24**: 337–350.

Klironomos, J., 2002. Feedback with soil biota contributes to plant rarity and invasiveness in communities. *Nature*, **417**: 67–70.

Kosztarab, M., and Schaefer, C.W., eds., 1990. *Systematics of the North American Insects and Arachnids: Status and Needs.* Blacksburg, VA: Virginia Agric. Exp. Station Information Series, p. 247.

Krantz, G.W., and Ainscough, B.D., 1990. Acarina: Mesostigmata (Gamasida). In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 583–666.

Kühnelt, W., 1961. *Soil Biology: With Special Reference to the Animal Kingdom.* (trans. Walker, N.), 3rd edn. of Kuhnelt 1950. London: Faber & Faber, p. 397

Labandeira, C.C., Philips, T.L., and Norton, R.A., 1997. Oribatid mites and the decomposition of plant tissues in Paleozoic coal-swamp forests. *Palaios*, **12**: 319–353.

Lal, R., 1988. Effects of macrofauna on soil properties in tropical ecosystems. *Agric. Ecosyst. Environ.*, **24**: 101–116.

Lavelle, P., 1997. Faunal activities and soil processes: adaptive strategies that determine ecosystem function. *Adv. Ecol. Res.*, **27**: 93–132.

Lavelle, P., and Spain, A.V., 2002. *Soil Ecology.* Dordrecht, The Netherlands: Kluwer.

Lavelle, P., Bignell, D.E., and Lepage, M. 1997. Soil function in a changing world: the role of invertebrate ecosystem engineers. *Eur. J. Soil Biol.* **33**: 159–193.

Lousier, J.D., and Bamforth, S.S., 1990.Soil Protozoa, In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 97–136.

Lussenhop, J., 1992. Mechanisms of microarthropod–microbial interactions in soil. *Adv. Ecol. Res.*, **23**: 1–33.

Lussenhop, J., Fogel, R., and Pregitzer, K., 1991. A new dawn for soil zoology: videoanalysis of root–soil–microbial–faunal interactions. *Agric. Ecosyst. Environ.*, **34**: 235–249.

Macfadyen, A., 1962. Soil arthropod sampling. In Cragg, J.B., ed., *Advances in Ecological Research,* Vol. 1, pp. 1–34.

Meier, F.A., Scherrer, S., and Honegger, R., 2002. Faecal pellets of lichenivorous mites contain viable cells of the lichen-forming ascomycete *Xanthoria parietina* and its green algal photobiont, *Trebouxia arboricola. Biol. J. Linnean Soc.*, **76**: 259–268.

Mikola, J., Bardgett, R.D., and Hedlund, K., 2002. Biodiversity, ecosystem functioning and soil decomposer food webs. In Loreau, M., Naeem, S., and Inchausti, P., eds., *Biodiversity and Ecosystem Functioning: Synthesis and Perspectives.* Oxford: Oxford University Press, pp. 169–180.

Moore, J.C., and De Ruiter, P.C., 1991. Temporal and spatial heterogeneity of trophic interactions within below-ground food webs. *Agric. Ecosyst. Environ.*, **34**: 371–398.

Moore, J.C., Walter, D.E., and Hunt, H.W., 1988. Arthropod regulation of micro- and mesobiota in below-ground detrital food webs. *Ann. Rev. Entomol.*, **33**: 419–439.

Muchmore, W.B., 1990. Terrestrial Isopoda. In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 805–818.

Müller, P.E., 1879. Studier över Skovjord, som bidrag til skovdyrkingens theori. I. Om bogemuld og bogemor pas sand og ler. *Tidsskr. Skovbr.*, **7**: 1–232.

Nelson, D.R., and Higgins, R.P., 1990. Tardigrada. In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 393–420.

Paoletti, M.G., and Pimentel, D., eds., 1992. *Biotic Diversity in Agroecosystems.* Amsterdam: Elsevier.

Paoletti, M.G., Favretto, M.R., Stinner, B.R., Purrington, F.F., and Bater, J.E., 1991. Invertebrates as bioindicators of soil use. *Agric. Ecosyst. Environ.*, **34**: 341–362.

Parkinson, D., 1988. Linkages between resource availability microorganisms and soil invertebrates. *Agriculture, Ecosyst. Environ.*, **24**: 21–32.

Pawluk, S., 1986. Soil micromorphology and soil fauna: problems and importance. *Quaest. Ent.*, **21**: 473–496.

Persson, T., and Lohm, U., 1977. Energetical significance of the annelids and arthropods in a Swedish Grassland Soil. *Ecol. Bull.*, **23**: 1–211.

Phillipson, J., ed., 1977. Methods of study in quantitative soil ecology. *I.B.P. Handbook*, Vol. 18. Oxford: Blackwell, p. 297.

Ponge, J.F., 1991. Food resources and diets of soil animals in a small area of Scots pine litter. *Geoderma*, **49**: 33–62.

Potter, C.S., and Meyer, R.E., 1990. The role of soil biodiversity in sustainable dryland farming systems. In Singh, R.P., Parr, J.F., and Stewart, B.A., *Dryland agriculture: strategies for sustainability. Advances in Soil Science*, Vol. 13. New York: Springer-Verlag, pp. 241–251.

Rabatin, S.C., and Stinner, B.R., 1988. Indirect effects of interactions between VAM fungi and soil-inhabiting invertebrates on plant processes. *Agric. Ecosyst. Environ.*, **24**: 135–146.

Rusek, J., 1986. Soil microstructures – contributions on specific soil organisms. *Quaest. Ent.*, **21**: 497–514.

Scheu, S., 2002. The soil food web: structure and perspectives. *Eur. J. Soil Biol.*, **38**: 11–20.

Scheu, S., and Falca, M., 2000. The soil food web of two beech forests (*Fagus sylvatica*) of contrasting humus type: stable isotope analysis of a macro- and a mesofauna-dominated community. *Oecologia*, **123**: 285–286.

Schwert, D.P., 1990. Oligochaeta: Lumbricidae. In Dindal, D.L., ed., *Soil Biology Guide.* New York: John Wiley & Sons, pp. 341–356.

Seastedt, T.R., 1984. The role of microarthropods in decomposition and mineralization processes. *Ann. Rev. Ent.*, **29**: 25–46.

Shear, W.A., Bonamo, P.M., Grierson, J.D., Rolfe, W.D.I., Smith, E.L., and Norton, R.A., 1984. Early land animals in North America: evidence from Devonian age arthropods from Gilboa, New York. *Science*, **224**: 492–494.

Sherwood-Pike, N.A., and Gray, J., 1985. Silurian fungal remains: probable records of the class Ascomycetes. *Lethaia*, **18**: 1–20.

Tullgren, A., 1917. Ein sehr einfacher Auslese apparat für terricole Tierformen. *Z. angew. Ent.*, **4**: 149–150.

Wallwork, J.A., 1970. *Ecology of Soil Animals.* New York: McGraw-Hill, p. 283.

Wallwork, J.A., 1976. *The Distribution and Diversity of Soil Fauna.* London: Academic, p. 355.

Walter, D.E., 1988. Nematophagy by soil arthropods from the shortgrass steppe, Chihuahuan Desert and Rocky Mountains of the central United States. *Agric. Ecosyst. Environ.*, **24**: 307–316.

Walter, D.E., and Proctor, H.C. 1999. *Mites: Ecology, Evolution and Behaviour.* Sydney/Wallingford: University of NSW Press/CABI, 322 pp.

Walter, D.E., Kethley, J., and Moore, J.C., 1987. A heptane flotation method for recovering microarthropods from semiarid soils, with comparison to the Merchant-Crossley high-gradient extraction method and estimates of microarthropod biomass. *Pedobiologia*, **30**: 221–232.

Walter, D.E., Kaplan, D.T., and Perman, T.A., 1991. Missing links: a review of methods used to estimate trophic links in soil food webs. *Agric. Ecosyst. Environ.*, **34**: 399–405.

Wardle, D.A., and van der Putten, W.H., 2002. Biodiversity, ecosystem functioning and above-ground–below-ground linkages. In Loreau, M., Naeem, S., and Inchausti, P., eds., *Biodiversity and Ecosystem Functioning: Synthesis and Perspectives.* Oxford: Oxford University Press, pp. 155–168.

Wolters, V., Silver, W.L., Bignell, D.E., Coleman, D.C., Lavelle, P., van der Putten, W.H., de Ruiter, P., Rusek, J., Wall, D.H., Wardle, D.A., Dangerfield, J.M., Brown, V.K., Giller, K.E., Hooper, D.U., Sala, O., Tiedje, J., and van Veen, J.A., 2000. Global change effects on above- and belowground biodiversity in terrestrial ecosystems: Interactions and implications for ecosystem functioning. *BioScience*, **50**: 1089–1098.

Yeates, G.W., Bongers, T., De Goede, R.G.M., Freckman, D.W., and Georgieva, S.S. 1993. Feeding habits in Soil Nematode Families and Genera – an outline for Soil Ecologists. *J. Nematol.*, **25**(3): 315–331.

Ziegler, F., and Zech, W., 1992. Formation of water-stable aggregates through the action of earthworms Implications from laboratory experiments. *Pedobiologia*, **36**: 91–96.

Zwart, K.B., and Brussaard, L., 1991. Soil fauna and cereal crops. In Firbank, L.G., Carter, N., Darbyshire, J.F., and Potts, G.R., eds., *The Ecology of Temperate Cereal Fields.* Oxford: Blackwell Scientific Publications, pp. 139–168.

Cross-references

Biodegradation
Degradation
Humic Substances
Microhabitats
Rhizosphere
Soil Biology

FEN

Low land covered wholly or partially with shallow water, or subject to frequent inundations; a tract of such land, a marsh. Fens have a neutral or slightly basic pH, a distinction from bogs, which are acid. A further distinction is that fens are fed by runoff and ground-waters as well as rainwater, whereas bogs are fed only by rainwater.

Cross-reference

Mire Wetland

FERRALITIC

Ferralitic soils are highly weathered and leached soils of the humid tropics enriched in iron and aluminum relative to silica and all major cations. Primary minerals are generally absent except for quartz, and the dominant secondary minerals are some combination of kaolinite, gibbsite, goethite and hematite. In Soil Taxonomy, soils with an oxic B horizon, and in the WRB system, Ferralsols are exemplars. Latosols is an older term for the same kind of soil.

Cross-references

Acid Soils
Acrisols
Ferralsols

FERRALITIZATION

The processes by which ferralitic soils are formed, specifically the enrichment of Fe and Al relative to Si. A soil-forming process characteristic of the humid tropics.

Cross-reference

Biomes and their Soils

FERRALSOLS

These are the classic, red and yellow soils of the humid tropics. The name derives from L. *ferrum*, iron, and *alumen*, alum indicative of the iron and aluminum rich mineralogy of Ferralsols.

Definition

Soils

1. having a *ferralic* horizon at some depth between 25 and 200 cm from the soil surface, and
2. lacking a *nitic* horizon within 100 cm from the soil surface, and
3. lacking an *argic* horizon that has 10% or more water-dispersible clay within 30 cm from its upper boundary unless the soil material has *geric* properties or contains more than 1.4% organic carbon.

General characteristics

Ferralsols are highly weathered soils, strongly to extremely leached, with a clay mineralogy essentially made up of kaolinite and Fe and Al oxides. They are deep to very deep soils. The depth of these soils can vary from 1 to 20 m and the most common depths of the solum (A + B) vary from 3 to 10 m. The soils are very homogeneous in color, texture, structure and mineralogy along the profile, being difficult to distinguish the B horizon that presents gradual and diffuse transitions between the B sub-horizons (Figure F2).

Figure F2 Rhodic Ferralsol in Patos de Minas, Brazil.

Morphology

The texture of Ferralsols varies from sandy loam to clay, with the absence of a significant textural gradient between the A horizon and the top of the B horizon. The structure of loamy and clayey Ferralsols can be formed by moderate to weak subangular blocky aggregates that break up in to highly stable microgranular aggregates. In sandy loam Ferralsols microgranular aggregates dominate between the grains of sand (Figure F3).

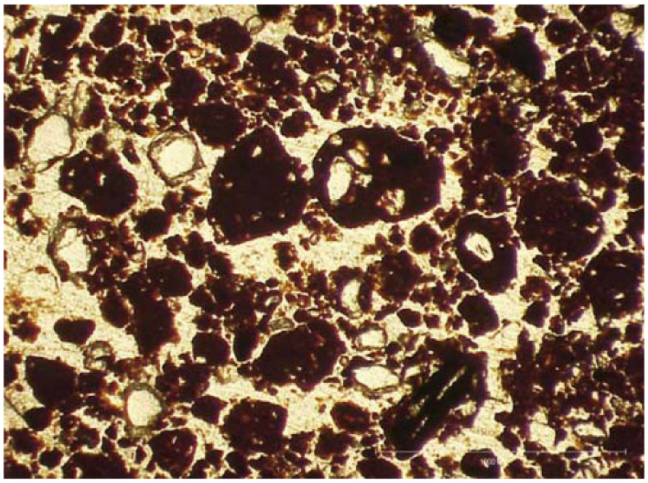


Figure F3 Microaggregation and packing pores of a ferralic horizon.

Parent material

They derive from various parent materials, except those with very high quartz content. Many of these soils are derived from unconsolidated re-worked materials that could have presented ferralic characteristics at their origin. They can also be formed from volcanic ashes. In areas of igneous crystalline parent materials, they are frequently superposed to saprolites which depth can be 3 to 5 times that of the solum. They are typically tropical soils.

Climate

Formation of Ferralsols occurs under climatic conditions that favor both leaching and intense weathering: conditions common in regions with a wet tropical/monsoonal, subtropical or warm temperate climate. Ferralsols that occur in other climates, as those that occur on table mountains in the Brazilian semiarid tropical regions, are remnants of past, more humid climates.

Topography

Ferralsols occur mainly in stable landscapes with low declivity. Old pediplains (from Tertiary to Pleistocene) and their respective erosion/deposition surfaces are the landscapes that present the largest extents of these soils in the humid and semi-humid tropical world (Buol and Eswaran, 2000). Although this is a good generalization, Ferralsols can also occur in hilly and even mountainous landscapes, mainly in perudic humidity regimes.

Genesis

The main soil formation process is ferralitization, or in less intense weathering regimes, fermonosilitization, that leads to a mineralogical assembly with mixtures of kaolinite and iron, aluminum and titanium oxides. They are soils that present less than 4% of weatherable primary minerals in the sand fraction, having, consequently, a very low mineral reserve.

The microaggregate formation of these soils has been the object of much study. Biological activity is implicated, mainly by termites, ants and other animals, and is clearly indicated by channels and biological pores found in the soil matrix. Many authors claim an important role for biological processes in the formation of microaggregates, though others believe that geochemical processes are more relevant. On the whole, the great uniformity of Ferralsols, and their long time of formation, it is reasonable to assume that the activity of the soil fauna is indeed a major factor in the formation of these soils.

Special attention has to be given to termites. These small insects have been around since the Tertiary, and their great ability in transporting soil materials allows them to bioturbate the soil many times over, thereby eliminating any sign of other horizonation processes such as clay migration or argilluviation, that would have stopped during a given physico-chemical context (pH and colloid type). Together with these biological processes, geochemical processes of alteration generate compounds such as iron and aluminum oxides that stabilize the 1:1 clay microaggregates. The activity of termites in the soil bioturbation has been related to medium and small sized particles, leaving the coarse sand and gravel behind. In the passage of time, this may result in the formation of a stone-line. The activity of the termites would occur to the depth of the stone-line. Note, however, that other processes of stone-line formation exist – soil creep in sloping terrain for example.

Lower level units of Ferralsols

Soil color varies from yellow (7,5 to 10YR) to dark red (2YR to 7,5R) and the content of iron oxides from 1 to 70%. Xanthic Ferralsols are yellow, Rhodic Ferralsols red, and Orthic Ferralsols red-yellow. Darker Ferralsols, with a higher accumulation of organic matter (OM) and a more intense and deeper development of the umbric epipedon, are called Humic Ferralsols.

A special type, differing notably from the rest of the Ferralsols, is Plinthic Ferralsol. With drainage restrictions at its base these soils have a clayey layer or horizon, poor in organic matter and rich in iron oxides. It is dense and with low porosity in the upper 125 cm of the soil profile, which limits the circulation of water and can also limit root growth.

Concordance with other classifications

In Soil Taxonomy the different types of Ferralsols correspond essentially with suborders of the oxisols, perox, udox, ustox and torrox except aquox. Other designations for the Reference Group include Latosols (Brazil), sols ferralitiques (France), lateritic soils, ferralitic soils (Russia) and Ferralsols (FAO).

Distribution

The area occupied by Ferralsols is estimated at some 750 million ha, almost all distributed in the humid tropics on the continental shields of South America (Brazil) and Africa (Zaire, southern Central African Republic, Angola, Guinea and eastern Madagascar). Outside the continental shields, Ferralsols are restricted to regions with easily weathering basic rock and a hot and humid climate, e.g., in Southeast Asia.

Map

Figure F4.

Physical and chemical properties

The physico-chemical behavior of Ferralsols can be unusual, as is the case of the Acric Ferralsols, whose CEC is lower than 1.5 $\mathrm{cmol_c\ kg^{-1}}$ clay. These soils, depending on the value of pH, may show charge reversion in the B horizon, from CEC to AEC, and have a very low reserve of nutrients. Independently of whether they are acric or not, and as a consequence of their age and intensity of weathering, they have a very low CEC. Consequently, their fertility will depend on the maintenance of the natural levels of soil OM.

By definition, the clay CEC of a ferralic horizon cannot exceed 16 $\mathrm{cmol_c\ kg^{-1}}$ clay (1 M ammonium acetate, buffered at pH 7). Ferralsols are normally desaturated, dystrophic and commonly have $\mathrm{Al^{3+}}$ dominating the exchange sites. Rarely the soils are eutrophic, in which case they are normally associated with rich parent materials, such as basalt, and with a relatively short time of weathering. As the buffering capacity of these soils is very low, the addition of amendments and fertilizers can render the soils eutrophic, an example of anthropic influences in soil genesis.

Water dynamics, erodibility and degradation

Macropores (structural pores) dominate micropores (textural pores) in the morphology of Ferralsols. This favors a high hydraulic conductivity and low water retention (Figure F5). Even when clay-rich, Ferralsols are well to excessively drained soils, due to the well-developed packing pores that confer a rapid drainage, and that are a consequence a very strongly developed microaggregation. Although these characteristics favor high water infiltration and percolation through the soil profile, it can

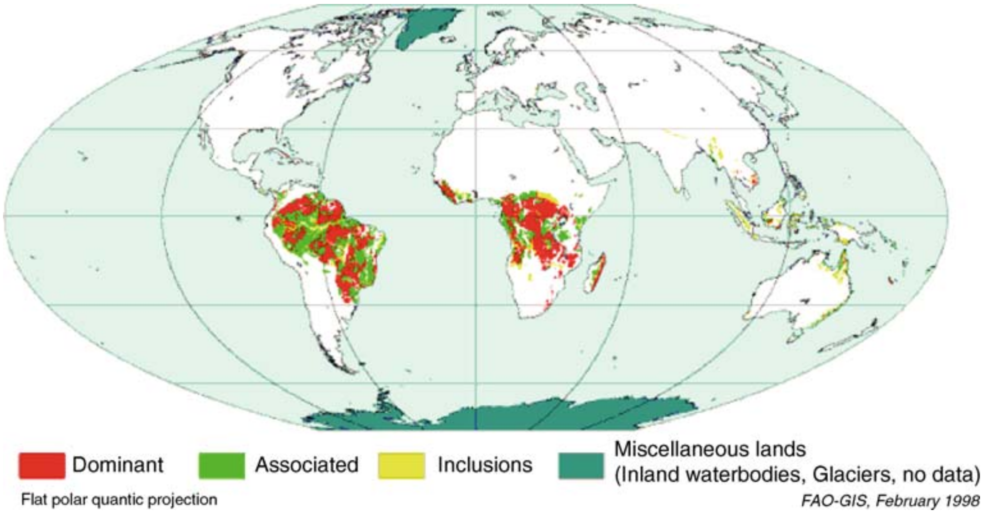


Figure F4 Distribution of Ferralsols in the World (FAO, 2001).

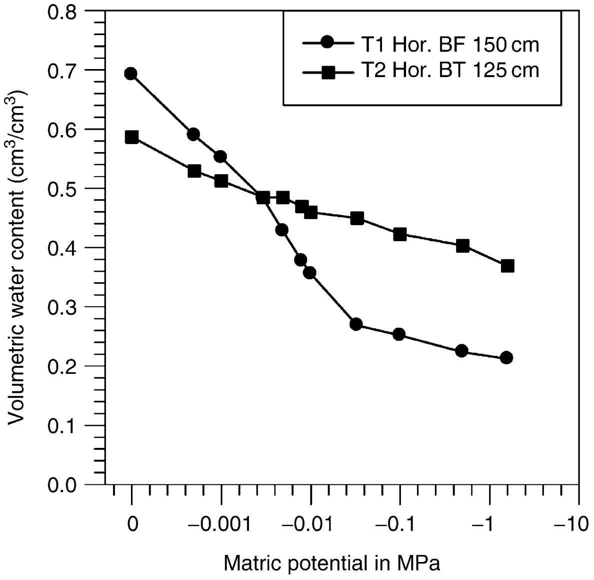


Figure F5 Comparison of the water retention curves between a Bt and a Bf horizon.

Figure F6 Soy beans planted on Ferralsols in Central East region of Brazil (photograph: Alexandre P.B. Franco, 2005).

cause water deficiency problems for the plant population, in extended dry periods or drought.

The high water infiltration allied to the depth of these soils and the relatively flat landscapes on which they develop determine the low erodibility and high soil loss tolerance of Ferralsols. Consequently, erosion-risk is low, thus eliminating the necessity of costly conservation techniques of soil erosion control. In most cases good soil cover management is sufficient to control soil erosion in Ferralsols. Where soil erosion eventually occurs, the high physical homogeneity and the good physical quality of these soils allied, once again, to their depth of solum and their stable landscape position facilitates the recuperation of these soils. In most cases, the recuperation of Ferralsols consists in restoring the soil physico-chemical attributes lost during soil erosion mainly by addition of soil organic matter and other amendments to the soil surface.

Intensive use of Ferralsols may lead to compaction problems. These soils are highly susceptible to compaction due to their aggregate and pore morphology. Compaction occurs by diminishing the void spaces between the microgranular aggregates leading to a consequent increase in bulk density and penetration resistance. Restricting the traffic on these soils, and adding soil organic matter, either directly or using soil covers, helps in recuperation. Mechanical solutions to soil compaction, such as the use of chisels, can be applied in highly compacted Ferralsols.

Use

After being considered for a long time to be soils with a low agricultural potential, Ferralsols in fact respond to highly technical interventions and with high levels of investment. The Brazilian Central Plateau in the region of the Cerrado (Savanna) provides examples. Here, advances in soil amending techniques (liming and gypsum application) and fertilizer management after the 1960s, have resulted in high productivities of soy beans (Figure F6), corn, cotton, sugar cane, coffee, and eucalyptus.

These soils are very friable and are easy to manage, which together with the favorable landscape, facilitate mechanization. As these soils are very porous, present a low CEC and quick drainage, problems with lixiviation of certain nutrients, as K, can occur. On the other hand, they are soils with a strong specific adsorption of P, immobilizing this nutrient mainly those soils with high contents of gibbsite and iron oxides.

Pablo Vidal-Torrado and Miguel Cooper

Bibliography

Buol, S.W., and Eswaran, H., 2000. Oxisols. *Adv. Agron.*, **68**: 151–195.

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

Muggler, C.C., 1998. Polygenetic oxisols on tertiary surfaces, Minas Gerais. PhD Thesis. Brazil: Soil Genesis and Landscape Development, Wageningen Agricultural University.

Cross-references

Acid Soils
Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils
Tropical Soils

FERRAN

See *Cutan*.

FERRI-ARGILLAN

See *Cutan*.

FERRODS

See *Classification of soils: Soil Taxonomy*.

FERROLYSIS

A two-step process of acidification in waterlogged soils. The first step takes place by reduction, with organic matter as the source of electrons:

$$CH_2O + 4Fe(OH)_3 + 7H^+ = 4Fe^{2+} + HCO_3^- + 10H_2O$$

This brings Fe^{2+} into solution, and the consumption of protons, thereby raising pH. The Fe^{2+} displaces Ca^{2+}, K^+ and other cations, on the exchange sites of clay minerals. As pH rises to 5 or 5.5, Al^{3+}-ions hydroxylate and polymerize into ring structures. If these become trapped between layers of the clay structures, hydroxyl-interlayered clays are formed. If the soil dries out, a second step begins. Exchangeable Fe^{2+} is re-oxidized, and precipitates as Fe^{3+}-hydroxide, producing two H^+-ions for each Fe^{2+}-ion oxidized:

$$4Fe^{2+} + O_2 + 10H_2O = 4Fe(OH)_3 + 8H^+$$

A hydrogen clay then forms and is then converted to an Al-Mg clay as H^+ is replaced by cations released from the octahedral layer of the clay structure. At the same time Si is released from the tetrahedral layer. It may be leached or may precipitate in amorphous form as the soil dries out. With the next wet season, the cycle starts anew.

Bibliography

Brinkman, R., 1970. Ferrolysis, a hydromorphic soil forming process. *Geoderma*, **3**: 199–206.

Cross-references

Gleysols
Planosols

FERSIALLITIZATION

Fersiallic pedogenesis, or fersiallitization, is characteristic of regions of hot-wet, and contrasted climates (in which cool wet seasons alternate with hot dry ones – the Mediterranean littoral is a typical example). It is the least weathered of the three stages of weathering recognized by Duchaufour (1982) in such environments, and is characterized by minerals inherited from parent material together with neoformed iron oxides and clays of dominantly 2:1 type. A Bt-horizon is common at this stage. Continued weathering removes the inherited minerals (except for quartz) and the clays are transformed into 1:1 types, and eventually to gibbsite, as the system progresses through the other two stages of weathering, namely ferrugination and ferrallitization.

Bibliography

Duchaufour, P., 1982. *Pedology, Pedogenesis and Classification* (trans. Paton, T.R.). London: Allen and Unwin, 448 pp.

FERTILIZER RAW MATERIALS

All plant nutrients, except nitrogen, are ultimately derived from geological resources. In many developed and developing countries these resources are industrially transformed into fertilizer that is used mainly for agriculture and horticulture. Soil nutrient depletion by cropping ('soil mining') is one of the principal biophysical causes for the downward trend of food production in many parts of the developing world. Farmers use various nutrient inputs, including fertilizers and manures, to reverse this trend and increase soil productivity, food production and food security. In the following the raw materials for the production of fertilizers with the macronutrients nitrogen, phosphorus, potassium as well as the secondary soil nutrient sulfur are reviewed.

Nitrogen

Nitrogen is the only major plant nutrient that is not completely supplied by geological raw materials. The main source of nitrogen is the atmosphere, which is made up of 79.1% nitrogen, 20.9% oxygen and 0.036% carbon dioxide and other trace gases.

Some plants are specialized in 'mining' nitrogen from the atmosphere. Leguminous crops such as beans, groundnuts and soybeans, and leguminous trees, *Leucena* and *Acacia* for example, are able to extract nitrogen from the air with the aid of root bacteria. During this process of biological nitrogen fixation (BNF) symbiotic bacteria 'fix' and convert N from the inorganic elemental form in the atmosphere into organic N-forms available to the host plants.

Synthetic ammonia

Ammonia is produced from water, air and energy. Approximately 77% of the world ammonia production is based on the use of natural gas using the Haber-Bosch process, named after its developers, Fritz Haber and Carl Bosch. The development of the process by the chemist Haber in 1909 and its subsequent technical application by the chemical engineer Bosch has been called the most important invention of the 20th century (Smil, 1999).

Resource of natural gas is used as an energy source and a feedstock for the production of synthetic ammonia. Atmospheric nitrogen is industrially 'fixed' from the air and combined with hydrogen, aided by a catalyst, to produce ammonia, according to the simplified equation:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The process is possible only under extremely high pressure (200 to 400 atmospheres) and high temperature (400 to 650° C) and thus requires large amounts of energy.

Nitrogen for this process is derived directly from the air and the hydrogen is supplied predominantly by means of fossil fuels (hydrocarbons). The Haber-Bosch process is applied in large-scale industrial operations (up to 1500 t NH_3 per day) close to the energy sources, e.g., natural gas fields. Nitrogen from the air is the principal N-raw material for the production of ammonia, which can be either used directly as anhydrous ammonia, and other N and N-P fertilizer products. Ammonia produced by the Haber-Bosch process represents the basis for approximately 97% of all nitrogen fertilizers produced. Nitrogen fertilizer products include anhydrous ammonia, urea, ammonium nitrate, ammonium sulfate, and other N-fertilizers, as well as N-P fertilizers like mono-ammonium and di-ammonium phosphates.

In the first part of the twentieth century, nitrogen fertilizers were mainly produced in North America, Western Europe and Japan. However, in the 1970s, the construction of N-fertilizer plants shifted to large N-fertilizer consuming countries, like China and India, and natural gas-rich countries, specifically countries of the Caribbean and the Middle East. In 2004, developing countries accounted for over 50% of the world's ammonia production of a total of 107 million t (U.S. Geological Survey, 2005).

Environmental aspects of industrial N-production using the Haber-Bosch process

Ammonia production requires large amounts of energy. The fertilizer industries using the Haber-Bosch process use approximately 1% of the world's total energy. The main environmental issue of industrial nitrogen production is the use of hydrocarbon based energy and feedstock sources, principally natural gas. These are finite and non-renewable resources. Over the past 25 years energy consumption of ammonia plants has been reduced from 60 GJ t^{-1} NH_3 to 32–35 GJ t^{-1} NH_3 (UNEP, 1996).

The basic technology of the Haber-Bosch process has not changed for almost a century and has become more energy efficient through improved reactor design, improved catalytic conversion and reduced losses of gases during the process. CO_2 is a by-product of the hydrogen production from natural gas and is required, together with NH_3, for the production of urea ($CO(NH_2)_2$). The losses of the greenhouse gas CO_2 to the environment have been widely reduced in newly erected plants through better engineering. The typical CO_2 emissions from modern ammonia plants are 0.5 t of CO_2 per t of NH_3 (UNEP, 1996).

Natural nitrate resources

The only commercial source of nitrogen from a geological resource is nitrates from the Atacama Desert in northern Chile. Albeit of only minor economic significance in comparison with the synthetic ammonia produced by the Haber-Bosch process, the production of nitrates from Chile provides a natural source of nitrates for specialty crops, greenhouse crops and tobacco.

Nitrate minerals are highly soluble, and as a result there are few deposits occurring in near-surface environments. Small nitrate mineral deposits of local importance are found in cave deposits with soda niter ($NaNO_3$) and niter (KNO_3) being the main naturally occurring nitrate minerals. Nitrates are found at or near the surface in extremely arid, vegetation-free conditions that have persisted for a very long time, such as in the Atacama Desert in Northern Chile. Here, the nitrate accumulations are found in a belt about 30 km wide and 700 km long between the western coastal range and the Andes to the East in closed basins. Economically viable nitrate deposits occur there as layers of 'caliche', a 1–3 m in thick crust under 2–3 m overburden. The nitrate content of the caliche varies but average caliche ore contains 7–25% $NaNO_3$, 2–3% KNO_3, 4–10% NaCl and 10–30% $NaSO_4$, together with various concentrations of Mg, Ca, K, B, and I. To produce one ton of nitrate, it is necessary to mine approximately 16 t of ore at 7% $NaNO_3$. In the Chile nitrate deposits, the nitrate ore is excavated in large-scale operations, crushed, leached in large vats for about 80 hours, concentrated in a cooling circuit, and the nitrate 'melt' (at 325 °C) is sprayed from a prilling tower, where the nitrate solidifies into spherical pellets (prills) during its fall. The finished product contains 98.5% $NaNO_3$.

Smaller accumulations of nitrates are also known from the Nevada desert, from small sedimentary deposits in northern Kenya, and in soils of the Antarctic desert. Long periods of aridity are key factors for the formation of nitrate accumulations, and the lack of vegetation, since plants would consume the near-surface nitrates.

Reserves and resources

Nitrogen resources are extremely extensive as the gas nitrogen forms more than 2/3 of the atmosphere. However, for the industrial production of nitrogen-based fertilizers other finite non-renewable resources are required, the main one being natural gas. The world's natural gas reserves were estimated at 5501 trillion cubic feet in Jan. 2003. Approximately 67% of these natural gas reserves are located in the Middle East and the Russian Federation (Figure F7).

The world's ratio of proven natural gas reserves to production at current levels is between 60 and 100 years, representing the time in which the remaining reserves would last if the present costs and levels of production were maintained.

Natural gas as critical feedstock for the production of N fertilizers, accounting for 70–90% of the cash production costs of nitrogen based fertilizers. There is thus a strong linkage between prices for natural gas and N-fertilizers. North American natural gas prices almost doubled from mid-2002 to mid-2003 (from U.S.$3.65 per million British thermal units (mbtu) to more than U.S.$ 6 per mbtu). This sharp increase in natural gas prices resulted in a steep rise in N-fertilizer prices in the same period, from U.S.$140 to U.S.$250 per t of ammonia and from U.S.$120 to U.S.$210 for urea. However, the increase in N fertilizer prices failed to cover the increased costs of fuel, forcing at least one U.S. company to file for bankruptcy protection in May 2003 (Harben, 2003). In the first half of 2005, the price for North American natural gas ranged from U.S.$6.50 per mbtu to U.S.$7.0 per mbtu and the corresponding price for urea ranged from U.S.$250 to 270 per t (Fertilizer Works, 2005).

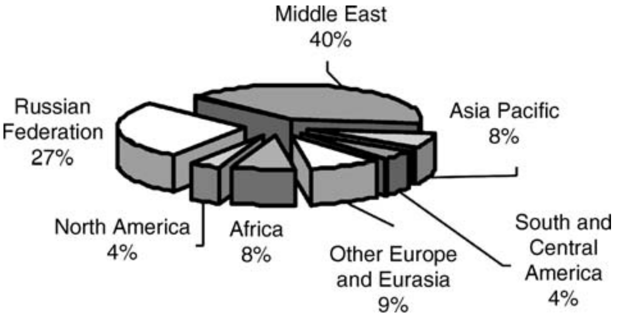


Figure F7 Distribution of proven natural gas reserves (%) in 2004 (source: UNCTAD, 2005, http://r0.unctad.org/infocomm/anglais/gas/market.htm#reserves.

New potential resources as feedstock for the synthesis of ammonia are coal methane and natural gas hydrate. It is expected that coal bed methane found in many major coal basins of the world becomes a significant supply source of methane. It is currently estimated that more than 146 Trillion cubic feet (Tcf) of methane can be recovered in the United States alone. Another potential source for the production of synthetic N-fertilizers is methane from gas hydrates, located in ocean sediments and on land in sediments underlying the Arctic permafrost zone, but there are major technical, economical and environmental barriers to be overcome before these resources may be developed.

Phosphorus

The primary resource to manufacture phosphate fertilizers and phosphate chemicals is phosphate rock, more than 75% of which is of marine origin, 10–15% of igneous provenance and only a small proportion of bird and bat guano. Phosphate deposits are widely distributed throughout the world with the largest resources concentrated in North Africa and the Middle East (Morocco, Tunisia, Jordan), the USA, China and Russia.

The commonest phosphates are the calcium phosphates of the apatite group. Other phosphate minerals include crandallite group minerals, as well as variscite and strengite, which are Al- and Fe-containing phosphates found in secondary weathering environments. The main phosphate minerals of the apatite group are:

- Fluor-apatite ($Ca_{10}(PO_4)_6F_2$), mainly associated with igneous rocks, for example, carbonatites, and mica-pyroxenites,
- Hydroxy-apatite ($Ca_{10}(PO_4)_6(OH)_2$), found mainly in biogenic bone deposit, but also in igneous and metamorphic environments,
- Carbonate-hydroxy-apatites ($Ca_{10}(PO_4, CO_3)_6(OH)_2$), commonly found on islands and in caves, as part of bird and bat guano,
- Francolite ($Ca_{10-x-y}Na_xMg_y\ (PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$), found predominantly in marine environments (whereby x ranges 0−0.35, y ranges 0–0.14 and z ranges to about 1.26 (McClellan and Lehr, 1969)).

The geological environments in which most of the known economic phosphate rock resources occur are:

- sedimentary, mainly shallow marine,
- igneous, mainly associated with alkaline complexes,
- guano and guano related.

Sedimentary phosphate deposits (also known as phosphorites) occur in many regions of the world (Figure F8). They are by far the largest and most easily extractable source of phosphate rock. Sedimentation of most phosphorites took place in shallow coastal and near-shore platform environments. The phosphorites mined today form beds a few decimeters to several meters thick. They are composed of grains of cryptocrystalline francolite together with grains of quartz, clay, and carbonates, and in some places framboidal pyrite. Phosphate deposits are commonly interbedded with shales and chert. The main sedimentary phosphate deposits are located in North Africa and the Middle East, in the United States, China and Russia.

Phosphate deposits of igneous origin make up approximately 10–15% of the global phosphate resources. Most of the extracted igneous phosphate rocks come from Russia, South Africa, Brazil and Finland. Typical rock associations with commercial phosphate accumulations are:

- carbonatites and alkaline complexes,
- biotite pyroxenite complexes,
- anorthosite–gabbro complexes.

The main phosphate bearing carbonatite complexes are located along deep seated tectonic structures such as the rift

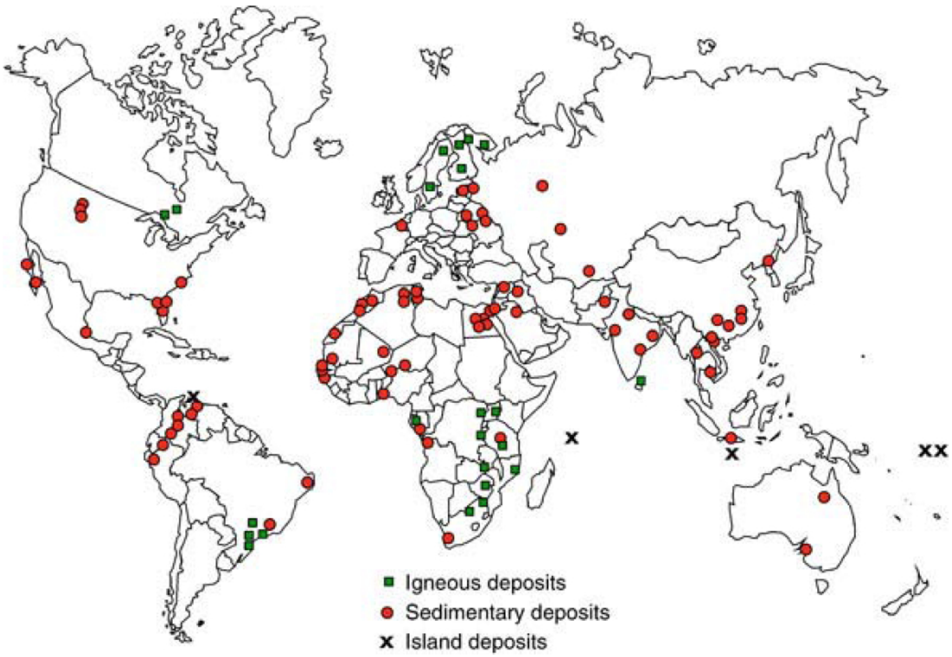


Figure F8 Economic and potentially economic phosphate rock deposits of the world (modified after Van Kauwenbergh, 2003).

systems in Eastern and Southern Africa and along extensive linear fault systems in Brazil, parts of southwest Africa, and Central-East Canada.

Extensive low-grade phosphate deposits are mined from soils or regoliths overlying carbonatites and other igneous phosphate deposits. Tropical weathering of carbonatites for example, results in the decomposition and leaching of the more soluble minerals such as the carbonates, leaving behind apatite, magnetite and other Fe-oxides as residual material. Many of the large igneous phosphate deposits in tropical countries, such as Brazil, Uganda, Sri Lanka, Mozambique, Gabon, but also in Canada (Cargill, Martison) are residual phosphate deposits, derived from igneous and metamorphic phosphate rock deposits. Other economic phosphate deposits are residual soils overlying carbonatites and other igneous phosphate bearing igneous rocks.

Unprocessed phosphate rock was applied in the past, with varying success, directly to the soils. Some of the phosphate rocks, especially highly carbonate-substituted francolites, have shown very good agronomic effectiveness on acid Ca-deficient soils. While the yield response of crops on fertilization with sedimentary phosphate rocks from North Carolina, Tunisia and Peru for example is comparable to triple superphosphate on acid tropical soils (Figure F8), the yield response to sparingly soluble igneous fluorapatite phosphate rock (for example from carbonatites Jacupiranga, Catalão, Tapira in Brazil) is commonly too low to be economically viable and of interest to farmers (Figure F9).

The production of superphosphates involves the reaction of phosphate rock with sulfuric and phosphoric acid. Single superphosphate is produced by the reaction of phosphate rock with sulfuric acid (H_2SO_4). Single superphosphate contains approximately 30% $Ca(H_2PO_4) \cdot H_2O$, about 45% gypsum $(CaSO_4) \cdot 2H_2O$, some 10% calcium biphosphate ($CaHPO_4$), 10% iron oxide, silica and aluminumsilicates, and about 5% water.

The main chemical reaction in the wet (sulfuric acid) process involves pure F-apatite representing phosphate rock concentrate is as follows:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 10nH_2$$
$$\rightarrow 10CaSO_4 \cdot nH_2 + 6H_3PO_4 + 2HF$$

whereby n is 0, 1/2 or 2 depending on the hydrate form in which the Ca-sulfate crystallizes.

In recent years, N-P fertilizers have been the trend, for example Mono-ammonium phosphate (MAP) and Di-ammonium phosphate (DAP), both reaction products of ammonia with phosphoric acid.

Reserves and resources

Phosphate rocks are finite non-renewable resources. In 2004, the global phosphate rock production was 138 million t (U.S. Geological Survey, 2005). The main producing countries expressed as percentage of the total production were: USA (27%), Morocco (17%), China (17%), Russia (8%), Jordan (5%) and Israel (3%) (Figure F10). Reserve and resource estimates of phosphate rock are highly variable. Global reserves (deposits that can be extracted profitably under current economic and technical conditions) are estimated by the U.S. Geological Survey (2005) to be 18 000 million t phosphate rock. Global resources, known reserves plus all other geological mineral resources that may eventually become available are in the range of 50 billion t (U.S. Geological Survey, 2005). Under current technical and economic conditions, and with the current rate of phosphate rock production, the reserves would be sufficient for 130 years. However, when phosphate rock prices increase, some of the resources will become reserves and the life time will increase considerably.

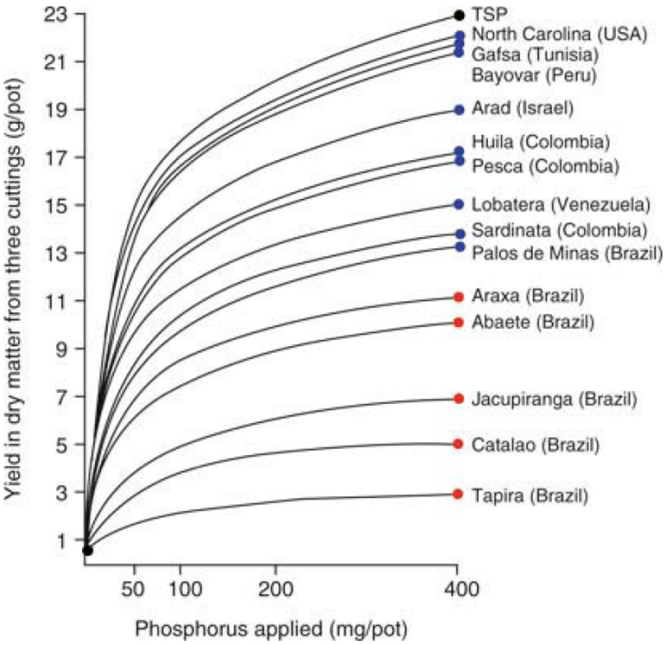


Figure F9 Response of guinea grass to application of various phosphate rock (modified from Léon et al., 1986).

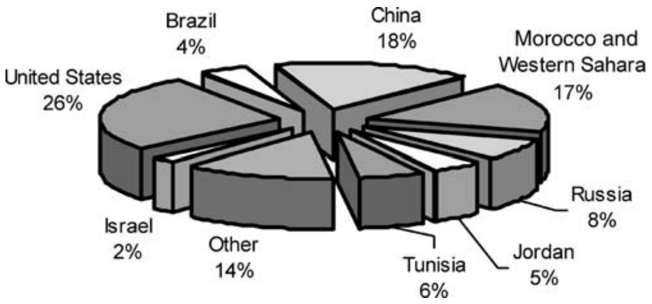


Figure F10 Global phosphate rock production in 2004 (source: U.S. Geol. Survey, 2005).

Environmental aspects of phosphate production

Environmental concerns related to the production of phosphate fertilizers can be classed into several categories, from mining to processing of phosphate rock and finally application of phosphate fertilizers.

The main environmental issues with regards to mining are related to the large footprint of surface extraction, related topographic changes ('moonscapes' due to surface mining), and use of large amounts of water from local aquifers (to lower the groundwater table for open pit mining). In many countries, land reclamation of open pit phosphate mining operations has been mandatory and the reclaimed land is used for agricultural and other land use practices.

Another issue concerns the inherent chemical characteristics of the phosphate ore as some of the natural phosphate rocks have elevated concentrations of Cd, As, and radionuclides. Especially the high Cd concentrations in sedimentary phosphates and in some of the manufactured P-fertilizers are a matter of concern. The high toxicity, bioavailability and potential for plants to accumulate Cd prompted several European countries to introduce legislation that limits the allowable concentration of Cd in phosphate fertilizers.

The production of high-grade soluble phosphate fertilizers involves initially the physical upgrading (beneficiation) of the phosphate ore with the concomitant production of large amounts of mineral wastes, especially sands and clays. This process requires large amounts of water and results in large amounts of phosphorus rich residues, which need storage or re-use.

The processing of phosphate concentrate (28–42% P_2O_5) requires the reaction between phosphate concentrate with acids. Phosphate processing plants in North America and other parts of the world use mainly sulfuric and phosphoric acids for this purpose, in Europe the use of nitric and other acids is prevalent. During the wet-process for the production of triple superphosphate (TSP), large amounts of gypsum are discharged into phospho-gypsum tailings ponds and piles, or in some cases directly into the ocean. During this process, approximately 11–14 t of phospho-gypsum waste is generated for each ton of fertilizer-P (5–6 t phospho-gypsum per ton of P_2O_5). The storage of these often slightly radioactive materials requires extensive areas for safe storage. In Florida, the phospho-gypsum piles reached more than 1 billion t material by the end of 2 000.

Potassium minerals and compounds

Water-soluble potassium containing minerals and compounds are widely known as potash, named after 'pot' and 'ash' derived from the discovery of potassium carbonate (K_2CO_3) in the oluble fraction of hardwood ash. Historically, this 'pot-ash' was largely used in the manufacture of glass and soap as well as a potassium-bearing plant nutrient source.

Today, the term potash refers to a variety of naturally occurring and mined potassium salts as well as manufactured salts that contain the element potassium in a water-soluble form. The main naturally occurring soluble K-mineral is sylvite, potassium chloride (KCl), which in the fertilizer industry and farming communities is also known as 'muriate of potash' (MOP). Other naturally occurring soluble K minerals include langbeinite, a potassium magnesium sulfate – $K_2SO_4 \cdot 2MgSO_4$, carnallite, a hydrated potassium magnesium chloride ($KCl \cdot MgCl_2 \cdot 6H_2O$), and kainite (potassium chloride magnesium sulfate – $4KCl \cdot 4MgSO_4 \cdot 11H_2O$). While the above-mentioned K minerals are naturally occurring, the potash fertilizer 'sulfate of potash' (SOP)–K_2SO_4 is a manufactured fertilizer, a reaction product of KCl and sulfuric acid. This K fertilizer is the principal non-chloride source of potassium that is widely used in high value crops such as fruits, vegetables, coffee, ornamentals and tobacco. The second most important non-chloride K fertilizer used in special applications is KNO_3, which is manufactured at nitrate plants in Chile's Atacama Desert. The process to produce K-nitrate involves the following reaction in solution:

$$NaNO_3 + KCl = KNO_3 + NaCl$$

Resources

Potassium bearing salts are finite non-renewable resources. The main potash deposits are found in large salt deposits, also called 'saline giants', which were formed in restricted shallow marine basins during periods of high evaporation rates from increasingly concentrated seawater. Evaporite sequences commonly start with the precipitation of carbonates and sulfates, followed by halite (NaCl), Mg-sulfates. Potassium-bearing salts precipitate at the end of the evaporation cycle and occur near the top of halite beds as thin layers of either Mg-sulfate rich K salts (e.g., carnallite) or Mg-free minerals such as sylvite.

Other potassium salt deposits are found in rift settings associated with K-rich brines, as well as in sabkha deposits, which are salt accumulations in desert coastal salt flats and tidal flats, and saline inland lakes in arid environments (Williams-Stroud et al., 1994; Kendall and Harwood, 1996).

Potassium-rich deposits are found in many parts of the world (Adams and Hite, 1983). The largest K-salt deposits of the world were formed in epicontinental seas during the Devonian (for example in Canada) and the Permian (in Europe, the Urals of Russia and in the USA). K deposits of Mesozoic and Cenozoic age, are mostly related to rift or paleo-rift environments, for example K deposits in the Rhine Graben of France, and in Congo and Brazil, as well as in Israel and Jordan. The most recent K-salt deposits are found in coastal sabkhas (supra-tidal salt flats) or saline inland lakes, like Searles Lake in the United States.

Bedded potash deposits are either mined by underground methods (for example 'room and pillar' extraction) or through solution mining, utilizing the selective dissolution of potassium chloride. Various upgrading techniques are used to concentrate the potassium salts for use as fertilizers, including solar evaporation, artificial crystallization-evaporation cycles, flotation and electrostatic separation techniques. Some potash salts are won through evaporation of lake and subsurface K-rich brines.

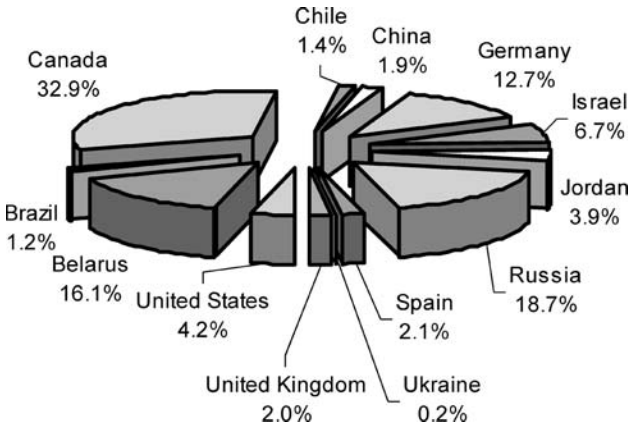


Figure F11 Global potash production 2004 (source: U.S. Geol. Survey, 2005).

The global potash production in 2004 was 30 million t of K_2O equivalent with Canada, Russia, Belarus and Germany being the main producers followed by Israel, Jordan and the United States (Figure F11).

The global reserves of potash are estimated at 8.3 billion t K_2O equivalent. Global resources total about 250 billion t K_2O equivalent (U.S. Geological Survey, 2005).

Environmental aspects of potash production

The main environmental concern associated with potash mining and processing is related to the quantity and composition of the tailings. For example, in the main potash producing region of Canada, Saskatchewan, the total annual production of K salts is 10 million t with associated tailings accumulation of 28 million t of NaCl and clays and disposal of 11 million m^3 saline brines. Engineering challenges are mainly related to the containment of seepage and runoff of brines from tailings into the environment.

Sulfur

Sulfur is regarded as an essential for soil and plant nutrition in two different ways, directly as a plant nutrient and indirectly for its importance in the production of sulfuric acid, which is used in the processing of phosphate rock into phosphate fertilizers.

Many of the currently used fertilizers contain little or no sulfur. In addition, the decreasing amounts of sulfur deposited with acid rain have resulted in lower sulfur deposition and consequently lower sulfur concentrations in soils. The best way to retain sufficient sulfur in soils is through good management of soil organic matter and recycling.

Sulfur in its elemental form is only rarely used in agriculture and horticulture, mainly to reduce alkalinity in soils. More common is the use of sulfur-bearing minerals and products, such as gypsum ($CaSO_4 \cdot 2H_2O$) – sometimes as a component in single superphosphate SSP – or as products such as ammonium sulfate, or potassium sulfate.

Resources

Raw materials for the production of sulfuric acid are derived from discretionary geological resources and non-discretionary sulfur. The latter sulfur is a by-product of the petroleum refining, natural gas processing, coking plants. In addition, sulfuric acid is a by-product from roasting of metal sulfides.

Elemental sulfur

Discrete accumulations of sulfur or sulfur-bearing minerals occur in specific geological environments. Elemental sulfur, or 'native sulfur' is derived from the oxidation of hydrogen sulfide, H_2S, formed by sulfur-oxidizing bacteria in cap rocks of salt domes, and in discrete layered deposits associated with gypsum/anhydrite deposits in hydrocarbon-bearing evaporate basins, e.g., Poland, Iraq, USA. Small amounts of elemental sulfur occur in active volcanic areas, in the Philippines, Indonesia, and Italy.

Native sulfur is extracted by open pit methods or by the so-called Frasch process, a method that uses super-heated water to melt sulfur and then transport it to the surface by compressed air. Many of the native sulfur deposits associated with caprocks of salt domes have been extracted by this method. The recovery of elemental sulfur by the Frasch extraction methods is declining. The last Frasch mine in the United States, the Main Pass Mine, closed in 2000, and today the Frasch process is used only in Poland.

Elemental sulfur is mainly used to produce sulfuric acid for superphosphate fertilizer production. Sulfur is oxidized (with the aid of catalysts) and reacted with water to form H_2SO_4. Elemental sulfur is also used to coat urea (sulfur coated urea) or phosphate rock.

Pyrite

Apart from elemental sulfur, there are other discrete sulfur-bearing geological resources used to produce sulfuric acid for the production of phosphate fertilizers, for example pyrite (FeS_2). Pyrite is found in a number of different geological environments, including volcanogenic, hydrothermal, and sedimentary environments. The main pyrite producing countries in the world are China, Finland, Russia, South Africa and Spain/Portugal. However, only a few pyrite deposits are mined for pyrite alone. Mostly, pyrite is won as a by product from the processing of other earth resources, for example from processing of Cu-Zn-Pb ores as well as gold ores ('flotation pyrites') and from upgrading of S-rich coals ('coal pyrites').

Pyrite with low concentrations of metals is widely used for the production of sulfuric acid. Pyrite is crushed, screened, and separated from other minerals, then oxidized at high temperatures ('roasted') to produce SO_2, which subsequently is converted to sulfuric acid. In recent years, however, the production of sulfuric acid has switched from pyrite roasting to the use of elemental sulfur as the costs to cleaning up the pollution created by pyrite roasting is becoming more and more prohibitive.

In some parts of the world, for example India, sedimentary pyrite is used as a soil amendment, especially on alkaline soils. On these soils the oxidizing pyrite lowers the pH and adds S and Fe. However, pyrite is often contaminated with heavy metals such as nickel, cobalt, copper, lead, arsenic, manganese, and zinc. Ground pyrite has also been used in composting systems, lowering the pH and providing Fe and SO_4^{2-}.

By-product sulfur

Elemental sulfur as by-product from petroleum refining, from natural gas processing and from coking plants accounts for approximately 2/3 of the total sulfur produced. The recovery process of elemental sulfur from petroleum and gas processing, prompted largely by environmental concerns, has turned into a business opportunity. The sour gas (H_2S) recovered by various processes from the refining of petroleum and natural gas is converted to elemental sulfur by the modified Claus process in

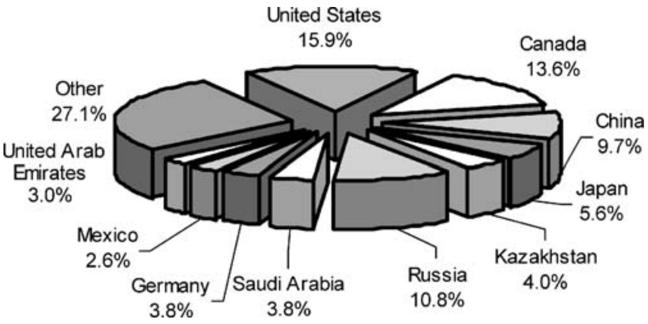


Figure F12 World production of sulfur and sulfur products in 2004 (source: U.S. Geological Survey, 2005).

which H_2S is oxidized under controlled conditions, producing elemental sulfur which is stored in 'formed sulfur' as slates, prills, and briquettes.

$$\begin{array}{c} H_2S + 1.5O_2 \rightarrow SO_2 + H_2O \\ 2H_2S + SO_2 \rightarrow 3S + 2H_2O \\ \hline 3H_2S + 1.5O_2 \rightarrow 3S + 3H_2O \end{array}$$

The total resources of elemental sulfur from evaporite and volcanic sources, as well as sulfur associated with natural gas, with tar sands and metal sulfides amounts to 5 billion t. The sulfur contained in gypsum and anhydrite is 'almost limitless' and the sulfur contained in coal, oil shale and shale rich organic matter exceeds 600 billion t (U.S. Geol. Survey, 2005) (Figure F12).

By-product sulfuric acid

Sulfuric acid as a by-product of Cu-, Pb-, Mo- and Zn-roasters and smelters accounts for approximately 20% of the total production of sulfur in all forms. Major sulfuric acid production as by-product is reported from Canada, China, Japan and the United States.

Sulfuric acid

Most of the sulfur extracted, either as discrete native sulfur, or as pyrite, or indirectly produced as by-product sulfur is converted to sulfuric acid, the prime acid to convert insoluble phosphate rock into soluble P-fertilizers.

In the production of single superphosphate (SSP) the sulfur is part of the gypsum, which makes up approximately 50% of SSP. However, in the more prevalent phosphoric acid production of triple superphosphate and ammoniated phosphate fertilizers (MAP, DAP), the sulfur from the sulfuric acid is finally released in the form of phospho-gypsum, causing major environmental concerns.

Environmental aspects of sulfur production

One of the main environmental challenges related to the production of superphosphates is the safe deposition of phospho-gypsum, a waste material from the production of triple superphosphate and phosphoric acid. Phospho-gypsum piles in Florida, USA, for example have accumulated to a volume of 1 billion t and pose a major environmental concern due to elevated concentrations of P, F, Ra, and radionuclides.

Also, the expected oversupply of elemental sulfur will result in increasing accumulations of stockpiled sulfur, which will cause serious environmental challenges with respect to potential acidification of the immediate surrounding of these stockpiles.

Several companies in North America are investigating the possibilities of re-injecting excess sulfur into sour gas reservoirs, or using the heat produced by burning elemental sulfur and injecting the produced SO_2 into sour gas reservoirs. There are major technical and operational challenges ahead to prevent gases to migrate into nearby aquifers.

Peter van Straaten

Bibliography

Adams, S.S., and Hite, R.J., 1983. Potash. In Lefond, S.J., ed., *Industrial Minerals and Rocks,* 5th edn. New York: AMIE, pp. 1049–1077.

Fertilizer Works, 2005. http://www.fertilizerworks.com/html/market/BasketPrice.pdf.

Harben, P., 2003. Enervating times – cost conundrum for U.S. minerals. *Ind. Min.*, 64–69.

Kendall, A.C., and Harwood, G.M., 1996. Marine evaporites: arid shorelines and basins. In Reading, H.G., ed., *Sedimentary Environments: Processes, Facies and Stratigraphy,* 3rd edn. Oxford, UK: Blackwell Science, pp. 281–324.

Léon, L.A., Fenster, W.E., and Hammond, L.L., 1986. Agronomic potential of eleven phosphate rocks from Brazil, Colombia, Peru and Venezuela. *Soil Sci. Soc. Am. J.*, **50**: 798–802.

McClellan, G.H., and Lehr, J.R., 1969. Crystal chemical investigation of natural apatites. *Am. Mineralogist*, **54**: 1374–1391.

Smil, V., 1999. Detonator of the population explosion. *Nature*, **400**: 415.

UNCTAD (United Nations Conference on Trade and Development), 2004. http://r0.unctad.org/infocomm/anglais/gas/market.htm#reserves.

UNEP (United Nations Environmental Programme), 1996. Mineral fertilizer production and the environment. *Technical Report 26*, 150 pp.

U.S. Geological Survey, 2005. Commodity statistics and information. http://minerals.usgs.gov/minerals/pubs/commodity/.

Van Kauwenbergh, S.J., 2003. Mineralogy and characterization of phosphate rock for direct application. In Rajan, S.S.S., and Chien, S.H., eds., *Direct Application of Phosphate Rock and Related Appropriate Technology – Latest Developments and Practical Experiences.* Proceedings of an International Meeting, International Center for Soil Fertility and Agricultural Development (IFDC), Muscle Shoals, Alabama USA, Special Publications IFDC-SP-37, pp. 28–49.

Williams-Stroud, S.C., Searls, J.P., and Hite, R.J., 1994. Potash resources. In Carr, D.D., ed., *Industrial Minerals and Rocks,* 6th edn. Littleton, CO: Society for Mining, Metallurgy, and Exploration Inc., pp. 783–802.

Cross-references

Agrogeology
Fertilizers, Inorganic
Geology and Soils
Macronutrients
Nitrogen Cycle
Phosphorus Cycle
Potassium Cycle
Soil Fertility
Sulfur Transformations and Fluxes

FERTILIZERS, INORGANIC

Legal definitions of fertilizers vary from state to state and from country to country. In order to bring about uniformity in fertilizer laws in the USA and Canada, a "Model State Fertilizer Bill" (California Fertilizer Association, 1990 and 1998) was drafted by the Association of American Plant Food Control Officials. This bill has been passed into law by many states. In this act "the term *fertilizer* means any substance containing one or more recognized plant nutrient(s) which is used for its plant nutrient content and which is designed for use or claimed to have value in promoting plant growth, except unmanipulated animal and vegetable manures, marl, lime, limestone, wood ashes and other products exempted by regulations by the" individual state or country. The bill specifies further:

1. "A *fertilizer material* is a fertilizer which either:
   a. contains important quantities of no more than one of the primary plant nutrients: nitrogen (N), phosphorus (P) and potassium (K), or
   b. has 85% or more of its plant nutrient content present in the form of a single chemical compound, or
   c. is derived from a plant or animal residue or by-product or natural material deposit which has been processed in such a way that its content of plant nutrients has not been materially changed except by purification and concentration.
2. A *mixed fertilizer* is a fertilizer containing any combination or mixture of fertilizer materials.
3. A *specialty fertilizer* is a fertilizer distributed for non-farm use.
4. A *bulk fertilizer* is a fertilizer distributed in a non-packaged form."

Many details of this model law such as regulations covering registration, labeling, reporting of tonnage, violations, fees, are still regulated regionally. For example

• Total Nitrogen (N)	per cent
• Available Phosphoric Acid (P_2O_5)	per cent
• Soluble Potash (K_2O)	per cent

The actual minimum percentages still vary between regions. The western fertilizer handbook (California Fertilizer Association, 1990) defines *Amendment* as

> "any material, such as lime, gypsum, sawdust or synthetic conditioners, that is worked into the soil to make it more productive. Strictly, a fertilizer is also an amendment, but the term amendment is used more commonly for added materials other than fertilizer."

Manure as "generally, the refuse from stables and barnyards, including both animal excreta and straw or other litter. In some other countries the term manure is used more broadly and includes both farmyard or animal manure and chemical manures, for which the term fertilizer is nearly always used in the United States". *Compost* as "a mixture that consists largely of decayed organic matter and is used for fertilizing and conditioning soil."

In other countries the classification may be altogether different. A minimum concentration is missing and in Germany or in Switzerland for example, the term fertilizer may be used for inorganic, organic fertilizers (including nitrification inhibitors for example) and for other fertilizers such as CO_2. In some European countries the law contains lists of specific fertilizers that are admitted for trade.

This article is concerned only with inorganic fertilizers. It is the custom to include urea, although it is actually the first organic substance known to have been synthesized artificially.

Expressions of fertilizers and their nutrient content

Laws in the United States and in many other countries require that fertilizer bags be clearly marked and the contents of nutrients be listed. A "*complete fertilizer*" contains the three major fertilizer nutrients nitrogen, phosphorus, and potassium and the label on the bag must give the contents in that order in terms of N, P_2O_5, and K_2O. Thus, a 10 : 20 : 10 fertilizer contains 10% nitrogen, 20% P_2O_5, and 10% K_2O. The antiquated oxide description of nutrients is used in the fertilizer industry and in trade for phosphorus and potassium and in some regions also for other nutrients such as calcium and magnesium. In contrast, the scientific community has changed to elemental designations. Some conversion factors are given in Table F2.

Table F2 Conversion factors for changes (a) from the oxide form to the elemental form, (b) from the elemental form to the oxide form

Nutrient	a	b
Phosphorus	2.29	0.436
Potassium	1.20	0.83
Calcium	1.40	0.715
Magnesium	1.66	0.60

Example: CaO (in %) × 0.715 = Ca (in %).

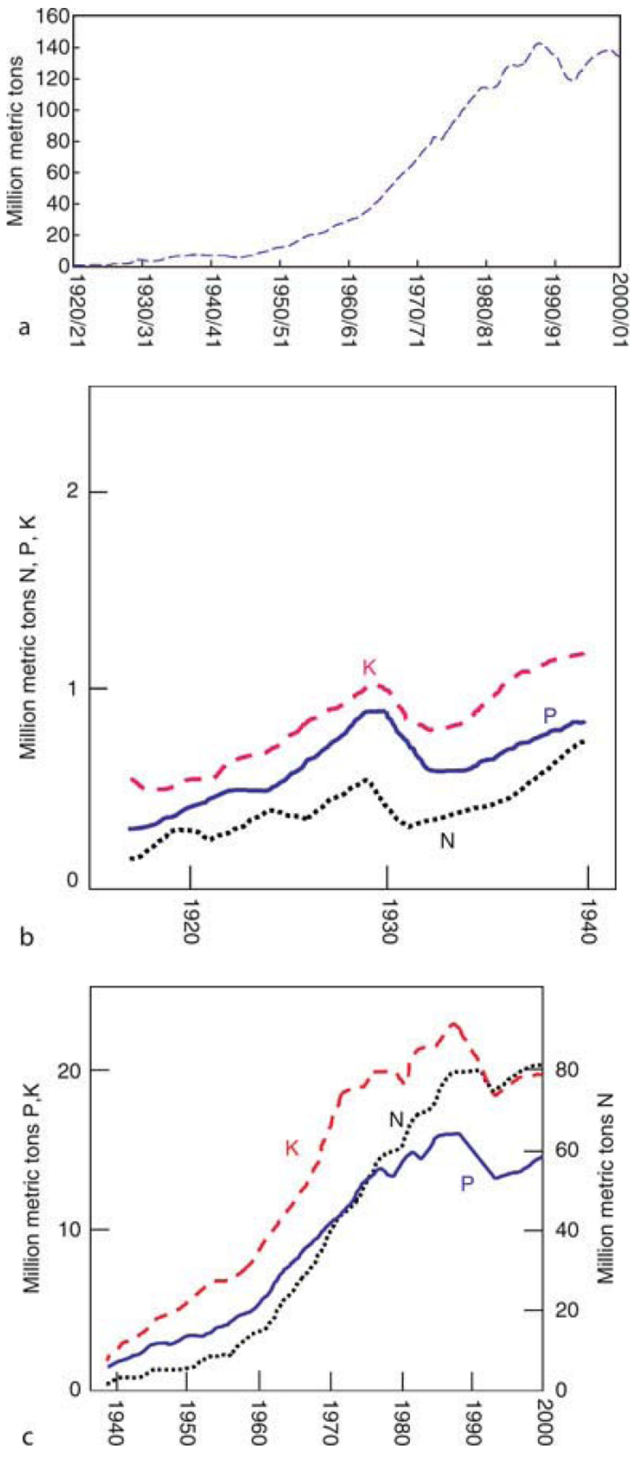
History

Observations that certain substances such as manure stimulate plant growth are as old as agriculture. They are mentioned by ancient Greek writers and the Roman agronomist, Columella emphasizes the need for applying organic and inorganic materials to the soil in order to maintain fertility. A systematic application of inorganic nutrient fertilizers began only after the development of modern chemistry, about two hundred years ago. In 1830, a first boat load of Chile saltpeter (mainly sodium nitrate) arrived in London, but further developments were hindered when a "patent fertilizer" of Liebig proved to be a failure because the nutrients P and K were present in an unavailable form and nitrogen was missing. In the second half of the last century it became possible to produce superphosphate in which the nutrient P is present in a more soluble form. Nitrogen remained a problem and Chile saltpeter was virtually the only inorganic source of this nutrient. Although some inorganic nitrogen fertilizers were being synthesized around the turn of the century, the decisive breakthrough occurred with the synthesis of ammonia by Haber-Bosch early in the 20th century (Cotton et al., 1999; Smil, 1999), through fixation of atmospheric nitrogen:

$$N_2 + 3H_2 = 2NH_3$$

World use of inorganic fertilizers

Worldwide consumption of the nutrient elements is shown in Figure F13a, and is broken down into the components nitrogen (N), phosphorus (P), and potassium (K) in inorganic fertilizers in Figure F13b and F13c. Figure F13b shows that a rather steady increase in fertilizer consumption after World War I was interrupted by the Depression of the early 1930s. Subsequent to World War II (Figure F13c) however, production and consumption, especially of nitrogen, increased greatly, though with a leveling off in the last fifteen years or so. This is a consequence of stagnating consumption in the industrialized countries of Europe and North America. Prior to WW II, phosphorus and potassium were used in greater amounts than nitrogen, but by 1970 the amount of nitrogen used was more than twice that of the other two elements. By 2000, nitrogen consumption was approximately five times that of



phosphorus and four times that of potassium. At present the dramatic increases in fertilizer consumption are seen in the developing countries, particularly China, India, Brazil and Bangladesh (Figure F14).

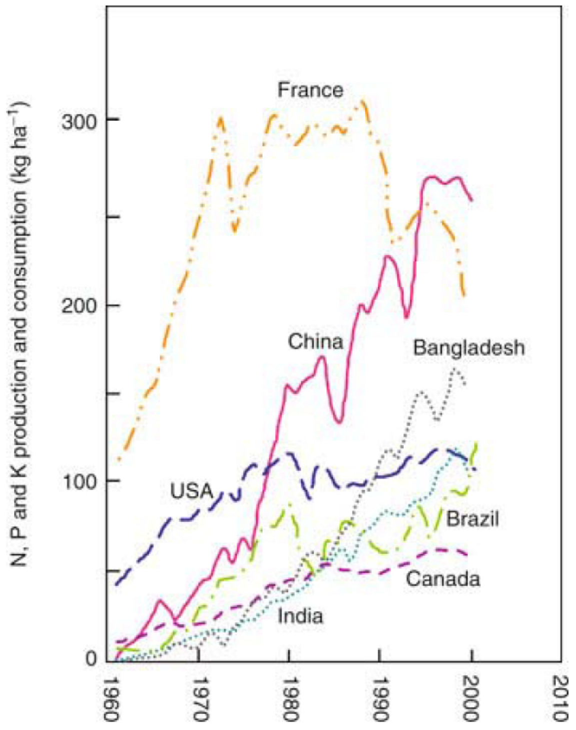


Figure F14 Recent production and consumption of inorganic nitrogen, phosphorus, and potassium fertilizers in developed and developing countries (from http://earthtrends.wri.org).

Diagnosis of fertilizer needs

Fertility maintenance and improvement must rest on information as to which fertilizers in which form are needed, when, at what rates and by which method they should be applied. In practice, a farmer may rely entirely on past experience at the one extreme, or on sophisticated tests of various kinds at the other. The enhanced interest in environmental protection has increased the demand in precise and accurate tools for diagnosing the nutrient status of soils. Risks to the environment are often the result of excessive application of fertilizers that are not fully utilized by plants and, therefore, also represent a financial loss to the farmer. Thus, both farming and environmental protection have the goal of limiting fertilizer applications to the actual needs of the production system. Suitable tests are necessary to inform users about the present state of soil nutrients in order to apply appropriate amounts of the fertilizer. Tests consist chiefly of chemical analyses and biotests. Both kinds of tests are currently in use and neither one is completely successful.

Chemical analyses of soils

Sparks (1996) provides a comprehensive view of the topic.

Analyses for total nutrient contents

Analyses for total nutrient contents usually make use of aggressive reagents such as hydrofluoric acid in order to bring all of a certain element into solution. Total contents are used in the legislation of some countries in order to set safety limits of heavy metals in soils. For example, Table F3 shows values used in the UK and which are similar to those in other jurisdictions. Total

Table F3 Maximum permissible concentrations of potentially toxic elements in soil after application of sewage sludge and maximum annual rates of addition (Pescod, 1992)

Potentially toxic element (PTE)	Maximum permissible concentration of PTE in soil (mg kg^{-1} dry solids)				Maximum permissible average annual rate of PTE addition over a 10-year period (kg ha^{-3})
	pH[1] $5.0 < 5.5$	pH[1] $5.5 < 6.0$	pH 6.0–7.0	pH[2] > 7.0	
Zinc	200	250	300	450	15
Copper	80	100	135	200	7.5
Nickel	50	60	75	110	3
Cadmium	3[5]				0.15
Lead	300				15
Mercury	1				0.1
Chromium	400 (provisional)				15 (provisional)
Molybdenum[4]*	4				0.2
Selenium*	3				0.15
Arsenic*	50				0.7
Fluoride*	500				20

* These parameters are not subject to the provisions of Directive 86/278/EEC.

[1] For soils of pH in the ranges of $5.0 < 5.5$ and $5.5 < 6.0$ the permitted concentrations of zinc, copper, nickel and cadmium are provisional and will be reviewed when current research into their effects on certain crops and livestock is completed.

[2] The increased permissible PTE concentrations in soils of pH greater than 7.0 apply only to soils containing more than 5% calcium carbonate.

[3] The annual rate of application of PTE shall be determined by averaging over the 10-year period ending with the year of calculation.

[4] The accepted safe level of molybdenum in agricultural soils is 4 mg kg^{-1}. However, there are some areas in the UK where, for geological reasons, the natural concentration of this element in the soil exceeds this level. In such cases there may be no additional problems as a result of applying sludge, but this should not be done except in accordance with expert advice. This advice will take account of existing soil molybdenum levels and current arrangements to provide copper supplements to livestock.

[5] For pH 5.0 and above.

contents are also contained in the "transfer coefficient" which is the ratio of the amount taken up by plants to the total content in soils. As an example, this coefficient has been applied to assess the uptake of fallout-radioisotopes or of heavy metal pollutants from soils. However, the total content of a substance in soils is worthless as a tool for diagnosis, because it lacks predictability for future uptake or of environmental hazard. Uptake by plants is related to the *available* amount of nutrients, which usually stands in no relation to the total amount. The availability expresses the ease with which a nutrient or any substance can be taken up by plants.

Selective extractants

These are the most frequently used methods for soil analyses. Numerous procedures using varying ratios of solution to soil have been proposed. Some of the more important methods for general and phosphate soil analyses are given in Table F4. With the exception of a very few isolated cases these methods neither measure the availability nor the total amount available of nutrients. The methods are thus empirical and require calibration. The calibrations may vary significantly from soil to soil.

Methods related to the nutrient uptake mechanism

There are good indications that nutrient uptake is related to concentration in the soil solution. As nutrients are taken up, their concentration in the soil solution falls. A re-supply from the solid phase through ion exchange, dissolution and other processes buffers the soil solution. Figure F15 shows two buffering curves, one of a soil that is highly buffered and one that is less so. The buffering capacity at any point is the slope of the curves:

$$\text{buffering capacity} = \frac{\partial(\text{amount})}{\partial(\text{availability})}$$

This represents the amount that can be removed until the availability changes by one unit. Soil 1 is much better buffered than soil 2 and in order to improve the availability by one unit, a much larger dose of fertilizer is required. Iron and aluminum rich Ferralsols (oxisols) are examples of soils with a high capacity for buffering phosphate.

Schofield (1955) suggested using the chemical activity as a measure of availability, but since in a strict sense, a chemical activity of an ion cannot be determined, the activity of calcium phosphate or the ratio of potassium to the square root of calcium plus magnesium were suggested as measures of the availability. These expressions of availability are correct only if phosphate is taken up together with calcium or if potassium is taken up in exchange for calcium. This is hardly correct. Further complications arise due to the fact that the concentration in the actual soil solution and not in the extract is relevant for the ease of nutrient uptake. It is no simple matter to calculate the natural concentrations from those of the extract made usually with a high water to soil ratio. The uptake of nutrients by plants differs with species; hence the availability is a plant-oriented property. The morphology and physiology of the root account for these differences. A mechanistic model using a number of variables, which affect plant growth, has been developed by Barber (1984).

Biotests

Several biotests, with many modifications, have been developed to assess soil fertility. These tests are conducted in the field, in the greenhouse or in the laboratory. With *field-test plots*, fertilizers are added directly to soils in the field in different amounts and combinations. The plots are selected according to some statistical pattern. The main advantage of field tests is that crops are grown under normal conditions on relatively large areas with few boundary effects. On the other hand, many variables are beyond control. *Pot tests*, which are normally conducted in the greenhouse, provide a more rapid means of assessing fertilizer applications. Climatic conditions are under better control but they may not necessarily be representative for the field. The *Mitscherlich technique*, by which soil is mixed

Table F4 Examples of extractants for general and phosphate-specific soil analyses

Name	Extractant	Nutrient	Reference
Mehlich I	0.05 N $HC1$ 0.025 N H_2SO_4	general	Jones (1990)
Mehlich II	0.2 N CH_3COOH 0.2 N NH_4C1	general	Mehlich (1984)
Mehlich III	0.2 N CH_3COOH 0.25 N NH_4NO_3 0.014 N NH_4F 0.013 N HNO_3 0.001 M EDTA	general	Jones (1990)
	0.01 M $CaCl_2$	general	Houba et al. (1990) Gupta and Hani (1989) Angelone et al. (1991)
Dirks-Scheffer EDTA (ethylene-diaminetetra-acetic acid)	CO_2-saturated water	general	
	0.05 M Na_2EDTA	general	
	1 N NH_4HCO_3 0.005 M DTPA	general	Soltanpour and Schwab (1977)
	0.5 N CH_3COOH 0.5 N NH_4-acetate 0.02 M EDTA	general	Cottenie et al. (1982)
	0.5 N NH_4-acetate 0.02 M EDTA	general	Gupta und Hani (1989)
	Ionexchange resins	P, general	Amer et al. (1955)
Bray I	0.03 N NH_4F 0.025 N $HC1$	P, general	Bray and Kurtz (1945)
Bray II	0.03 N NH_4F 0.1 N $HC1$	P, general	Bray and Kurtz (1945)
CAL (calcium acetate-lactate)	0.1 N Ca lactate 0.1 N Ca acetate	P, general	Schiiller (1969)
AL (ammonium lactate)	0.3 N CH_3COOH 0.1 M NH_4 lactate	P, general	Scheffer and Schachtschabel (1989)
DL (double lactate)	0.4 M CH_3COOH	P, general	Scheffer and Schachtschabel (1989)
	0.02 M Ca lactate 0.02 M $HC1$	P	Van der Paauw (1969), Olsen et al. (1954), Trimm and Farley (1991)
	H_2O, 1:60 0.5 N $NaHCO_3$ 50 g Na_2EDTA	P	
	100 g $(NH_4)_2$ citrate 75 ml NH_4OH (1:1) in 2 l H_2O	P	Scheffer and Schachtschabel (1989)
	isotopic exchange with ^{32}P	P	Scheffer and Schachtschabel (1989)
	0.5 M H_2SO_4		McDonald et al. (1991)
	0.5 M H_2SO_4		Simard et al. (1991)
	Bioassay (e.g., ^{32}P)		
	0.02 M $SrCl_2$ 0.05 M citric acid		
DTPA (diethylentriaminepentaacetic acid)	0.005 M DTPA 0.01 M $CaCl_2$ 0.1 M triethanolamine	P	Micronutrients, Lindsay and Norvell (1978)
EUF	Electro-ultrafiltration	N, general	Nemeth et al. (1988)

with sand in special pots, and the *Neubauer technique*, by which nutrients are extracted by 100 rye seedlings from a soil-sand mixture in a definite ratio, are both used in certain countries.

Microbiological assays

The growth of *Asperqillus niger* is sometimes used as a test for zinc, iron, molybdenum, copper, potassium and phosphorus. *Azotobacter* has been used in assays for calcium, phosphorus, and potassium. *Algae* have been used as test organisms for nitrogen, phosphorus, and potassium.

Diagnosis at the growing plant

The appearance and the chemical composition of the plant growing in the field can be used for diagnostic purposes. *Deficiency symptoms*, which are often typical for a given element, occur when the supply is too low for satisfactory growth. By the time the symptoms appear, however, corrective measures often occur too late to avoid a loss in yield. Pictures of deficiency symptoms are found in a number of compendia (Bold et al., 1984 and later, Bergmann, 1988; Sprague, 1964).

Plant composition provides much information on the amounts of nutrient elements removed by crops (Table F5). The many factors that affect nutrient uptake are thus integrated in the nutrient concentration of plants, which reflects the result of past events and does not necessarily permit predictions of the future. However, crop removal of nutrients (Table F5) has not proved to be a satisfactory basis for estimating fertilizer needs. Better information is obtained from analyses of

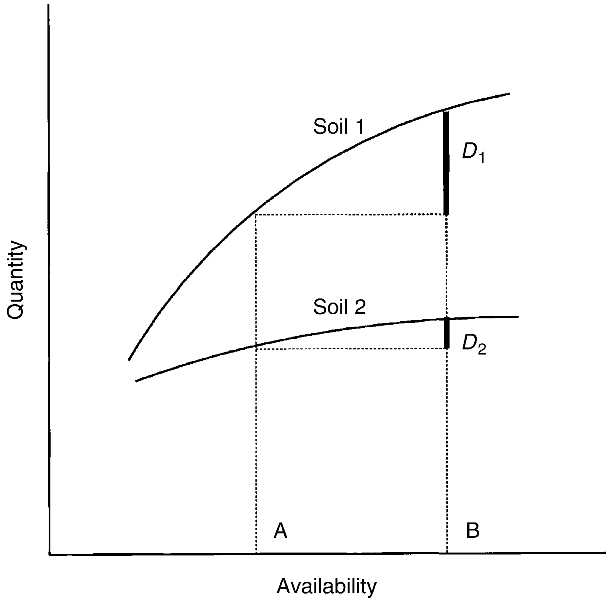


Figure F15 Schematic buffering curves of two soils. A larger quantity of nutrients (*D*) has to be added to the well buffered soil 1 compared to the poorly buffered soil 2, in order to increase the availability from A to B.

Table F5 Approximate yield in t ha^{-1} and nutrient removal in kg ha^{-1}

Plant	Yield	N	P	K	Mg	S
Alfalfa	22.4	672	49	558	59	57
Orchard grass	13.4	336	49	349	28	39
Coastal Bermuda	22.4	560	68	391	56	56
Clover-grass	13.4	332	44	335	34	34
Corn						
grain	12.5	168	43	53	20	17
stover	9.0	130	13	194	53	20
Sorghum						
grain	9.0	134	29	28	16	25
stover	9.0	146	15	158	34	18
Corn silage	71.7	298	56	248	73	37
Cotton		105	19	41	12	8
lint 1.7 To, seed 2–5 Tp		96	12	76	27	26
stalks, leaves, burrs						
Oats						
grain	3.6	90	12	19	6	9
straw		39	7	116	16	12
Peanuts						
nuts	4.5	157	11	33	6	11
vines	5.6	112	8	139	22	12
Potatoes, Irish						
tubers	27.3	194	36	260	16	17
vines	16.4	108	8	246	40	8
Potatoes, Sweet						
roots	16.4	82	17	157	9	–
vines		93	15	139	11	–
Rice						
grain	7.8	86	22	26	9	6
straw	7.8	39	7	112	7	8
Soybeans						
grain	4.0	269	22	78	19	13
straw	7.8	94	8	54	11	15
Tobacco, flue-cured						
leaves	3.4	95	7	144	17	13
stalks	4.0	46	5	95	10	8
Tobacco, burley						
leaves	4.5	194	8	176	24	27
stalks	4.0	129	9	122	12	24
Tomatoes						
fruit	67.2	112	11	200	9	24
Vines	4.9	90	12	112	22	22
Wheat						
grain	5.4	103	22	25	13	6
straw	6.7	47	5	126	13	17
Barley						
grain	5.4	123	20	33	9	11
straw	45	7	107	10	11	
Sugar beets						
roots	67.2	140	7	232	30	11
tops	36	146	12	279	59	39
Sugar cane						
stalks	224	179	44	311	45	60
tops, trash	224	32	256	67	36	

individual tissues such as leaves or petioles. Two approaches are currently popular: the critical level concept and the DRIS system (Diagnosis and Recommendation Integrated System).

The basis of the *critical level system* is represented by Figure F16, which shows the yield as a function of the concentration of an individual nutrient in the tissue. The yield may consist of the total biomass or of that specific part of the plant, which is of commercial interest (e.g., grains or fruit). Leaves or petioles are usually used as tissues. Tissues must be selected very carefully lest their nutrient concentrations are not representative of the nutrient status. In practical applications, foliar analyses are often restricted to recently matured leaves. Note that as the nutrient concentrations increases (Figure F17) in the deficiency range, the yield also increases. At higher nutrient concentrations, yields remain constant over the range of luxury consumption. Yield is depressed again at very high nutrient levels when nutrient concentrations in tissues are large enough to become toxic. The inflection in the curve where the tissue nutrient concentration shifts from deficient to adequate is called the *critical level:* it is often taken as the nutrient concentration at which the yield is 90% of the maximum rather than the maximum itself.

In foliar diagnosis a calibration curve, as shown in Figure F17, is established in greenhouse or field experiments for a particular nutrient and a certain crop. The plants are grown with differing nutrient regimes, some being deficient. Yields are then plotted as a function of foliar nutrient concentrations. The same type of tissues is then sampled in the field, analyzed, and the nutrient concentrations compared to the previously established calibration curve. If foliar analyses fall on the ascending branch of the curve, a nutrient deficiency is indicated and remedies through fertilization are necessary. No information as to the amount of fertilizer required is obtained, but past experience could be helpful. Periodic analyses of tissues in the luxury consumption range can indicate approaching deficiencies. Corrective measures must be taken before production falls.

As the plant ages, foliar nutrient concentrations do not remain constant: those of N and P tend to decrease, those of Ca and Mg to increase. For this reason, ratios of N:P or Ca:Mg or products of Ca and N remain more constant during the development of plants than individual nutrient concentrations. A deviation from an optimum ratio is thus an indicator of a nutritional problem. In the case of ratios, the deviation may be caused either by an excess of one nutrient or by a deficiency of the other. In order to use this system, standard values, i.e., *DRIS norms* for optimum conditions, must first be established. Walworth and Sumner report DRIS

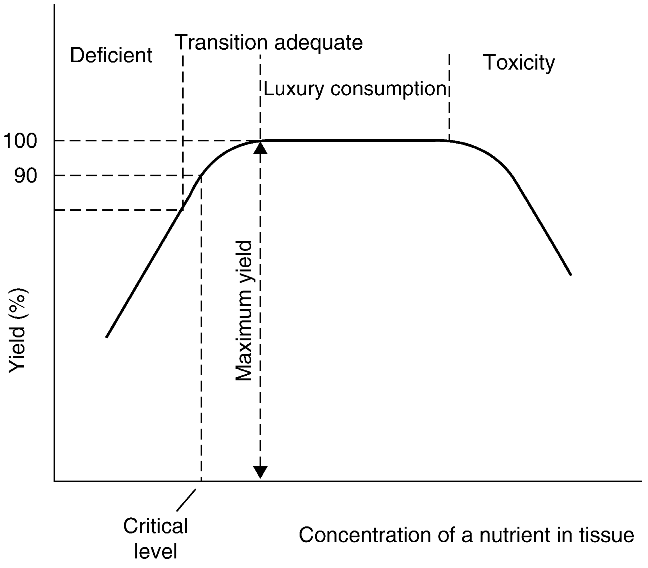


Figure F16 Schematic calibration curve for foliar diagnosis.

Calcium nitrate	Ammonium sulfate	Ammonium sulfate nitrate	Ammonium nitrate	Urea	Calcium cyanamid	Single-, triple superphosph.	Diammonium phosphate	Basic slag	Soft rock phosphate	Potassium chloride	Potassium (+Mg) sulfate	Calcium carbonate (lime)	
	◒	◒	◒	●	◒	●	◒	◒	◒	◒	◒	◒	Calcium nitrate
		○	●	◒	●	○	○	●	○	○	○	●	Ammonium sulfate
			○	●	●	○	○	●	◒	◒	○	●	Ammonium sulfate nitrate
				●	●	◒	○	●	○	◒	◒	●	Ammonium nitrate
					●	●	○	○	○	◒	○	◒	Urea
						●	●	○	○	◒	○	○	Calcium cyanamid
							◒	●	○	○	○	●	Single-, triple superphosph.
								●	○	○	○	●	Diammonium phosphate
									○	○	○	○	Basic slag
										○	○	○	Soft rock phosphate
											○	○	Potassium chloride
												○	Potassium (+Mg) sulfate
													Calcium carbonate (lime)

○ Miscible
◒ Conditionally miscible
● Immiscible

Figure F17 Mixing diagram of fertilizers (after Finck, 1991).

norms for corn: N/P = 10.04, N/K = 1.49, K/P = 6.74 for high yielding plants. A ratio is still considered adequate if it does not deviate by more than 2SD/3 from the optimum value, where SD is the standard deviation of the population from which the optima were determined. Deviations between 2 SD/3 and 4 SD/4 indicate slightly imbalanced nutrient relations. Larger deviation are said to be markedly imbalanced.

For a large number of nutrients A, B, C, ..., N (e.g., K, N, P, Zn, ...), the calculation of a DRIS index has been proposed:

$$A\ \text{index} = \frac{f\left(\frac{A}{B}\right) + f\left(\frac{A}{C}\right) + f\left(\frac{A}{D}\right) + \ldots + f\left(\frac{A}{N}\right)}{z} \tag{84}$$

$$B\ \text{index} = \frac{-f\left(\frac{A}{B}\right) + f\left(\frac{B}{C}\right) + f\left(\frac{B}{D}\right) + \ldots + f\left(\frac{B}{N}\right)}{z} \tag{85}$$

$$N\ \text{index} = \frac{-f\left(\frac{A}{N}\right) - f\left(\frac{B}{N}\right) - f\left(\frac{C}{N}\right) - \ldots - f\left(\frac{M}{N}\right)}{z} \tag{86}$$

and for $A/B < a/b$

$$f\left(\frac{A}{B}\right) = \left[\frac{(A/B)}{(a/b)} - 1\right]\frac{1000}{CV} \tag{87}$$

The various functions are calculated for $A/B \geq a/b$ by

$$f\left(\frac{A}{B}\right) = \left[1 - \frac{(a/b)}{(A/B)}\right]\frac{1000}{CV} \tag{88}$$

A/B: ratio of concentrations of elements A and B in tissues; a/b: ratio of optimum concentrations (of norms), CV: coefficient of variations of norms, z: number of functions contained in the index. A number of researchers consider the DRIS System superior. However, more analytical work is required in comparison to establishing a critical level curve. The more negative an index the greater the nutrient deficiency, relative to the others.

Specific fertilizers and their reactions in soils

Refer to Table F6 for specific fertilizer compositions.

Nitrogen fertilizers

Ammonium fertilizers. Ammonia, synthesized by the Haber-Bosch reaction, is applied as a fertilizer or is used for the synthesis of many other nitrogen fertilizers.

$$3H_2 + N_2 = 2NH_3$$

The process requires energy. Early in the century when the synthesis was developed, coal was utilized to produce hydrogen. Today methane from natural gas is the main source of hydrogen and of energy needed for this process. *Anhydrous ammonia* is a major form of nitrogen fertilizer on the North American continent and in Australia. It is an inexpensive, highly concentrated form, requiring, however, special equipment for its application. The boiling point is −33.4 °C and, therefore, it tends to vaporize rapidly and must be injected 10–15 cm into the soil in order to minimize gaseous losses into the atmosphere. It must either be stored in special tanks that withstand the high vapor pressure at room temperature or the vapors, which escape from a continuously boiling liquid at atmospheric pressure, are recondensed by refrigeration machines and returned to the storage tank. Liquid ammonia can be toxic to plants and should preferably be applied 10–15 days before planting. Due to its toxicity it initially inhibits nitrification for a few days. *Aqua ammonia* is prepared by dissolving anhydrous ammonia in water to give 20–40% NH_3. Due to the lower vapor pressure, it is easier to handle and requires less expensive equipment, but the lower concentration adds to transportation and labor costs. It can be used in liquid fertilizer mixtures together with other nutrients. Upon reaction with sulfuric, hydrochloric, nitric, phosphoric, and "carbonic" acids the respective ammonium salts are formed. *Ammonium sulfate* is the oldest ammonium fertilizer. It consists of white, readily soluble needles, which are barely hygroscopic. It tends, however, to acidify soils. *Ammonium*

Table F6 Elemental composition of fertilizers (in % element)

Fertilizer material	Formula	Elemental composition						
		N	P	K	Ca	Mg	S	Cl
Anhydrous ammonia	NH_3	82.2						
Aqua ammonia	NH_4OH	20.0						
Ammonium sulfate	$(NH_4)_2SO_4$	20.5					23.4	
Ammonium chloride	NH_4Cl	28.0						67
Ammonium nitrate	NH_4NO_3	32.5						
Ammonium nitrate + lime		20.0			7.1	4.1	0.6	
Ammoniated ordinary super-phosphate		3–6	7		16.4	0.3	10.0	0.3
Monoammonium phosphate	$NH_4H_2PO_4$	11.0	20.9		1.4	0.3	2.6	
Diammonium phosphate	$(NH_4)_2HPO_4$	20.0	23					
Ammonium phosphate	e.g., 40% $NH_4H_2PO_4$	16.5	8.7				15.4	
Ammonium sulfate	60% $(NH_4)_2SO_4$							
Nitric phosphates		14–20	6–8.7		5.7–7.1		0.4	
Calcium cyanamid	$CaCN_2$	22.0			38.6	1.5	0.6	0.2
Calcium nitrate	$Ca(NO_3)_2$	15.5			19.3			
Sodium nitrate	$NaNO_3$	16.0						0.6
Potassium nitrate	KNO_3	13.4		37	0.7	0.3	0.2	1.2
Urea	$(NH_2)_2CO$	46.0						
Urea sulfur		40.0					10	
Urea formaldehyde Urea ammonium	35.4% $(NH_2)_2CO$	38.0						
		32.0						
Urea nitrate solution	44.3% NH_4NO_3	15.0	25					
Ammoniumpolyphosphate								
Magnesium ammonium phosphates		8	17			14		
Superphosphate single	50% $CaSO_4$		7.9–8.7		13–15		12	
	30% $Ca(H_2PO_4)_2$							
Superphosphate double, triple	$Ca(H_2PO_4)_2$		18–20		9–10		1	
Liquid phosphoric acid	H_3PO_4		23–24		0.2			
Superphosphoric acid			34					
Diacalcium phosphate	$CaHPO_4$		23		29			
Potassium phosphate			18–22		29–45			
Acidulated bonephosphate			6–6.5					
Rock phosphate			11–17		33–36	3		
Basic slag			3.5–8		32		0.2	
Defluorinated P			9		20			
Phosphate rock						8.4		
Magnesium silicate glass			10		20	0.3		
Rhenania phosphate			10		30			
Calcium metaphosphate	$Ca(PO_3)_2$		27	29–32	19			
Potassium metaphosphate	KPO_3		24–25	56				
Potassium carbonate	K_2CO_3			39				
Potassium bicarbonate	$KHCO_3$			52				48
Potassium chloride	KCl			44				
Potassium sulfate	K_2SO_4			18–22		11	18	
Sulfate of potash magnesia	K_2SO_4 $2MgSO_4$		2		0.7		11–15	

chloride is preferred in rice fields in SW Asia because, under reductive conditions in rice paddies, the sulfate is reduced to hydrogen sulfide. If metal ion concentrations (iron, manganese) are insufficient to precipitate the sulfide, hydrogen sulfide injuries to plant roots could occur. It is suspected that the Akiochi disease (late summer disease) is caused by hydrogen sulfide (Armstrong and Armstrong, 2005). The chloride form is not recommended for chloride sensitive plants such as potatoes or the avocado tree. *Ammonium phosphates* are two-nutrient fertilizers. The monoammoniumphosphate ($NH_4H_2PO_4$) gives an acid solution upon hydrolysis and the diammoniumphosphate ($(NH_4)_2HPO_4$) a basic solution. In the long run, due to nitrification, both fertilizers will cause a more acid soil reaction. *Ammonium nitrates* contain the nutrient nitrogen in two forms. They will be discussed under "nitrate fertilizers". *Ammonium carbonates* have substantial importance as inorganic fertilizers in China. They are also present as carbonates and bicarbonates in guano, a commonly used "organic" fertilizer in the past.

Nitrate fertilizers. Chilean nitrate is mined from natural deposits in Chile. It was the main source of nitrogen when inorganic fertilizers began to be used. It contains valuable impurities of trace elements such as boron (important for sugar beet) and iodine (important for animal nutrition). Synthetic nitrates can be formed directly, e.g., in the light arc or more frequently now through oxidation of ammonia. Both reactions yield energy, although the spontaneous formation of nitrate from air at room temperature is not observed. Synthesized *sodium nitrate* is not different from Chilean nitrate except for the trace elements. Potassium nitrate is a valuable two-nutrient fertilizer, which is used more for intensively grown crops. *calcium nitrate*, in spite of its low nitrogen concentration and its hygroscopicity, is sometimes preferred because of the beneficial effect of calcium on the soil structure. It is synthesized by reacting nitric acid with lime. *Ammonium nitrate* has a relatively high concentration of nitrogen in a more rapidly available form (nitrate) and a form that is exchangeable and, consequently, less subject to leaching (ammonium). It is the preferred fertilizer in some European countries. Upon contact with organic substances such as oils it becomes an explosive. After coating the grains with lime (26%) or gypsum, the material becomes non-explosive, but the nitrogen concentration will then have been reduced.

Amid fertilizers. Amid fertilizers, although organic substances, are usually included with inorganic fertilizers. Urea (carbamide, ($CO(NH_2)_2$)) is a frequently used fertilizer in SE Asia but its popularity is increasing in other countries too. It has the highest N-concentration of any solid fertilizer in use, is highly water soluble and suitable for liquid fertilizers. It is synthesized in a two-step process:

$$2NH_3 + CO_2 \rightarrow NH_2CO_2NH_4 \rightarrow CO(NH_2)_2 + H_2O$$

During urea synthesis at high temperatures a by-product, *biuret* (NH_2)-CO-NH-CO-NH_2), is formed which is toxic to plants but not to animals. Improved methods of synthesis have now eliminated this problem. In soils or on leaf surfaces after foliar applications, urea is hydrolyzed enzymatically (urease) to the ammonium form:

$$2H_2O + CO(NH_2)_2 \xrightarrow{\text{Urease}} (NH_4)_2CO_3 \rightarrow NH_4^+$$

In soils, urea acts more slowly than ammonium or nitrate fertilizers; if sprayed on leaves, it is a quick acting nitrogen supply. Large granules (supergranules) of urea have been tested on rice cultures. Calcium cyanamid. obtained from the reaction of N_2 with calcium carbide (CaC_2), releases nitrogen into the soil through a stepwise uptake of water:

$$CaCN_2 \rightarrow Ca(HCN_2)_2 \rightarrow H_2CN_2 \rightarrow CO(NH_2)_2$$

Urea is then broken down as shown above. It is assumed that other minor pathways of breakdown also occur. Because some intermediates in this reaction sequence are toxic, this fertilizer must be applied two to three weeks before a crop is planted. On account of its toxicity, calcium cyanamid can also be used as a weed killer. One of the intermediates, dicyandiamid ($(NCNH_2)_2$), formed in a minor breakdown pathway inhibits nitrification and is now available as a nitrification inhibitor.

Slow release or controlled release fertilizers

Nitrates are not readily adsorbed on the solid phase of soils and are, therefore, subject to rapid leaching. Ammonium nitrogen can be lost through volatilization. In order to minimize these processes, which represent losses to the farm operator and pollute the environment, fertilizers are being developed that release nutrients at rates as required by the plants. These fertilizers will be discussed later in a separate section.

Reactions of fertilizer nitrogen in soils

Uptake by plants: Both ammonium-N and nitrate-N are readily taken up by plants. With a supply in the form of ammonium, most nutrients are absorbed as cations. Electroneutrality in the external solution is maintained through an increase in protons. Thus, the soil solution in the rhizosphere will become more acid. *Exchange reactions:* Ammonium nitrogen, like other cations, participates in ion exchange in soils. Its position in the lyotropic series (see *Ion exchange*) is similar to that of potassium. Nitrate, on the other hand, is present in the soil solution and thus subject to leaching. Inhibitors of nitrification keep nitrogen for extended periods in the less leachable ammonium form. *Ammonium fixation:* Ammonium ions can be held by a number of 2:1 clays, especially illite, in a non-exchangeable form from where they are released only slowly into the soil solution. Ammonium fixation can be the reason why nitrogen-deficient plants respond only unsatisfactorily to additions of nitrogen fertilizer. Nitrification: Ammonium nitrogen is usually converted to nitrate nitrogen within a few weeks, although some ammonium ions are adsorbed by the exchange complex. Fixed ammonium is converted at a much slower rate. With the conversion of ammonium-N to nitrate-N, the acidity of the soil is increased. This greater acidity (a lower pH) can be desirable in soils that are alkaline in reaction, and it may increase the availability of phosphates; however, lime must be added to most soils in humid regions to offset the increased acidity that follows a prolonged continued use of nitrogen fertilizers in the reduced form. Nitrification is mediated by microorganisms that derive their energy from the processes. It occurs in two steps: the first one from ammonium to nitrite through the activity of a number of microorganisms such as *Nitrosomonas*, the second step is from nitrite to nitrate through *Nitrobacter*:

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^-$$

In soils, the second reaction is usually sufficiently fast to prevent any accumulation of the toxic nitrite. At high pH values, the second reaction is inhibited more than the first

Table F7 Examples of nitrification inhibitors

Names	Chemical composition
Dicyandiamide (DCD)*	$(CH_2N_2)_2$ (Didin)
Carbon disulphide	CS_2
Ammonium thiosulphate	$(NH_4)_2S_2O_3$ (ATS)
Nitrapyrin (NP)(N-Serve)	2-Chloro-6-(trichloromethyl) pyridine
Various triazoles, e.g.	
Etridiazol (ED)	5-Ethoxy-3-trichloromethyl-1,2,4-tridiazol
ATC	4-Amino-1,2,4-triazole · HCl

* IUPAC name: 2-cyanoguanidine.

one, causing accumulations of harmful amounts of nitrite (Chapman and Liebig, 1952). In highly acid soils, nitrification is slow but nevertheless present (Becquer et al., 1990). In order to reduce loss of nitrates through leaching, nitrification inhibitors have been studied intensively over the past decades (Keeney, 1986; Powell, 1986) and two of them, N-Serve and Didin (Table F7) have found considerable application in agriculture. A natural inhibition of nitrification has also been observed, but at least in some situations it is caused by a reaction of ammonium nitrogen with organic substances in the soil, thus depriving the nitrifying microorganisms of their substrate (Kholdebarin and Oertli, 1992). *Denitrification:* Nitrification requires aerobic conditions. Under temporary anaerobic conditions, as might occur after irrigation or a rainfall, nitrates are reduced again. The end-products are N_2O (laughing gas) and N_2 (atmospheric nitrogen). Nitrification itself can also produce some N_2O. *Volatilization:* Ammonium nitrogen tends toward equilibrium with the volatile ammonia:

$$NH_4^+ \rightarrow NH_{3(aq)} + H^+ \;(pK = -9.5)$$

From the law of mass action it is apparent that losses will be greater when the soil pH is high. Losses can be appreciable whenever nitrogen is added to soils in the form of ammonium or ammonia. This includes liquid manures.

Phosphorus fertilizers

Most phosphorus fertilizers are derived from mined *rock phosphates*. The major deposits are concentrated in a few countries (Morocco, USA, Russia, China). The availability of phosphorus from rock phosphate is extremely low in most soils, in acid peat soils it may be a suitable, inexpensive fertilizer, but even so the material must be ground to a fine powder to be effective. *Liquid phosphoric acid* or *green phosphoric acid*, produced by treating rock phosphate with sulfuric acid and separating the liquid phosphoric acid from the calcium sulfate, is occasionally used as a phosphorus fertilizer in irrigated agriculture (fertigation) where it can be added directly to the water. For example, the low pH prevents the clogging up of the fine orifices in drip irrigation. Phosphoric acid is also used in the manufacture of a number of solid fertilizers and liquid fertilizer mixtures. *Superphosphoric acid* is obtained by burning rock phosphate in an electric furnace to produce elemental white phosphorus, which reacts with water to give phosphoric acid. Enrichment with phosphorus pentoxide forms superphosphoric acid, which is actually a mixture of ortho- pyro-, and polyphosphates. It is the basis for phosphorus-rich fertilizers, especially liquid mixtures. The high production costs are partly offset by lower storage and transportation expenses. Fixation of phosphates from polyphosphates seems to be delayed. *Superphosphates* are manufactured by treating rock phosphates with an acid so that different quantities of monocalcium phosphates are obtained:

$$\underset{\text{fluorapatite}}{Ca_3(PO_4)_2\,CaF_2} + 6H^+ \rightarrow Ca(H_2PO_4)_2 + 3Ca^{2+} + 2HF$$

Normal or *single superphosphate* is made by treating rock phosphate with sulfuric acid so that a mixture of monocalcium phosphate and gypsum in about equal amounts is formed. *Triple superphosphate*, also called *treble*, *double* or *concentrated superphosphate*, is manufactured by treating rock phosphate with phosphoric acid. *Nitric phosphates* are formed by treating rock phosphate with nitric acid. The superphosphates tend to react acidic, and hence they are more suitable for basic soils. Ammonium and potassium can also be introduced as nutrient cations which permit the formulation of multinutrient fertilizers of various N:P:K ratios.

Thermophosphates (Rhenaniaphosphates) are manufactured by reacting Rock phosphates with soda and quartz:

$$\begin{aligned} &Ca_5(PO_4)_3F + 2NaCO_3 + SiO_2 \\ &\quad \rightarrow \underset{\text{rhenaniaphosphate}}{3\,CaNaPO_4CaSiO_4} + NaF + 2CO_2 \end{aligned}$$

Rhenaniaphosphate reacts basic and is therefore, more efficient on acid soils. On neutral or basic soils, they react more slowly. Ammoniumphosphates are produced when ammonia is added to phosphoric acid, and various ratios of N:P are commercially available. Diammoniumphosphate is basic at first and monoammoniumphosphate acidic, but due to nitrification the soil pH will drop a few weeks after the addition of either one. *Ammoniumpolyphosphate* is a newer fertilizer that is obtained by treating ammonia with superphosphoric acid. *Ammonium phosphate nitrate* are water-soluble mixtures of ammonium phosphates and ammonium nitrates. *Metal ammonium phosphates* are slow-release nitrogen-phosphorus fertilizers. They are used for special purposes only. *Potassium phosphates* are highly water-soluble and are sold mainly to home gardeners. *Dicalcium phosphate* is not widely used as a fertilizer but rather as a feed supplement to animals. *Metaphosphates:* potassium and calcium salts of the metaphosphoric acid (HPO_3) are high-P fertilizers of a low water solubility. *Biosuper* consists of rockphosphate granules that are coated with sulfur. Microorganisms such as *Thiobacillus thiooxidans* oxidize the sulfur to sulfuric acid, which then reacts with the phosphate granule similar to the production of superphosphates. Elemental *red phosphorus* is a highly concentrated fertilizer that must first be oxidized to orthophosphates before being useful to plants. Some phosphate fertilizers do not originate from phosphate deposits. *Basic slag* (Thomas slag) is a by-product of steel manufacturing by the Bessemer and open-hearth processes. This fertilizer is widely used in some countries and is about as efficient as superphosphate. Its reaction is basic and it contains various other nutrients as contaminations. *Bone products* are offered on the market with various pretreatments. Bone meal fertilizers are more expensive and, therefore, used mainly for high value crops (greenhouses, homes).

Reactions of fertilizer phosphorus in soils

Fertilizer phosphates react rapidly with soils within a few days. Subsequently, further, slower reactions are observed, an aging process that continues for months and even years. In acid soils, fertilizer phosphates are gradually rendered unavailable through the reaction with aluminum and iron compounds. In alkaline soils they are precipitated as calcium phosphates, which then undergo slow changes toward more insoluble forms and perhaps to apatites. Highest solubilities of phosphates are observed at near neutral or slightly acid soil pH values. The fixation of phosphates is a serious problem in the management of many soils. Fixation effects can be reduced by local, concentrated placement of fertilizer and by adjustment of the application rate. A substantial amount of phosphorus is found in the soil organic matter.

Potassium fertilizers

Potassium is mined from marine deposits. Germany has been a leading nation in potassium fertilizer production but larger deposits have been found in Canada. Potassium deposits are usually mixed with sodium, and the potassium must be separated by recrystallization, flotation or by electrostatic separation. *Potassium chloride* (muriate of potash) is the most widely used potash fertilizer. It is sold as *Kainit* (manure salts) of an indefinite composition, or more frequently as 40%, 50%, or 60% potassium as K_2O. It is highly water soluble, and some sensitive plants can be injured by the dissolved salt or by the chloride. Potato, tobacco, grapevine and avocado are examples of chloride sensitive plants, whereas spinach, cabbage and celery are tolerant. *Potassium sulfate* (sulfate of potash) is preferred where chlorides may injure sensitive crops. This fertilizer has good handling properties and contains the plant nutrient sulfur. *Potassium nitrate* supplies both potassium and nitrogen in highly soluble forms, as does potassium magnesium sulfate for potassium, magnesium and sulfur. *Potassium phosphates* are good fertilizers, supplying both potassium and phosphorus. They are not widely used, however, because of high production costs. *Potassium hydroxide* is primarily applied as a special liquid fertilizer.

Reactions of fertilizer potassium in soils

Potassium is adsorbed by the cation exchange complex for which reason leaching losses are normally small. The equilibrium between exchangeable and soluble potassium is rapidly established and potassium taken up by plants from the soil solution is replaced at once by exchangeable potassium. In some soils the added potassium in fertilizers is, however, made less available by fixation between layers of certain clay minerals.

Sulfur, calcium, magnesium

The elements sulfur, calcium, and magnesium, although macronutrients are considered secondary fertilizer nutrients, because they often need not be added. Sulfur is often added when soils are fertilized with nitrogen (ammonium sulfate) or phosphorus (single super phosphate). It is also a major component of acid rain, which might supply more than sufficient sulfur to the soil. Sulfur deficiency is alleviated by the addition of calcium sulfate (gypsum), elemental sulfur, sulfuric acid or by mixed fertilizers that contain sulfur. Calcium is required in soils for satisfactory root growth and nutrient uptake, and it is a valuable ion necessary to keep the soil in adequate physical condition. Calcium deficiencies can be corrected by the addition of calcium containing fertilizers such as calcium nitrate. Calcium deficiency of apples (bitter pit) can be alleviated by sprays of calcium chloride. Adding dolomitic limestone for pH correction not only improves soil calcium but also magnesium (see *Lime*).

Micronutrients

Deficiencies of micronutrients (Table F8) are of great local importance, and various means have therefore been found to correct or avoid them, including applications of the required elements to soils as salts or as components of fertilizers, in foliar sprays, as nails in tree trunks and as chelates. Required quantities are sometimes so small that direct applications to the soil are difficult. For example, the required amount of molybdenum is in the range of 100 g ha^{-1}. Elements such as manganese, zinc, copper and molybdenum have been added to soils in the form of salts or have been incorporated in small quantities into fertilizers of major nutrients.

Foliar sprays have been used successfully for applications of manganese, zinc, and boron (Alexander, 1986). Zinc has also been added by driving galvanized nails into tree trunks and by drilling holes and filling them with salts. Special care is necessary in foliar applications so as not to injure leaves with excessive concentrations of nutrients. This is particularly important with boron because of the narrow margin between deficient and toxic levels.

The treatment of iron deficiency has been a difficult problem. Most soils contain sufficient quantities of iron, which are, however, in an unavailable form. Fertilizing with inorganic salts is of no avail since the iron is rapidly rendered unavailable. Likewise, foliar sprays with inorganic salts have not worked well. In recent years, correcting or avoiding iron deficiencies in plants has become much easier because of chelates. Chelates are compounds in which iron atoms are bound at two or more sites by organic molecules (ligands). Chelates can be applied to soils or used in foliar sprays. Iron-EDTA (ethylene-diamine-tetraaceticacid) has been used since 1951 (Jacobson, 1951). For calcareous soils, iron-EDDHA (ethylene-diamine-di (O-hydroxy-phenylacetic acid)) is a much better source of iron. To be effective, an iron chelate must not decompose spontaneously and must also be resistant to microorganisms in soils. The iron-ligand must be more stable than the ligand with competing ions over a considerable range of pH. At the same time, the chelate must not be so stable that it cannot release iron to growing plants. Chelates of other micronutrients such as manganese and copper are also available.

In nature, plants also supply nutrients that are essential to animals, but not to themselves. It is generally more efficient to supply these nutrients directly to the animal when the food chain fails to provide adequate quantities. In some instances, such nutrients have been enriched in the plant. Small quantities of cobalt salts have been added to superphosphates in Australia and New Zealand. Direct applications of cobalt in foliar sprays are also made, a rate of 250 g ha^{-1} generally being enough to provide adequate levels in subterranean clover for grazing animals. In these cases, cobalt may also have been beneficial to nitrogen fixing soil microorganisms.

Fertilizer-pesticide combinations

Insects cause enormous crop damage by feeding on plants and acting as vectors of important diseases. Weeds cause losses in crop production amounting to several billion dollars per year in the United States alone, and fungal diseases are an enormous problem in crop production. To reduce such losses, chemicals other than fertilizers i.e., *pesticides* are applied to both soils and plants. Depending on their functions, they are known as “insecticides”, “herbicides”, “fungicides”, etc. Combinations of fertilizers and pesticides are applied in some instances to reduce costs of labor. Mixtures may be no more than small amounts of fertilizer included in foliar pesticide spray to add small quantities of nutrients that can be quickly absorbed and result in rapid action. Combinations must be adjusted to the requirement of an individual crop. Field mixing is often preferable to bulk mixing because amounts can then be adjusted to the specific

Table F8 Micronutrient fertilizers

Name	Formula	Content (%)	Remarks
Iron			
Ferrous sulfate	$FeSO_4 \cdot 7H_2O$	19	soluble, rapid oxidation of Fe and precipitation as $Fe(OH)_3$
Ferric sulfate	$Fe_2SO_4 \cdot 4H_2O$	23	soluble, precipitation of $Fe(OH)_3$
Ferrous ammonium sulfate	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	14	soluble, precipitation of $Fe(OH)_3$ after oxidation of Fe
Iron frits	A fritted glass	20–40	slow release
Iron chelate	NaFeEDTA	5–14	soluble, ethylenediamintetraacetate
Iron chelate	NaFeHEDTA	5–9	soluble, N-hydroxyethylethylenediamin triacetate
Iron chelate	NaFeEDDHA	6	soluble, ethylenediamine di(o-hydroxy-phenylacetate)
Iron chelate	NaFeDTPA	10	
Iron lignosulfonates		50–80	
Boron			
Boric acid	H_3BO_3	17	soluble
Borax	$Na_2B_4O_7 \cdot 10H_2O$	11	soluble
Colemanite	$Ca_2[B_3O_4(OH)_3]_2 \cdot 2H_2O$*	10–(16)	low solubility
Solubor	$Na_2B_4O_7 \cdot 5H_2O + Na_2B_{10}O_{16} \cdot 10H_2O$	20	partially dehydrated borax
Boron frits	Fritted glass	2–6	slow release
Manganese			
Manganese sulfate	$MnSO_4(1 \text{ or } 4)H_2O$	23–28	soluble, fast action
Manganese chloride	$MnCl_2$	17	soluble, fast action
Manganese chelate	MnEDTA	5–12	soluble, fast action
Manganese lignosulfate		5	soluble, fast action
Manganous oxide	MnO	41–68	insoluble
Manganese frits	Fritted glass	10–35	slow release
Zinc			
Zinc chloride	$ZnCl_2$	48–50	soluble
Zinc sulfate	$ZnSO_4 \cdot H_2O$	36	soluble
Zinc sulfate	$ZnSO_4 \cdot 7H_2O$	23	soluble
Zinc nitrate	$Zn(NO_3)_2 \cdot 6H_2O$	22	soluble
Basic zinc sulfate	$ZnSO_4 \cdot 4Zn(OH)_2$	55	low solubility
zinc oxide	ZnO	50–80	insoluble
Zinc chelate	Na_2ZnEDTA	14	soluble
Zinc chelate	Na_2ZnHEDTA	9	soluble
Zinc chelate	NaZnNTA	9	soluble, nitrilotriacetate
Zinc lignosulfate		5–8	
Copper			
Cupric chloride	$CuCl_2$	47	soluble
Cupric sulfate	$CuSO_4 \cdot H_2O$	35	soluble
Cupric sulfate	$CuSO_4 \cdot 5H_2O$	25	soluble
Basic cupric sulfates	$CaSO_4 \cdot 3Cu(OH)_2$	13–53	low solubility
Cupric oxide	CuO	75	insoluble
Cuprous oxide	Cu_2O	89	insoluble
Copper chelate	Na_2CuEDTA	13	insoluble
Copper chelate	NaCuHEDTA	9	soluble
Copper lignosulfonate		5–8	soluble
Molybdenum			
Sodium molybdate	$Na_2MoO_4 \cdot 2H_2O$	39	soluble
Ammonium molybdate	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	54	soluble
Molybdenum trioxide	MoO_3	66	low solubility
Molybdic acid	$H_2MoO_4 \cdot H_2O$	53	low solubility
Molybdenum frits	Fritted glass	20–30	slow release
Chlorine			Deficiencies are extremely rare. Possible fertilizers are KCl, NaCl, $CaCl_2$,NH_4Cl

* Different formulas are given by Mortvedt (1991), Martens and Westermann (1991). Here, the formula of Cotton et al. 1999 has been used.

situation. Chemicals of both kinds must be compatible so as to form homogeneous mixtures suitable for application. A concern in mixing fertilizers and pesticides is that the latter may represent health hazards. In many countries fertilizer-pesticide combinations must be registered with appropriate government agencies.

Controlled-release fertilizers

The control of nutrient release from fertilizers assures plants of a continuous supply of nutrients, lowers leaching losses, reduces groundwater contamination, volatilization, denitrification and pollution of the atmosphere. It permits a single, labor-saving application of large quantities of nutrients without danger of salt injury (Oertli, 1980). Slow-release fertilizers are especially desirable for nitrogen, phosphorus and, to a lesser extent, for potassium. Losses of nitrogen due to leaching and volatilization are lessened, fixation rates of phosphorus are reduced. There are several methods of regulating the release of fertilizer nutrients. These include: coating fertilizer grains with a diffusion barrier between nutrients and soil (coats of dicyclopentadiene plus an oil derived from soybean seeds or from linseed, sulfur, latex etc.), using organic compounds that break down slowly to release nitrogen (urea formaldehydes, crotonylidene diurea, oxamid, dicyandiamid, isobutylidenediurea, etc.), applying inorganic compounds of low solubility (metal ammonium phosphates, glassy frits of micronutrients); and adding processed waste products such as ammoniated sawdust or nitrogen enriched oxidized coal. Some control of nutrient release is possible through use of inhibitors of microbial activity. Nitrification inhibitors, for example, reduce leaching losses by keeping nitrogen in the exchangeable ammonium form. Controlled-release fertilizers must meet additional requirements in addition to those of regular fertilizers. The additional constituents, for example, must never produce toxic by-products and the release rate must be predictable, never exceeding the tolerance limits of a specified crop. A disadvantage of these fertilizers is that the release of nutrients continues frequently in the absence of crops, thus leading to salinity problems (Oertli, 1980).

Many other products that have been used as nutrient supplies show slow release activities. Table F9 lists some of the more important organic materials (see *Fertilizers, organic*).

Mixed fertilizers

A *complete fertilizer* contains the three nutrient elements nitrogen, phosphorus and potassium. Mixed fertilizers allow more uniform and balanced fertility management with reduced application costs. During the past decades, the use of bulk-blended dry fertilizers has greatly increased. Many fertilizers are compatible in blends, but some materials should not be mixed, for example urea and ammonium nitrate, which form hygroscopic mixtures (Figure F17). Materials that are blended together must have similar particle size distributions to avoid resegregation.

Mixed liquid fertilizers are relatively new. The mixtures are produced either by dissolving various fertilizer materials in water or by neutralizing phosphoric acid with anhydrous ammonia followed by additions of more nitrogen and potassium carriers. Suspension fertilizers (slurries) are liquid fertilizers in which nutrients are stored, shipped and even applied in concentrated forms exceeding the solubilities of some salts. Technologies have been developed to maintain homogeneous suspensions. The applications require special equipment. Liquid fertilization (fertigation) permits greater variation in mixing nutrients and thus better adjustment to requirements of a particular situation than bulk blending where usually only a few standard mixtures are available. Labor costs are lower, application rates higher, and combined applications with pesticides are possible. On the other hand, large quantities of water have to be transported and some fertilizers are unsuitable for liquid fertilization.

Timing and rate of fertilization

Successful fertilization requires that the right fertilizer be placed properly at optimum rates. Sufficient quantities of nutrients of an adequate availability should be present for crop production. The decision on how to proceed depends on the crop species and cultivar, availability of labor and equipment, soil conditions, weather and climate and also on the economic goal. Plant species differ in their requirements for nutrients as well as in their ability to extract native nutrients from the soil. Fertilization practices must be adjusted accordingly. Wet soils

Table F9 Average composition of some natural organic materials

Organic material	Percent composition							
	N	P	K	Ca	Mg	S	Cl	Organic
Activated sewage sludge	6.0	1.0		1.8	0.9	0.4	0.5	
Blood, dried	13.0			0.4			0.6	
Bone meal (raw)	3.5	19.8		22.5	0.6	0.2	0.2	
Bone meal (steamed)	2.0	12.2		23.6	0.3	0.2		
Castor pomace	6.0	0.6	0.4	0.4	0.3		0.3	
Cacao meal	4.0	0.6	2.1	0.4	0.6			
Cacao shell meal	2.5	0.4	2.5	1.1	0.3			
Cacao tankage	2.5	0.6	1.0	12.0				
Cottonsead meal	6.6	1.1	1.2	0.4	0.9	0.2		
Fish scrap (acidulated)	5.7	1.3		6.1	0.3	1.8	0.5	
Fish scrap (dried)	9.5	2.6		6.1	0.3	0.2	1.5	
Garbage tankage	9.5	0.6	0.8	3.2	0.3	0.4	1.3	
Peanut meal	7.2	0.6	1.0	0.4	0.3	0.6	0.1	
Peanut hull meal	1.2	0.2	0.7					
Peat	2.7			0.7	0.3	1.0	1.1	
Peruvian guano	13.0	5.5	2.1	7.9	0.6	1.4	1.9	
Process tankage	8.2			0.4		0.4		
Soybean meal	7.0	0.5	1.3	0.4	0.3	0.2		
Tankage, animal	7.0	4.3		11.1	0.3	0.4	0.7	
Tabacco stems	1.5	0.2	4.2	3.6	0.3	0.4	1.2	
Whale guano	8.5	2.6		6.4	0.3			
Manure source								
Dairy manure	0.7	0.1	0.5					30
Goat manure	2.8	0.6	2.4					60
Hog manure	1.0	0.3	0.7					30
Horse manure	0.7	0.1	0.4					60
Poultry	1.6	0.5	0.8					50
Rabbit	2.0	0.6	1.0					50
Sheep	2.0	0.4	2.1					60
Steer	2.0	0.2	1.6					60

should never be subjected to heavy equipment. From this point of view, a fall application of fertilizers would thus be preferable in temperate zones. A fall application, however, extends the period during which severe nutrient losses will occur: nitrogen mainly through leaching of nitrates and some volatilization of ammonia, phosphorus through reaction with soils resulting in a fixation that renders it unavailable. Therefore, spring applications are usually recommended, restricting fall fertilization to the minimum necessary to give certain crops such as winter wheat an adequate start. It has become the practice to split fertilization during the main growing season. This practice reduces fertilizer losses and environmental problems and brings about a better adjustment of the nutrient supply to the plant's requirement. Figures F18 and F19 show biomass production as well as the cumulative uptake (not necessarily the need) of wheat and sugar beet. Obviously nutrient uptake varies with species, stage of development and kind of nutrient. Soil properties must also be considered when formulating fertilizing strategies. The risk of loosing nitrogen through leaching, thus polluting the groundwater, is far greater in a light (sandy) than in a heavy (clay) soil. Thus, in sandy soils, rates of application of nitrate, or substances that are converted to it should be small but frequent, whereas in a heavy soil fewer but larger applications are permissible. Economic considerations also modify fertilization practices. Should one fertilize for maximum yield as one would in case of starvation or for maximum financial return? These two objectives are not identical. Fertilization strongly affects the composition of the product. Carbohydrates are produced with sugar cane and sugar beet. These plants respond to high and late nitrogen fertilization by converting some carbohydrates into proteins. In the case of wheat grains, this is desirable, since there is a shortage of proteins in some regions of the world. The baking quality of wheat flour is also improved by the higher protein content. A good example as to how fertilization affects the quality of the product is shown in the production of barley, which, if used for animal fodder, should be well fertilized with nitrogen, whereas barley for brewing should be given only the minimum amount of nitrogen necessary to produce an adequate crop. Different cultivars are also used to optimize production. Potatoes grown for animal or human consumption must be better fertilized with nitrogen than those grown for alcohol production.

Placement of fertilizers

The placement of fertilizers in the soil is important for maximizing utilization of applied nutrients and minimizing environmental impacts. Through proper placement, losses can be kept to a minimum, and a larger share of the applied nutrients is kept in plant-available forms. A great variety of sophisticated equipment for applying fertilizers has been developed. Optimum placement of fertilizers depends on a number of factors, viz (1) the mobility of nutrients, (2) the depth and spread of the rooting system of the crop, (3) climatic conditions, (4) the type of soil, (5) the kind of fertilizer being used, and (6) the amount to be applied per dressing during various stages of development of plants.

Solid fertilizers

Broadcasting (top-dressing) consists of the uniform distribution of dry fertilizers on the soil surface. This inexpensive method is used most widely in grain fields, pastures, range land, and orchards where extensive areas must be covered. Problems are separation of mixed fertilizers and inaccurate applications leading to yellow stripes with nitrogen deficiencies or to stripes of lodging after excessive nitrogen applications. *Drilling* places fertilizers at a distance of 3 to 5 cm from the seed grain, usually below and/or to the side of the plant at the time of sowing or at a greater depth in case of sods. It is frequently used, e.g., in maize cultures. Drilling gives the seedling an early supply of nutrients, and it increases the period during which some of the phosphorus remains available. *Banding* places the fertilizer in one band on one side or in two bands on both sides of the seed row at or slightly below sowing depth. Distances between the

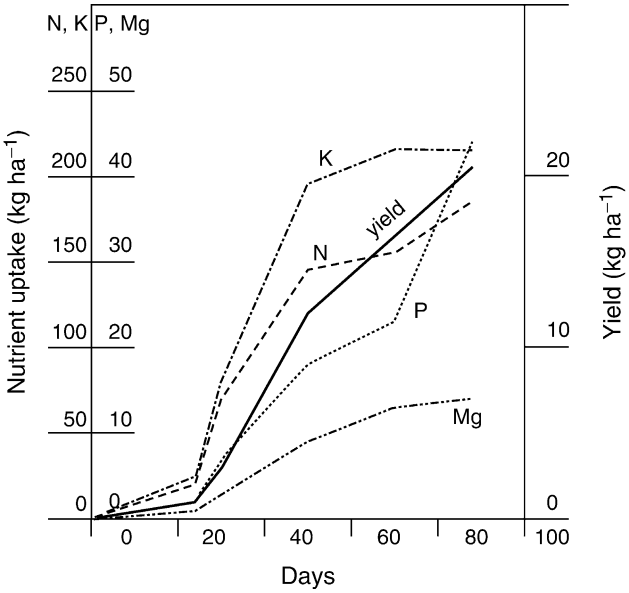


Figure F18 Time curve of nutrient uptake and biomass production by wheat (after Finck, 1991).

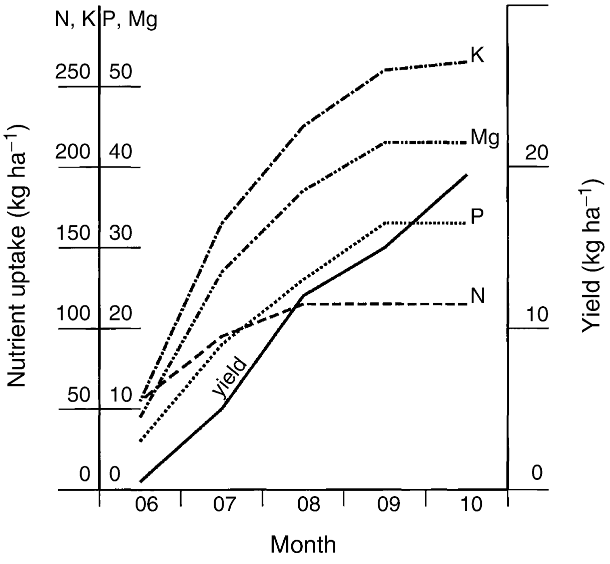


Figure F19 Time curve of nutrient uptake and biomass production by sugar beet (after Finck, 1991).

seeds and bands are adjusted to the individual crops, but bands are commonly 3–7 cm to the side of and about the same distance below the seeds. *Sidedressing* is banding of fertilizers after a crop has become established, at which time proper placement is especially important. The method is not well suited to phosphate fertilizers because of fixation and the resulting limited mobility. *Furrow placement* is actually a type of banding in which the fertilizer is placed at the bottom of a furrow below the future sides of plants. *Starter fertilizers* should provide the emerging rootlet with an immediate supply of nutrients. This may be achieved through coatings on the seed.

Liquid fertilizers

Broadcasting can also be achieved with liquid fertilizers. The advantages are: homogeneous distribution and easy adjustment of the nutrient mixture to plant and soil conditions. *Foliar sprays* consist of dilute solutions of fertilizers applied to plants by ground rigs or from airplanes. In the latter case, nutrients are applied without entering the field, thus reducing soil compaction. Foliar sprays of dilute nutrient solutions can generally be employed but are most frequently used for special purposes such as adding micronutrients or urea to orchard crops in order to produce a quick action. Nutrient solutions can also be used as *starter fertilizers* when added at the time of seeding. Application with irrigation water consists of adding dry or liquid fertilizer to the water at some central point before it is distributed (*Fertigation*). Sophisticated equipment has been invented to inject nutrient solutions into irrigation lines for drip and sprinkle irrigation.

Fertilization and environmental risks

The past three decades have seen an increasing concern about environmental impacts of human activities. Optimum crop production and environmental protection usually go hand in hand. Insufficient plant growth due to nutrient deficiencies may expose arable fields to erosion. Most of the environmental risks stem from inadequate fertilization practices. For example, too high an application rate incurs financial losses to the farm operator and increases the risk of environmental pollution.

Nitrate in the environment

Nitrates enter the food chain through drinking water, vegetables, treated meat products and some other, minor channels. Vegetables seem to be the major supply line, followed by drinking water. The significance of cured meat products has greatly decreased with the advent of refrigeration. The quantities of the various sources do not necessarily indicate the potential health risk, since it appears that vegetables might contain beneficial substances that counteract the injurious effect of nitrate.

Toxicology. Nitrates as such are hardly toxic. A fraction of nitrates, after being taken up by humans or animals, is reduced to nitrites, which react with various substances in the body and cause diseases (methemoglobinemia, cancer). Most of the nitrates are absorbed by the small intestines and are excreted with the urine. A small fraction of the absorbed nitrate – estimates are about one fourth – is excreted with the saliva into the oral cavity where, over a longer period of time, it is reduced by bacteria to nitrite. After absorption, nitrites react with hemoglobin and form methemoglobin by oxidizing the iron to the trivalent state. Methemoglobin cannot transport oxygen and, in severe cases (>10% methemoglobin), respiratory difficulties occur. Newborn babies are especially susceptible, because their stomach is less acid; a condition favorable to the reduction of nitrate to nitrite, and their ability to reconvert the methemoglobin back to hemoglobin is not yet fully developed. In the U.S., some deaths have occurred, but they are mainly connected with polluted well water and not with domestic water supplies (Maynard et al., 1976).

The second problem with nitrates stems from the reaction of nitrites with secondary and tertiary amines and amids forming nitrosoamines and nitrosoamids. In acid media:

$$\underset{\text{dimethylamine}}{(CH_3)_2NH} + \underset{\text{nitric acid}}{HNO_2} \rightleftharpoons \underset{\text{dimethylnitrosoamine}}{(CH_3)_2{-}N{=}O} + H_2O$$

in neutral media:

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

$$(CH_3)_2NH + N_2O_3 \rightleftharpoons (CH_3)_2{-}N{=}O + HNO_2$$

In experiments with animals, most of the nitrosoamines have been shown to be mutagenic, teratogenic or carcinogenic. Ascorbic acid and other reducing compounds decompose nitrous acid. It is perhaps for this reason that the consumption of vegetables reduces rather than increases the incidence of cancer of the stomach (Oertli, 1985). Nitrates obtained from drinking water may thus pose a greater health hazard than those obtained from vegetables.

Leaching of nitrates. The main transfer of nitrate to the ground water occurs in winter when there is a stronger net movement of water in downward directions (Figures F20, F21). This downward nitrate transport is extremely high in a plant-free soil even if this soil has not been fertilized. Little nitrate is lost from a grass-covered soil even if it has been reasonably well fertilized. A plant cover consisting of legumes (biological nitrogen fixation) (the clovers in Figure F21) lead to substantial losses of

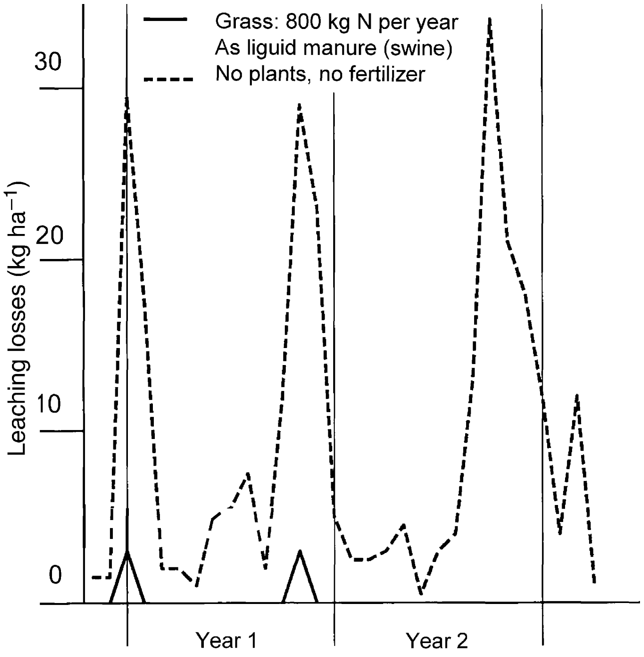


Figure F20 Leaching losses of nitrate from a non-fertilized barren a soil and a soil fertilized with 900 kg N yr^{-1} and cropped with grass (after Furrer et al., 1983).

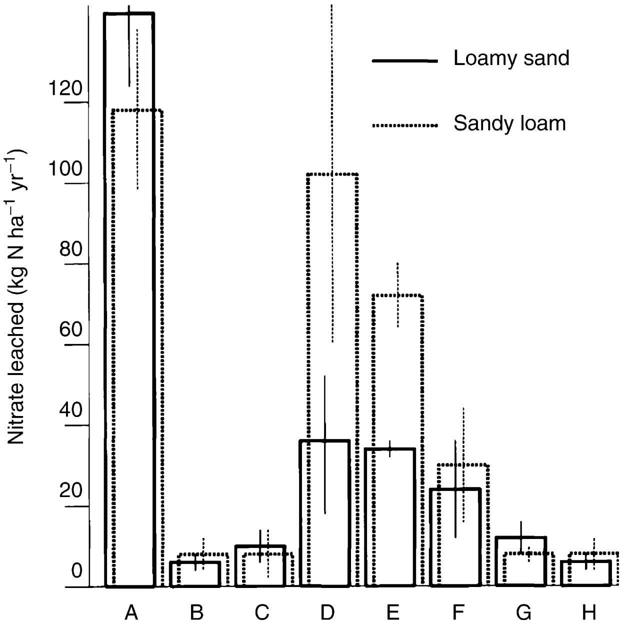


Figure F21 Effect of soil management on leaching losses of nitrate from a loamy sand and a sandy loam in lysimeter experiments. *A:* barren soil, no fertilizers; *B:* continuous grass, no fertilizers; *C:* continuous grass, complete fertilizers (N: 250 kg N yr^{-1}); *D:* clover, P and K added, no N; *E:* rotation, cropped in summer, plowed and barren in winter, complete fertilizer; *F:* as E but covercrop of rape in winter; *G:* continuous grass, sewage sludge at average annual rate of 412 kg N ha^{-1}; *H:* continuous grass, liquid animal manure at an annual rate of 738 kg N ha^{-1}. *Blocks* represent averages of 4 years (after Furrer, 1983).

nitrate due to leaching. These losses are especially large if a plant cover containing legumes is plowed under. Nitrates are released after plowing grass (Oakes, 1991) and are believed to be a major cause of increasing nitrate levels in European groundwater since World War II (Hill, 1991). The experimental variability of the clover treatment is high, because once some clover plants died leading to extreme nitrate levels in the leachate. Leaching losses are also high in a rotation with summer cropping, plowing in fall and keeping the soil barren during winter. The use of a covercrop of rape during winter reduces these losses to nominal values. The function of the covercrop is not clear; leaching may be reduced because of nitrate uptake, increased transpiration and increased denitrification (von Rheinhaben and Trolldenier, 1984). Similar to the treatments with mineral fertilizers, groundwater pollution with nitrates is also negligible when soils are fertilized with liquid animal manure or with sewage sludge provided a continuous plant cover is present.

The WHO set the safe limit for drinking water at 50 mg nitrate l^{-1}. This value has been adopted by a number of different countries and the EC, sometimes as an imperative, sometimes as a recommended limit. The U.S. ERA put the limit at 45 mg nitrate l^{-1}.

Nitrates in vegetables. The highest amounts of nitrate in the food chain originate from vegetables. Concentrations of several thousand mg NO_3 per kg fresh weight are not uncommon in plants like head lettuce, spinach, radish etc. While fertilizer management definitely influences nitrate levels in leaves, the dominating factor seems to be the duration and intensity of light.

Denitrification. Denitrification not only causes loss of a valuable nutrient, but one of its end products, nitrous oxide (N_2O), may also be an environmental hazard. It is, however, not clear whether the chemically stable nitrous oxide that escapes from soils and eventually reaches the stratosphere as a net effect strengthens or weakens the ozone layer (Johnston, 1982) which protects living organisms on the Earth's surface. Nitrous oxide is also a potent greenhouse gas and its importance is lessened only by its relatively low concentration in comparison to CO_2.

Volatilization of ammonia. Ammonia that is volatilized from soils is usually returned to the soil by diffusion or rain, sometimes at an undesirable location. It has been argued that, in forest soils, it causes an imbalance of nutrient supplies in favor of nitrogen and may thus be a contributing factor to the decline of forests.

Phosphorus in the environment

Phosphorus is probably the major nutrient causing eutrophication of surface waters. Rather small quantities of phosphorus suffice to induce a prolific growth of algae, which, after their death, are decomposed by bacteria, thus depriving the water of oxygen. Although large quantities of nitrogen can be transferred from soils to surface waters, their significance is smaller because some microorganisms can fix nitrogen biologically so that surface waters are supplied with this nutrient even in the absence of an external influx. Due to its chemical behavior in soils, leaching of phosphorus into ground water is an extremely rare event; the major pollution of surface water comes from soil erosion. Erosion control is, therefore, an efficient means of protecting surface waters from eutrophication. A second problem connected with phosphorus fertilization is that contaminants are present in rock phosphate. Cadmium has been of special concern. Rock phosphates of volcanic origin have very low Cd concentrations, e.g., only 0.9 mg Cd per kg P in deposits of the Kola Peninsula. In contrast, sedimentary deposits contain much higher concentrations. For example, North African deposits (Tunisia, Morocco) contain 200 to 400 and those in Florida 56 mg Cd per kg P. At present, preference is given to low-Cd deposits for manufacturing phosphate fertilizers, but in future it will be necessary to develop procedures to remove cadmium.

Potassium in the environment

Potassium, being exchangeable, resists transport into soil water and only rarely does its concentration in ground water reach concentrations that might be of concern such as in sandy soils. There are no guidelines from the WHO. The EEC recommends 10 mg K l^{-1} as an upper limit.

Sewage sludges in the environment

Sewage sludges contain valuable nutrients for which reason they are sometimes spread on agricultural land. Nutrients are thus recycled. Sewage sludge also contains heavy metals and limits have been set up for maximum levels of lead, zinc copper, nickel, cadmium and other contaminants (Table F3).

J. J. Oertli

Bibliography

Alexander, A., 1986. *Foliar Fertilization.* Dordrecht, Netherlands: Kluwer, 508 pp.

Amer, F., Boulin, D.R., Black, C.A., and Duke, F.R., 1955. Characterization of soil phosphorus by anion exchange resin adsorption and ^{32}P-equilibration. *Plant Soil*, **6**: 391–408.

Angelone, M., Vaselli, O., Bini, C., Coradossi, N., and Pancani, M.G., 1991. Total and EDTA-extractable element contents in ophiolitic soils from Tuscany (Italy). *Z. Pflanzenernahr. Bodenk.*, **154**: 217–223.

Armstrong, J., and Armstrong, W., 2005. Rice: sulfide-induced barriers to root radial oxygen loss, Fe^{2+} and water uptake, and lateral root emergence. *Ann. Bot.*, **96**: 625–638.

Barber, S.A., 1984. *Soil Nutrient Bioavailability, A Mechanistic Approach.* New York: Wiley-Interscience, 398 pp.

Beaufils, E.R., 1973. Diagnosis and recommendation integrated system (DRIS). *Soil Science Bulletin 1.* Petermaritzburg: University of Natal, 132 pp.

Becquer, T., Merlet, D., Boudot, J.-P., Rouiller, J., and Gras, F., 1990. Nitrification and nitrate uptake: Leaching balance in a declined forest ecosystem in eastern France. *Plant Soil*, **125**: 95–107.

Bergmann, W., 1983. *Ernahrungsstorungen bei Kulturpflanzen.* Stuttgart, Germany: Gustav Fischer Verlag, 614 pp.

Bould, C., Hewitt, E.J., and Needham, P., 1984 *Diagonsis of Mineral Disorders in Plants, Several Volumes.* New York: Chemical Publishing Co. Inc.and later.

Bray, R.H., and Kurtz, L.T., 1945. Determination of total, organic, and available forms of phosphorus in soils. *Soil Sci.*, **59**: 39–45.

California Fertilizer Association, 1990. *Western Fertilizer Handbook*, Horticulture edn. Sacremento: Prentice-Hall, 279 pp.

California Fertilizer Association, 1998. *Western Fertilizer Handbook*, Horticulture edn. New Jersey: Prentice-Hall, 290 pp.

Chapman, H.D., and Liebig, G.F., 1952. Field and laboratory studies of nitrite accumulation in soils. *Soil Sci. Soc. of Am. Proc.*, **16**: 276–282.

Cottenie, A., Verlod, M., Kiekens, L., and Carmerlynck, R., 1982. *Chemical Analysis of Plant and Soils.* Belgium: Laboratory of Analytical and Agrochemistry, State University Ghent, 63 pp.

Cotton, F.A., Wilkinson, G., Murillo, C.A., and Bochmann, M., 1999. *Advanced Inorganic Chemistry*, 6th edn. New York: Wiley, 1355 pp.

FAO, 2001. *Yearbook*, Vol. 51. Rome: Food and Agriculture organization of the United Nations, 212 pp.

FAO, 2002. *Yearbook*, Vol. 52. Rome: Food and Agriculture organization of the United Nations, 211 pp.

Finck, A., 1992. *Dunger und Dungung: Grundlagen und Anleitung zur Dungung der Kulturpflanzer*, 2nd edn. Weinheim, Germany: VCH Verlagsgellschaft, 390 pp.

Furrer, O., Stadelmann, F.X., and Stauffer, W., 1983. Grundwasserqualitat und Landwirtschaft. Wiener Mitteilungen: Wasser-Abwasser-Gewasser Bd, Vol. 51, pp. 1–33.

Gupta, S., and Hani, H., 1989. Methods of soil analysis. Eidg. Forschungsanstalt fur Agrikulturchemie und Umwelthygiene. Switzerland: Liebefeld-Bern.

Hill, M.J., 1991. Origins of nitrate in water. In Hill, M., ed., *Nitrates and Nitrites in Food and Water.* New York: Ellis Horwood, pp. 59–76.

Houba, V.J.G., Novozamsky, J., Lexmond, Th.M., and van der Lee, J.J., 1990. Applicability of 0.01 M $CaCl_2$ as single extraction solution for the assessment of the nutrient status of soils and other diagnostic purposes. *Commun. Soil Sci. Plant Anal.*, **21**: 2281–2290.

Jacobson, L., 1951. Maintenance of iron supply in nutrient solutions by a single addition of ferric potassium ethylenediaminetetra-acetate. *Plant Physiol.*, **26**: 411–413.

Johnston, H.S., 1982. Odd nitrogen processes. In Bower, F.A., and Ward, B.R., eds., *Stratospheric Ozone and Man,* Vol. I, Boca Raton, FL: CRC Press, pp. 87–140.

Jones, B., Jr., 1990. Universal soil extractants, their composition and use. *Commun. Soil Sci. Plant Anal.*, **21**: 1091–1101.

Keeney, D.R., 1986. Inhibition of nitrification in soils. In Prosser, J.I., ed., *Nitrification.* Special Publications of the Society for General Microbiology, Vol. 20. Oxford: IRI Press, pp. 99–115.

Kholdebarin, B., and Oertli, J.J., 1992. Allelopathic effects of plant seeds on nitrification: effects on ammonium oxidizers. *Soil Biol. Biochem.*, **24**: 59–64.

Lindsay, E.L., and Norvell, W.A., 1978. Development of DTPA soil test for zinc, iron, manganese, and copper. *Soil Sci. Soc. Am. J.*, **42**: 421–428.

Martens, D.C., and Westermann, D.T., 1991. Fertilizer applications for correcting micronutrient deficiencies, Chapter 15. In Mortvedt, J.J., Cox, F.R., Schuman, L.M., and Welch, R.M., eds., *Micronutrients in Agriculture,* 2nd edn. Madison, WI: Soil Science Society of America, pp. 549–592.

Maynard, D.N., Barker, A.V., Minotti, P.L., and Peck, N.H., 1976. Nitrate accumulation in vegetables. *Adv. Agron.*, **28**: 71–118.

McDonald, M.A., Malcom, D.C., and Harrison, A.F., 1991. The use of a ^{32}P root bioassay to indicate the phosphorus status of forest trees. 2. Spatial variation. *Can. J. For. Res.*, **21**: 1185–1193.

Mehlich, A., 1984. Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.*, **15**: 1409–1416.

Mortvedt., J.J., 1991. Micronutrient fertilizer technology, Chapter 14. In Mortvedt, J.J., Cox, F.R., Shuman, L.M., and Welch, P.M., eds., *Micronutrients in Agriculture,* 2nd edn. Madison, WI: Soil Science Society of America, pp. 523–548.

Nemeth, K., Bartels, H., Vogel, M., and Mengel, K., 1988. Organic nitrogen compounds extracted from arable and forest soils by electro-ultrafiltration and recover rates of amino acids. *Biol. Fertil. Soils*, **5**: 271–275.

Oakes, D., 1991. Nitrate in water. In Hill, M., ed., *Nitrates and Nitrites in Food and Water.* New York: Ellis Horwood, pp. 33–58.

Oertli, J.J., 1985. Gastric cancer, nitrates, consumption of vegetables and vitamins. *Schweiz. Landw. Forschung*, **25**: 1–13.

Oertli, J.J., 1980. Controlled-release fertilizers. *Fert. Res.* **1**: 103–123.

Pescod, M.B., 1992. *Wastewater Treatment and Use in Agriculture – FAO Irrigation and Drainage Paper 47.* Rome: Food and Agriculture Organization of the United Nations, 125 pp.

Powell, S.J., 1986. Laboratory studies of inhibition of nitrification. In Prosser, J.I., ed., *Nitrification. Special Publications of the Society for General Microbiology,* Vol. 20. Oxford: IRI Press, pp. 79–97.

von Rheinhaben, W., and Trolldenier, G., 1984. Influence of plant growth on denitrification in relation to soil moisture and potassium nutrition. *Z. Pflanzenernahr. Bodenk.*, **147**: 730–738.

Scheffer, F., and Schachtschabel, P., 2002. *Lehrbuch der Bodenkunde.* Heidelberg, Berlin: Spektrum Akademischer Verlag, 607 pp.

Schofield, R.K., 1955. Can a precise meaning be given to "available" soil phosphorus? *Soils Fert.*, **18**: 373–375.

Schuller, H., 1969. Die CAL-Methode, eine neue Methode zur Bestimmung des pflanzenverfugbaren phosphates in Boden. *Z. Pflanzenernahr. Bodenk.*, **123**: 48–63.

Smil, V., 1999. Detonator of the population explosion. *Nature*, **400**: 415.

Soltanpour, P.N., and Schwab, A.P., 1977. A new soil test for simultaneous extraction of macro- and micro-nutrients in alkaline soils. *Commun. Soil Sci. Plant Anal.*, **8**: 195–207.

Sparks, D.L., ed., 1996. *Methods of Soil Analysis: Part 3: Chemical Methods*, 3rd edn. Madison, WI: Soil Science Society of America/American Society of Agronomy, 1390 pp.

Sprague, H.B., 1964. *Hunger Signs in Crops: A Symposium*, 3rd edn. New York: McKay, 461 pp.

Trimm, J.R., and Parley, J.A., 1991. Rapid extraction of available phosphorus in fertilizers. *J. Assoc. Off. Anal. Chem.*, **74**: 809–811.

Van der Paauw, F., 1969. Entwicklung und Verwertung einer neuen Wasserextraktionsmethode fur die Bestimmung von pflanzenaufnehmbarer Phosphorsaure. *Landwirtschaftliche Forschung*, **23**: 102–109.

Walworth, J.L., and Sumner, M.E., 1987. The diagnosis and recommendation integrated system (DRIS). *Adv. Soil Sci.*, **6**: 149–188.

Cross-references

Fertilizer Raw Materials
Macronutrients
Micronutrients
Nitrogen Cycle
Phosphorus Cycle
Plant Nutrients
Potassium Cycle
Sludge Disposal
Soil Fertility
Sulfur Transformations and Fluxes
Trace Elements

FERTILIZERS, ORGANIC

Organic fertilizers are carbon (C) containing materials originating from plants, animals, and human activity that are added to soil to supply one or more elements essential for plant growth.

Some C-containing materials, such as urea and carbonaceous liming materials that are frequently added to the soil are not considered to be organic fertilizers (SSSA, 1987).

Organic fertilizers have been used since the beginning of agriculture to amend nutrient-poor soils and subsequently improve crop productivity. The Greek historians, Theophrastus and Xenophon, recommended the use of animal and green manures in crop production hundreds of years before Christ (Collings, 1955; Tisdale et al., 1985). Organic fertilizers continued to be a major source of nutrients for crops until the mid-20th century when their use declined in proportion to increased use of high-analysis, relatively low-cost inorganic fertilizers (NRC, 1989). Other factors contributing to declining organic fertilizer use include: (1) increased farm size; (2) increased farm specialization, in particular, separation of livestock and grain production systems; (3) adoption of high-density animal confinement systems; (4) government commodity programs that encourage farm specialization; and (5) agricultural research aimed primarily at increasing per-land-unit crop yields (NRC, 1989). These trends in agricultural management over the past few decades have, in large part, resulted in nutrient-bearing organic materials being viewed as a liability that must be dealt with in a disposal mode, rather than being viewed as a resource for crop production. However, even though modern crop production practices that rely heavily on inorganic fertilizers have resulted in a 2% per year increase in per-land-unit crop yields since 1940 (NRC, 1989), interest in organic fertilizer use in crop production has recently been renewed.

Revitalized interest in organic fertilizers is mainly owing to issues of soil quality, environmental pollution, energy costs, and sustainable agricultural productivity. Soil quality or productivity may be defined as the capability of a soil to produce a specified plant or sequence of plants under a defined set of management practices (USDA, 1957), and is directly linked to soil organic matter content (Parr et al., 1984). Reintroduction of organic fertilizers into crop production systems has the potential to increase inherent soil productivity via accumulation of soil organic matter. Environmental impetus for judicious use of organic wastes as fertilizers stems from the enormous amounts generated each year; Table F10 provides mass estimates for selected wastes produced annually in the USA and Europe. Land application offers the best solution to management of the enormous amounts of organic wastes generated each year (Loehr, 1974). However, concerns over potential environmental degradation due to land application of organic materials must be addressed. Proper management of these materials is the key to ensuring environmental compatibility and sustained biomass production. With respect to energy consumption, substantial amounts of non-renewable fossil fuels are used to produce chemical fertilizers, especially those containing nitrogen (N) (Tisdale et al., 1985). Indeed, N fertilizers represent the largest single energy input in many crop production systems (Wilkinson, 1979). Thus, using organic wastes as fertilizers, in place of chemical fertilizers, may reduce energy inputs into crop production systems. In addition to soil productivity, environmental, and energy cost considerations, premiums paid for "organically produced" crop and animal products have motivated some farmers to replace inorganic fertilizers with organic fertilizers (NRC, 1989).

Table F10 Annual production of organic wastes in the USA and Europe

Organic Material	Organic waste (dry Tg yr^{-1})	
	USA[†]	European Economic Community[‡]
Animal manure	156	950
Crop residues	385	–[§]
Sewage sludge	4	300
Food processing wastes	3	–
Industrial organics	7	160
Logging and milling wastes	32	–
Municipal refuse	130	150

[†] Miller and McCormack (1978).
[‡] Ferrero and L'hermite (1985).
[§] – = no data.

Types and composition

The major types of organic fertilizers include barnyard manures, liquid manures, processed organic materials, and crop residues returned directly to the soil (Simpson, 1986). Barnyard manures are relatively dry, bulky, solid materials that derive their nutrient value from animal excreta. In many cases barnyard manures are a combination of animal excreta and bedding materials (straw, wood chips, etc.) that have been used to absorb liquid fractions of the excreta. Liquid manures consist of animal excreta that has been deposited on solid or slatted floors, without bedding material, and then washed into lagoons or storage tanks. Processed organic materials are produced on-or off-farm and include composts, sewage sludge, food processing wastes, forestry by-products, industrial wastes, and municipal refuse. Crop residues include plant parts (straw, stover, roots, etc.) that remain on the land after crop harvest and green manure or cover crops grown for incorporation into the soil.

Organic fertilizers vary widely in their macronutrient, micronutrient, and heavy metal content; typical values are shown in Tables F11 and F12. Variability in elemental composition among and within organic fertilizer types stems from source differences and disparity among types of operations under which the materials are generated. Among barnyard and liquid animal manures, variation in elemental composition arises from: (1) animal species and breed, (2) confinement density, (3) feed conversion rate, (4) feed ration, (5) bedding material type and composition (if present), and (6) climatic conditions during manure accumulation. The elemental composition of processed organic materials reflects the nature of the industry or municipality from which they are derived. For example, sewage sludge tends to have higher heavy metal concentrations if industrial wastewater is processed along with domestic sewage, and spent refinery catalyst has a high phosphorus (P) content (Table F11) owing to phosphoric acid used in the oil refining process. Plant species, and, to a lesser extent, climatic conditions and soil fertility status generally control the composition of crop residues and green manures.

Because of variability among and within organic fertilizer types, some materials have greater nutrient value than others. Of the barnyard manures, those generated by birds tend to have the greatest plant nutrient value owing to their relatively high macronutrient content and low water content. Due to low dry matter concentrations, liquid manures typically have low macronutrient contents. Sewage sludges tend to have relatively high N concentrations, but contain less P and potassium (K). Although macronutrient content generally declines when organic wastes are composted (Witter and Lopez-Real, 1987), some composts, such as dead-bird compost (co-composted poultry mortalities and broiler litter (Table F11)), may have greater macronutrient contents than barnyard manures (Cummins et al., 1993). Crop residues (i.e., corn

Table F11 Representative macronutrient content of selected organic materials

Material	N	P	K	Dry matter
	g kg^{-1} (wet basis)			
	Barnyard manures			
Broiler litter[†]	33	14	19	800
Hen manure[‡]	17	6	6	290
Turkey manure[‡]	18	6	8	450
Cow manure[‡]	4	1	2	150
Beef feedlot manure[§]	13	5	15	655
Horse manure[‡]	7	2	5	320
Pig manure[‡]	6	3	3	210
	Liquid manures			
Chicken slurry[‡]	6	2	2	80
Cattle slurry[‡]	3	1	2	40
Pig slurry[‡]	4	1	2	40
	Processed materials			
Activated sewage sludge[¶, #]	40	20	4	–[‡]
Digested sewage sludge[‡]	14	4	1	340
Municipal refuse[¶, #]	7	2	3	–
Fruit processing waste[¶, #]	10	2	3	–
Vegetable processing waste[¶, #]	2	1	2	–
Spent mushroom compost[‡]	6	2	8	360
Dead-bird compost[‡‡]	39	18	21	640
Spent refinery catalyst[§§, #]	–	160	–	–
	Crop residues#			
Corn stover[¶¶]	11	2	13	–
Wheat straw[¶¶]	7	1	10	–
Rice straw[¶¶]	6	1	12	–
Cotton stover[¶¶]	18	2	14	–
Clover tops[##]	23	3	20	–
Alfalfa tops[†††]	20	2	15	–

[†] Stephenson et al. (1991).
[‡] Loehr (1974).
[§] McCalla et al. (1977).
[¶] Miller and McCormack (1978).
[#] Nutrient contents expressed on a dry weight basis.
[††] – = no data.
[‡‡] Cummins et al. (1993).
[§§] Wood and Westfall (1989).
[¶¶] Larson et al. (1978).
[##] Essig (1985).
[†††] Lanyon and Griffith (1988).

Table F12 Representative secondary- and micro-nutrient, and metal contents of selected organic materials

Element	Broiler litter[†]	Pig slurry[‡]	Digested sewage sludge[§]	Corn stover[¶]
	g kg^{-1} (dry basis)			
Ca	23	25	22	4
Mg	5	5	11	4
S	5	–[#]	9	1
Fe	2	–	36	0.2
A1	–	–	10	–
Na	–	15	3	–
	mg kg^{-1} (dry basis)			
Zn	315	150	2770	21
Cd	–	–	205	–
Cu	473	675	1370	10
Cr	–	–	2330	–
Ni	–	–	355	–
Mn	348	–	370	31
Pb	–	–	699	–
Hg	–	–	3	–

[†] Stephenson et al. (1990).
[‡] Loehr (1974).
[§] McCalla et al. (1977).
[¶] Barber and Olson (1968).
[#] – = no data.

and cotton stover, and wheat and rice straw (Table F11)) usually contain greater amounts of N and K but less P due to lower crop P uptake. Leguminous green manures (i.e., clover and alfalfa (Table F11)), due to their symbiotic N_2 fixation capability, can provide substantial amounts of residual N for succeeding crops.

Collection, transport, and application

The means by which organic fertilizers are collected, transported, and applied to land are controlled, in large part, by the moisture content of the material. Depending on the type of organic fertilizer, treatments prior to land application may enhance the usefulness of these materials as a source of plant nutrients.

Solid organic fertilizers (i.e., barnyard manure, de-watered sewage sludge, municipal refuse, composts, etc. that have >150 g dry matter kg^{-1}) do not flow hydraulically, and require handling techniques different from those used for liquid materials (Miner and Hazen, 1977). These materials generally have higher nutrient contents per unit volume than liquid organic fertilizers, which make their handling less costly.

Several treatment options exist for solid organic fertilizers. Drying of solid organic fertilizers on the wetter end of the spectrum, which is accomplished by static aeration or by mixing with drier materials, may be desirable from a weight reduction perspective, particularly if the materials are to be transported long distances. Because of the expense involved, mechanical drying of solid organic fertilizers is rarely practiced (Miner and Hazen, 1977). Storage of solid organic fertilizers under a roofed structure allows flexibility in timing of land application, and reduces the risk of environmental contamination as compared with exposed piles. Composting of solid organic materials occurs naturally when non-sterile organic substrates are combined with water and oxygen (Emerton et al., 1988). Microbial decomposition generates sufficient heat to raise the temperature of compost mixtures to the thermophilic zone (65–75 °C), which destroys pathogenic organisms and weed seed. Composting reduces the volume and weight of original organic substrates, and the end result of successful composting is a material that is biologically stable, odor-free, and useful as a potting media or soil amendment (Flynn et al., 1995; Flynn and Wood, 1996). Other treatments that may be desirable, particularly for municipal refuse, include shredding and grinding to improve spreading, and sorting to reclaim valuable by-products or to eliminate undesirable materials prior to spreading (Miner and Hazen, 1977).

Collection of solid organic materials is usually accomplished with machinery capable of scooping the material, such as front-end loaders. Transport to the field, depending on the distance, may be accomplished with spreader or large-bodied trucks. Spreading solid organic fertilizers on cropland is typically done with either open tank spreaders, which throw the material over the sides of the tank via flails, or with box type spreaders that utilize paddles, flails, or augers for spreading from the rear of the vehicle. Once spread on the soil surface, it is desirable to incorporate solid organic fertilizers into the soil; N loss of up to 50% of original N applied via ammonia (NH_3) volatilization has been reported for animal manures and sewage sludges remaining on the soil surface (Loehr, 1984; Sommers and Giordano, 1984; Marshall et al., 1998; Sherlock et al., 2002; Sullivan et al., 2003).

Liquid organic fertilizers contain <150 g dry matter kg^{-1} and include aforementioned materials, such as liquid animal manures, manure slurries, domestic sewage treatment plant effluent, and food processing wastewaters. While these materials are generally amenable to hydraulic pumping, those that contain between 40 and 150 g dry matter kg^{-1}, referred to as slurries, can present problems to pumping equipment owing to their viscosity and potential to plug orifices (Miner and Hazen, 1977). Solid-liquid separation via sedimentation, screening, or filtration may be necessary when liquid organic fertilizers with higher amounts of solids are to be pumped.

A wide variety of systems exist for handling liquid organic fertilizers between their point of origin and the fields on which they are to be spread. Commonly used systems for recovery of liquid organic fertilizers include scraping or washing into tanks, detention basins, aerobic or anaerobic lagoons, and oxidation ditches. Lagoons and oxidation ditches serve as storage reservoirs and allow for sedimentation and biological activity that decomposes organic fractions. Although these reservoirs enhance the hydraulic properties of these liquids with regard to ease of pumping, they often result in considerable loss of plant nutrients. Ammonia volatilization losses from these systems range from 25 to 80% of original N contained in liquids/slurries, and P and K losses due to sedimentation range from 5 to 50% of original P and K (Tisdale et al., 1985). Nitrogen losses are minimized when the liquids/slurries are added to the bottom of storage reservoirs instead of the surface (Loehr, 1984).

Liquid organic fertilizers are usually transported to the application site by either tank bearing equipment or pipelines. Slurries, owing to their viscosity, are typically pumped into tanks for transport. Pumping slurries requires agitation via paddles, augers, blow-back from vacuum-filled tanks, or submerged centrifugal recirculating pumps (Miner and Hazen, 1977). Upon arrival at the site of application, slurries can either be spread on the soil surface or injected into the soil. Surface spreading is accomplished either by application from tank wagons fitted with splash plates or by large bore nozzles (manure guns) that distribute the slurry from a pressurized line. Subsurface application consists of either direct injection below the soil surface, injection ahead of tillage devices, or surface application immediately followed by tillage operations. Liquid organic fertilizers containing <40 g dry matter kg^{-1} may be handled similarly to slurries or be pumped out of their storage reservoirs into pipeline systems. If handled in pipeline systems, liquid organic fertilizers are commonly applied to the soil surface with irrigation equipment. The type of irrigation system (i.e., flood, furrow, or sprinkler irrigation) required for application of liquid organic fertilizers is controlled by soil type, topography, crop management, and many other factors. As with solid organic fertilizers, losses of N via NH_3 volatization occur when liquid/slurry organic fertilizer forms are applied to the soil surface, making incorporation desirable when possible.

Crop residues and green manure crops fall outside the handling criteria for solid and liquid organic fertilizers, because their placement is usually directly on the land on which they are grown. A major consideration for handling these materials is the tillage system under which they are managed. Plowing in crop residues after harvest or green manure crops prior to planting a succeeding crop usually results in quicker release of nutrients in the materials when compared to leaving them on the soil surface, as is done in no-till systems (Huntington et al., 1985; Wilson and Hargrove, 1986; Groffman et al., 1987). Other studies (Wagger, 1989; Yarco et al., 1989), however, suggest that N from green manure crops can be released in a sufficiently timely manner under no-till so as not to limit yields of succeeding crops. While the issue of nutrient release from crop residues and green manure crops as impacted by tillage systems remains unclear, crop residues and green manures managed under no-till generally provide greater benefits to inherent soil quality (organic matter content, potential nutrient supplying capability, water relations, etc.) when compared to those managed under conventional plow/disk tillage systems (Frye et al., 1988; Wood et al., 1990, 1991; Wood and Edwards, 1992). In most field crop systems, green manure crops must be killed prior to physiological maturity, which is accomplished by plowing or herbicides, to allow timely planting of the succeeding crop. The time at which green manure crops are killed affects their nutrient content, particularly the N content of legumes. For example, in a two-year study in North Carolina, the aboveground portion of crimson clover contained an average of 105 kg N ha^{-1} at late bloom as compared to 68 kg N ha^{-1} at the late vegetative stage (Ranells and Wagget, 1992). Therefore, knowledge of chemical properties at various stages of growth is critical to derive the maximum nutrient credit from green manure crops.

Rates and timing of application

As previously discussed, considerable variability in elemental composition among and within organic fertilizer types exists. This variability promotes uncertainty with regard to amounts of organic fertilizers that should be applied to satisfy plant nutritional requirements without degrading the environment. Analyzing the plant nutrient content of organic materials prior to land application, along with soil tests and knowledge of crop nutrient requirements, aids land managers in determining application rates that result in sustained crop production and environmental compatibility. However, as discussed below, organic fertilizers must be decomposed by soil microbes to release their nutrients in a plant available form; this complicates decisions concerning land application rates.

Although organic fertilizers usually contain a host of elements essential for plant growth, land application rate is often based on a single plant nutrient. Most often, since N is the most limiting nutrient for crops (Tisdale et al., 1985), land application rates are based on N content of organic fertilizers. Much of the N in these materials is in organic combination, and since plants assimilate N as nitrate (NO_3) or ammonium (NH_4), mineralization (aminization, ammonification, and nitrification) of organic N to these inorganic forms is a prerequisite to plant uptake of organic fertilizer-N. Aminization and ammonification are affected by heterotrophic microbes in the soil that use the carbon (C) contained in the organic fertilizer as an energy source, while nitrification is accomplished by autotrophic soil bacteria. The ratio of C to N (C/N) of organic fertilizers is a major factor controlling whether the net change in mineral N is positive (mineralization) or negative (immobilization). In general, organic materials having a C/N less than 20 result in net mineralization, while those with a C/N greater than 30 result in net immobilization (Tisdale et al., 1985). Most barnyard and liquid manures, sewage sludges, and green manures have a C/N less than 20, while crop residues and forestry by-products typically have C/N ratios greater than 30. Other factors controlling the release of N from organic fertilizers include climatic and soil variables.

Mineralization of N from organic fertilizers immediately after application to the soil usually follows first order kinetics, and is represented mathematically as

$$IN(t) = NM_0(1 - e^{-kt}) \tag{1}$$

where IN is inorganic N present in the soil-organic fertilizer system at time t, NM_0 is potentially mineralizable N in the soil-organic fertilizer system at $t = 0$, and k is the rate coefficient. The N variables have units of N mass per mass of soil, while k is in units of reciprocal time. The variables in Equation (1) are usually determined in laboratory incubation experiments, and while assessment of NM_0 can provide good estimates of potentially available N from organic fertilizers that correlate well with N uptake by crops, the use of laboratory incubations on a routine basis prior to land application is usually prohibited by time and monetary constraints. For these reasons, researchers have sought for quick, reliable, availability indices that correlate well with N mineralization in laboratory incubations. Methods tried include determination of organic fertilizer volatile solids, inorganic N, organic N, total N, Walkley-Black C, NH_4 released by autoclaving, NH_4-N released by Walkley-Black digestion, NH_4-N released by acid permanganate extraction, and many others. Currently there is no standard method for estimating potentially available N from organic fertilizers. However, Douglas and Magdoff (1991) correlated N release in laboratory incubations from a variety of organic materials with several N availability indices, and found that NH_4-N released during Walkely-Black digestion was highly related ($r^2 = 0.89$; $P < 0.01$) to N mineralized in 67-day incubations. They caution, however, that this approach to determining potentially available N from organic fertilizers should be further tested before being put into widespread use.

Because much of the N in organic fertilizers must undergo microbial transformations in the soil before it is in a form that plants can assimilate, the N in these materials is not immediately available to plants. Thus, from a practical standpoint, applications based on N for maximum crop production are greater for organic fertilizers than for inorganic N sources. General decay constants describing the fraction of N that becomes available over successive years after application have been developed for some organic fertilizers (Table F13). Although the values in Table F13 are only indicative, and specific materials may have different decay constants, they serve to illustrate how availability indices could be utilized. For example, the data in Table F13 indicate that 75% of broiler litter N becomes available during the first year after application. Using a value of 33 g N kg^{-1} for broiler litter (Table F11), approximately 4.04 Mg broiler litter ha^{-1} would be required to supply 100 kg N ha^{-1} during the first year after application. Table F13 also serves to illustrate the residual effects of organic fertilizer applications, and the data suggest that organic fertilizer rates, when based on N content, should be reduced in years following initial application.

Appropriate timing of land application is critical to deriving the greatest nutrient credits from organic fertilizers while minimizing the risk of environmental contamination. Synchronizing nutrient release from organic fertilizers with the period of rapid crop growth and nutrient uptake will maximize crop nutrient utilization. Climatic conditions favorable for plant growth (i.e., warm soil temperatures and adequate soil moisture) also stimulate nutrient release from soil applied organic fertilizers. In contrast, applying organic fertilizers to frozen or snow-covered soils results in minimal biological activity, and little or no mineralization of applied N and P occurs (Overcash et al., 1983). Furthermore, losses of organically bound N and P, and in some cases inorganic N and P, from winter-applied manures via runoff can amount to a substantial fraction of applied N and P (Hensler et al., 1970; Minshall et al., 1970; Converse et al., 1976; Klausner et al., 1976).

In a practical sense, because it is desirable for available nutrients to be present at initiation of the rapid phase of plant nutrient uptake, organic fertilizers should be applied prior to

Table F13 Nitrogen decay constants for selected organic fertilizers

Material	Year after application			
	1	2	3	4
	N mineralized (%)[†]			
Broiler litter[‡]	75	10	5	5
Hen manure[‡]	90	10	5	5
Swine manure[‡]	90	10	4	3
Dairy cattle manure[‡]	50	15	5	5
Beef cattle manure (Fresh)[‡]	75	15	10	5
Beef cattle manure (Stockpiled)[‡]	20	10	5	3
Aerobically digested sewage sludge[§]	25	12	6	3
Anaerobically digested sewage sludge[§]	20	10	5	3
Composted sewage sludge[‡]	10	5	3	3

[†] Nitrogen mineralized for year 1 refers to the percentage released from the initial application; N mineralization for years 2 to 4 refers to the percentage released from that present at the beginning of years 2 to 4, respectively.
[‡] USDA (1979).
[§] USEPA (1983).

the onset of rapid vegetative growth. In general, organic fertilizer applications to field crops should occur just prior to planting, while applications to pasture or hay crops should be made immediately before the rapid phase of plant growth. Although synchronizing nutrient release from organic fertilizers with periods of greatest plant needs is the most desirable practice, this precept may impose operational constraints on land managers. Bouldin et al. (1984) lists several of these constraints: (1) storage facilities must be large enough to accommodate several months of accumulated organic fertilizer; (2) materials must be land-applied during a narrow period in the spring; (3) expensive spreading equipment is used for only a short time period; (4) labor demand is high during an already busy time period; and, (5) incorporation of organic fertilizers in the spring on fall-planted cereals is not feasible. Innovative measures should be developed by researchers to alleviate these palpable constraints on proper timing of organic fertilizer application to cropping systems.

Benefits to crop production

The literature is replete with examples of how organic fertilizers benefit crop production via their nutrient supplying capability, and herein no attempt will be made to cover the vast number of studies that have been conducted. Suffice it to say that organic fertilizers, when managed properly, can result in crop yields and quality of commodities equivalent to those produced with inorganic fertilizers.

Benefits to crop production, beyond nutrients supplied, can be realized when organic fertilizers are used as a nutrient source. Owing to their organic nature, these materials can build soil organic matter reserves, thus improving soil quality. The beneficial functions of soil organic matter include its capacity to: (1) serve as a nutrient reserve; (2) increase soil cation exchange capacity; (3) provide energy substrates for microbial transformations; (4) increase soil water-holding capacity; (5) stabilize soil structure; (6) reduce soil crusting; (7) increase water infiltration into soil; and, (8) buffer against rapid changes in acidity, alkalinity, and salinity (Tisdale et al., 1985).

Environmental concerns

Although salutary effects of organic fertilizers on crop production systems have been demonstrated, land application of these materials can cause environmental degradation. The major environmental concerns associated with land application of organic fertilizers include: (1) movement of soluble ions into groundwater, particularly NO_3-N; (2) movement of organically-bound and soluble nutrients, particularly P (Wood, 1998), and heavy metals (Wood et al., 1999), toxic organic compounds, and pathogenic organisms into surface water supplies; (3) excessive accumulation of nutrients, soluble salts, heavy metals, and toxic organic compounds in soil (Kingery et al., 1994, Wood et al., 1996); and, (4) emission of ammonia, greenhouse gases, and odors (Marshal et al., 1998, 1999). Many of these environmental concerns can have direct impacts on human and animal health, while others may limit plant growth. It should be noted that organic fertilizers, because of their chemical composition, vary in their pollution potential. For example, most barnyard manures are relatively benign when compared to industrial sludges. Furthermore, environmental problems arising from land application of organic fertilizers, in general, result only when these materials are mismanaged. Poor timing of application and excessive application rates are the avenues of organic fertilizer mismanagement that most often promote environmental problems.

Environmental contamination arising from mismanagement of land applied organic fertilizers, owing to its diffuse, land-based nature, is inherently nonpoint. Approaches to control pollution from these materials are generally some form of source management rather than collection and treatment of pollutants, as is typically done with point-source pollutants (Loehr, 1984). As pointed out by Bailey and Waddell (1979), source management to prevent environmental contamination from land application of organic fertilizers, commonly referred to as “best management practices” (BMPs), should be agronomically effective, environmentally effective, economically achievable, socially acceptable, and implementable. No single BMP will control the myriad of potential environmental problems arising from land application of organic fertilizers. Site-specific soil, topographical, climatic, operational, and crop factors, as well as the chemical composition of organic fertilizers are major considerations when developing BMPs for land applied organic fertilizers.

Future needs

Although organic fertilizers have been used in crop production systems for thousands of years, uncertainties in regard to proper management of these materials remain. In addition, human populations and intense livestock confinement systems continue to increase, which guarantees that greater amounts of organic wastes will necessarily be applied to land in the future. Research aimed at development of innovative systems for utilization of the massive amounts of organic materials generated that ensure environmental compatibility and sustained crop production, remains necessary.

A major constraint to proper utilization of organic fertilizers is knowledge of chemical and biological properties of the materials themselves. Although much laboratory work has been done in regards to mineralization of N from organic fertilizers, no standard, timely means of predicting N release from these materials is available. Since availability indices only account for potential N release, further knowledge of gaseous N losses from land applied organic fertilizers is needed to develop land application rate recommendations for organic fertilizers. Modeling based on data from a variety of climatic and soil conditions may offer a means of accounting for gaseous N losses from manures. Even more limited is information concerning the release of P and other nutrients or heavy metals from organic fertilizers. Most organic fertilizers, when applied on a N content basis, can result in excessive soil accumulations of P and/or other elements. This suggests that application rates for some organic fertilizers should be based on contents of elements other than N, which, in many cases would provide less than optimum amounts of N for crop production. Thus, research that addresses the need for supplemental N applications to crops fertilized with lesser amounts of organic fertilizer-N should be conducted.

Timing of organic fertilizer application can impact crop yield, farmers' operational schedules and labor and equipment costs, and the environment. Therefore, innovative application techniques and cropping systems should be designed that allow flexibility in application-timing without compromising crop yields, quality of commodities produced, and environmental quality. Little research has been aimed at developing systems for multiple applications of organic fertilizers within a single cropping period. Systems that allow application of organic fertilizers to a growing crop need further evaluation from both an engineering (spreading equipment design) and agronomic perspective. Furthermore, cropping systems that take advantage of residual nutrients from organic fertilizers during normally "non-crop" periods deserve further attention.

Much research has been done to assess the movement of chemical constituents of organic fertilizers from sites of land application. Although this research has provided a good view of potential environmental contamination when organic fertilizers are land-applied, presently there is little knowledge concerning off-site (e.g., downstream surface or ground waters) impacts of these materials. Data at the watershed level is needed to assess the real impacts that land application of organic fertilizers have on the environment. Finally, in a free, capitalistic society, the adoption of any system for utilization of organic fertilizers ultimately becomes a question of economics. Land managers, unless regulated, will not adopt a particular "best management practice" for handling these materials if it reduces profit. Organic fertilizers, by nature, are bulky materials with high transport costs relative to their value as nutrient sources. Thus, it is often more convenient to dispose of these materials on sites close to the source, rather than transporting them to sites where the maximum nutrient value could be obtained. This situation often promotes environmental degradation via poor timing of excessive application rates to land near the point of organic fertilizer origin. Economic research aimed at accounting not only for the costs associated with handling and utilizing these materials, but also at accounting for the more nebulous "environmental costs" associated with mismanagement of organic fertilizers, should be conducted.

C. W. Wood

Bibliography

Bailey, G.W., and Waddell, T.E., 1979. Best management practices for agriculture and silviculture: an integrated overview. In Loehr, R.C., Haith, D.A., Walter, M.F., and Nartin, C.S., eds., *Best Management Practices for Agriculture and Silviculture.* Ann Arbor, MI: Ann Arbor Sci. Pub., pp. 35–56.

Barber, S.A., and Olson, R.A., 1968. Fertilizer use on corn. In Nelson, LB., ed., *Changing Patterns in Fertilizer Use.* Madison, WI: Soil Science Society of America, pp. 163–188.

Bouldin, D.R., Klausner, S.D., and Reid, W.S., 1984. Use of nitrogen from manure. In Hauck, R.D., ed., *Nitrogen in Crop Production.* Madison, WI: American Society of Agronomy, pp. 221–245.

Collings, G.H., 1955. *Commercial Fertilizers.* New York: McGraw-Hill, 617 pp.

Converse, J.C., Bubenzer, G.D., and Paulson, W.H., 1976. Nutrient losses in surface runoff from winter spread manures. *Trans. Am. Soc. Agric. Eng.*, **19**: 517.

Cummins, C.G., Wood, C.W., and Delaney, D.P., 1993. Co-composted poultry mortalities and poultry litter: composition and potential value as a fertilizer. *J. Sustainable Agric.*, **4**(1): 7–19.

Douglas, B.F., and Magdoff, F.R., 1991. An evaluation of nitrogen mineralization indices for organic residues. *J. Environ. Qual.*, **20**: 368–372.

Emerton, B.L., Mote, C.R., Dowlen, H.H., Allison, J.S., and Sanders, W.L., 1988. Comparison of forced and naturally aerated composting of dairy manure solids. *J. Am. Soc. Agric. Eng.*, **4**(2): 159–164.

Essig, H.W., 1985. Quality and antiquality components. In Taylor, N.L., ed., *Clover Science and Technology.* Madison, WI: American Society of Agronomy, pp. 309–324.

Ferrero, G.L., and L'hermite, P.L., 1985. Composting – progress to date in the European Economic Community and prospects for the future. In Gasser, J.K.R., ed., *Composting of Agricultural and Other Wastes.* London, UK: Elsevier, pp. 3–10.

Flynn, R.P., and Wood, C.W., 1996. Temperature and chemical changes during composting of broiler litter. *Compost Sci. Util.*, **4**(3): 62–70.

Flynn, R.P., Wood, C.W., and Guertal, E.A., 1995. Lettuce response to composted broiler litter as a potting medium. *J. Am. Soc. Hort. Sci.*, **120**(6): 964–970.

Frye, W.W., Blevins, R.L., Smith, M.S., Corak, S.J., and Varco, J.J., 1988. Role of annual legume cover crops in efficient use of water and nitrogen. In Hargrove, W.L., ed., *Cropping Strategies for Efficient Use of Water and Nitrogen.* Madison, WI: American Society of Agronomy, pp. 129–154.

Groffman, P.M., Hendrix, P.F., and Crossley, D.A., Jr., 1987. Nitrogen dynamics in conventional and no-tillage agroecosystems with inorganic fertilizer or legume nitrogen inputs. *Plant Soil*, **97**: 315–332.

Hensler, R.F., Olsen, R.J., Witzel, S.A., Attoe, G.J., Paulson, W.H., and Johannes, R.F., 1970. Effect of manure handling on crop yields, nutrient recovery, and runoff losses. *Trans. Am. Soc. Agric. Eng.*, **13**: 726.

Huntington, T.G., Grove, J.H., and Frye, W.W., 1985. Release and recovery of nitrogen from winter annual cover crops in no-till corn production. *Commun. Soil Sci. Plant Anal.*, **16**: 193–211.

Kingery, W.L., Wood, C.W., Delaney, D.P., Williams, J.C., and Mullins, G.L., 1994. Impact of long-term land application of broiler litter on environmentally related soil properties. *J. Environ. Qual.*, **23**: 139–147.

Klausner, S.D., Zwerman, P.J., and Ellis, D.F., 1976. Nitrogen and phosphorus losses from winter disposal of dairy manure. *J. Environ. Qual.*, **5**: 47.

Lanyon, LE., and Griffith, W.K., 1988. Nutrition and fertilizer use. In Hanson, A.A., ed., *Alfalfa and Alfalfa Improvement.* Madison, WI: American Society of Agronomy, pp. 333–372.

Larson, W.E., Holt, R.F., and Carlson, C.W., 1978. Residues for soil conservation. In Oschwald, W.R., ed., *Crop Residue Management Systems.* Madison, WI: American Society of Agronomy, pp. 1–15.

Loehr, R.C., 1974. *Agricultural Waste Management.* New York: Academic Press, 576 pp.

Loehr, R.C., 1984. *Pollution Control for Agriculture.* New York: Academic Press, 467 pp.

Marshall, S.B., Wood, C.W., Cabrera, M.L., Guertal, E.A., and Mullen, M.D., 1998. Ammonia volatilization from fescue pastures fertilized with broiler litter. *J. Environ. Qual.*, **27**: 1125–1129.

Marshall, S.B., Cabrera, M.L., Braun, L.C., Wood, C.W., Mullen, M.D., and Guertal, E.A., 1999. Denitrification from Fescue Pastures fertilized with Broiler Litter. *J. Environ. Qual.*, **28**: 1978–1983.

McCalla, T.M., Peterson, J.R., Lue-Hing, C., 1977. Properties of agricultural and municipal wastes. In Elliot, L.F., and Stevenson, F.J., eds., *Soils for Management of Organic Wastes and Waste Waters.* Madison, WI: American Society of Agronomy, pp. 9–43.

Miller, R.H., and McCormack, D.E. (coleaders), 1978. Improving soils with organic wastes. *USDA Spec. Task Force.* Washington, DC: U.S. Department of Agriculture, U.S. Government Printing Office, 157 pp.

Miner, J.R., and Hazen, T.E., 1977. Transportation and application of organic wastes to land. In Elliot, L.F., and Stevenson, F.J., eds., *Soils for Management of Organic Wastes and Waste Waters.* Madison, WI: American Society of Agronomy, pp. 378–425.

Minshall, N.E., Witzel, S.A., and Nichols, M.S., 1970. Stream enrichment from farm operations. *Am. Soc. Chem. Eng. Div.*, **96**: 513.

National Research Council (NRC), 1989. *Alternative Agriculture*. Washington, DC: National Academy Press, 448 pp.

Overcash, M.R., Humenik, F.J., and Miner, J.R., 1983. *Livestock Waste Management*, Vol. II. Boca Raton, FL: CRC Press, 244 pp.

Parr, J.F., Miller, R.H., and Colacicco, D., 1984. Utilization of organic materials in developed and developing countries. In Bezcicek, D.F., ed., *Organic Farming: Current Technology and its Role in a Sustainable Agriculture.* Madison, WI: American Society of Agronomy, pp. 83–95.

Ranells, N.N., and Wagger, M.G., 1992. Nitrogen release from crimson clover in relation to plant growth stage and composition. *Agron. J.*, **84**: 424–430.

Sherlock, R.R., Sommer, S.G., Khan, R.Z., Wood, C.W., Guertal, E.A., Freney J.R., Dawson, C.O., and Cameron, K.C., 2002. Emission of ammonia, nitrous oxide and methane from pig slurry applied to a pasture in New Zealand. *J. Environ. Qual.*, **31**: 1491–1501.

Simpson, K., 1986. *Fertilizers and Manures.* New York: Longman, 254 pp.

Sommers, LE., and Giordano, P.M., 1984. Use of nitrogen from agricultural, industrial, and municipal wastes. In Hauck, R.D., ed., *Nitrogen in Crop Production.* Madison, WI: American Society of Agronomy, pp. 207–220.

SSSA, 1987. *Glossary of Soil Science Terms*. Madison, WI: Soil Science Society of America, 44 pp.

Stephenson, A.H., McCasky, T.A., and Ruffin, B.G., 1990. A survey of broiler litter composition and potential value as a nutrient source. *Biol. Wastes*, **34**: 1–9.

Sullivan, D.G., Wood, C.W., Owsley, W.F., Norfleet, M.L., Wood, B.H., Shaw, J.N., and Adams, J.F., 2003. Ammonia volatilization from a swine waste amended pasture. *Commun. Soil Sci. Plant Anal.*, **34** (11 & 12): 1499–1510.

Tisdale, S.L., Nelson, W.L, and Beaton, J.D., 1985. *Soil Fertility and Fertilizers.* New York: Macmillan, 754 pp.

USDA, 1957. *Soil – Yearbook of Agriculture*. Washington, DC: U.S. Government Printing Office.

USDA, 1979. Animal waste utilization on cropland and pastureland. *Utilization Research Report No. 6*. Washington, DC: Science and Education Administration.

USEPA, 1983. *Process Design Manual – Utilization of Municipal Sewage Sludge on Land*. Cincinnati, OH: Municipal Environmental Research Laboratory.

Varco, J.J., Frye, W.W., Smith, M.S., and MacKown, C.T., 1989. Tillage effects on nitrogen recovery by corn from a nitrogen-15 labeled legume cover crop. *Soil Sci. Soc. Am. J.*, **53**: 822–827.

Wagger, M.G., 1989. Cover crop management and nitrogen rate in relation to growth and yield of corn. *Agron. J.*, **81**: 533–538.

Wilkinson, S.R., 1979. Plant nutrient and economic value of animal manures. *J. Animal Sci.*, **48**(1): 121–133.

Wilkinson, S.R., 1992. Nitrogen carryover from broiler litter applied to coastal bermudagrass. In Blake, J., Donald, J., and Magette, W., eds., *Proc. Nat. Workshop on Poultry and Aquaculture Waste Management.* St. Joseph, MI: Am. Soc. Agric. Eng., pp. 166–170.

Wilson, D.O., and Hargrove, W.L., 1986. Release of nitrogen from crimson clover residue under two tillage systems. *Soil Sci. Soc. Am. J.*, **50**: 1251–1254.

Witter, E., and Lopez-Real, J.M., 1987. The potential of sewage sludge and composting in a nitrogen recycling strategy for agriculture. *Biol. Agric. Hort.*, **5**: 1–23.

Wood, C.W. 1998. Agricultural phosphorus and water quality: an overview. In Sims J.T., ed., *Soil testing for phosphorus: Environmental Uses and Implications*. SERA-17 USDA-CSREES Regional Committee Bull. No. 389. pp. 5–12.

Wood, C.W., and Edwards, J.H., 1992. Agroecosystem management effects on soil carbon and nitrogen. *Agric. Ecosyst. Environ.*, **39**:123–138.

Wood, C.W., and Westfall, D.G., 1989. Beneficial re-use of spent refinery catalyst as a P fertilizer for dryland winter wheat. *Hazard. Waste and Hazard. Mater.*, **6**(3): 241–250.

Wood, C.W., Westfall, D.G., Peterson, G.A., and Burke, I.C., 1990. Impacts of cropping intensity on potential C and N mineralization in no-till dryland agroecosystems. *Agron. J.*, **82**: 1115–1120.

Wood, C.W., Westfall, D.G., and Peterson, G.A., 1991. Soil carbon and nitrogen changes on initiation of no-till cropping systems. *Soil Sci. Soc. Am. J.*, **55**: 470–476.

Wood, B.H., Wood, C.W., Yoo, K.H., Yoon, K.S., and Delaney. D.P., 1996. Nutrient accumulation and nitrate leaching under broiler litter amended corn. *Commun. Soil Sci. and Plant Anal.*, **27**: 2875–2894.

Wood, B.H., Wood, C.W., Yoo, K.H., Yoon, K.S., and Delaney, D.P., 1999. Seasonal surface runoff losses of nutrients and metals from soils fertilized with broiler litter and commercial fertilizer. *J. Environ. Qual.*, **28**: 1210–1218.

Cross-references

Fertilizers, Inorganic
Humic Substances
Labile Pool
Macronutrients
Nitrogen Cycle
Plant Nutrients
Soil Microbiology
Tillage
Trace Elements

FIBRIC, HEMIC AND SAPRIC

Three terms for describing the state of organic material in peats and peaty soils (Histosols). Fibric marks an early stage in the decomposition of organic matter in the process of peat formation. Vegetable fibers are prominent and easily identified making up two thirds of the OM. Sapric relates to OM in which less than one sixth is recognizable as original plant material. Hemic is intermediate between the other two.

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

Cross-references

Histosol
Mire

FIELD CAPACITY

The amount of water remaining in a soil, when free drainage has effectively ceased two or three days after a wetting event.

FIELD pH

Soil pH is a fundamental property of soil systems and many inferences can be made regarding the chemical and agronomic properties of soils based on its value. It is considered a master variable of the soil system (McBride, 1994), and of weathering systems in general (Chesworth, 1992). Soil pH is a determination of the negative logarithm of the hydrogen ion (H^+) activity in soil solution, i.e., $pH = -\log_{10}(H^+)$, however, it is frequently more convenient to use H^+ ion concentration [H^+] rather than activity. A soil solution containing 1×10^{-7} mg H^+ l^{-1} would have a pH of 7.0. A solution of pH 5 contains 100 times more hydrogen ions than a solution of pH 7; similarly a solution of pH 9 is 100 times more alkaline than a solution of pH 7. Measured pH value is influenced by electrolyte concentration, soil to solution ratio, and time of equilibration (Bache, 1970; Davies, 1971; Mubarak and Olsen, 1976; Seatz and Peterson, 1964; Van Lierop, 1981).

The measurement of soil pH can be an important field operation for evaluating plant growth and for soil classification. Since soils in the landscape are spatially distributed, it is important to collect a soil sample that is representative of the area that is to be measured. Point measurements can be made but if the pH of a field is desired at least 20 to 25 small samples should be collected to provide a composite sample. This composite sample is thoroughly mixed and then subsampled for the pH determination.

Interpretation

Soils are seldom more acidic than pH 4 and rarely more alkaline than pH 9, even in extreme cases. Soil pH is well buffered above pH 7 and below pH 4 (Magdoff and Bartlett, 1985). The optimum pH for most field crops lies between 5.5 and 8.3. Below pH 5.5, free aluminum (Al^{3+}) and manganese (Mn^{2+}) can be present in the soil in concentrations that are high enough to reduce plant growth due to toxic amounts of these elements being taken up by plants. Above pH 8.3, excess Na^+ is usually present and can have adverse effects on soil properties and plant growth (Thomas, 2002). Data presented in Table F14 give broad guidelines for the interpretation of field pH values.

The availability of essential plant nutrients in soil is closely related to soil pH. For example, acid soils are often low in calcium and magnesium, two elements that are required in large amounts for the growth and reproduction of higher plants. Highly acidic elements such as manganese, iron, copper and zinc are also essential for plant growth but these elements, along with aluminum, can become too soluble at low pH and toxic concentrations are possible in plants growing on these soils. Conversely, too high a pH value could result in lowered solubility and plant deficiencies of essential elements.

Some crops are better adapted to extremes of pH. Knowledge of the acidity or alkalinity of a soil is therefore important from the crop suitability point of view. Also, pH is used as an indicator of when limestone ($CaCO_3$) must be incorporated into the soil to increase the pH value of an acidic soil to a point that is better suited to effective crop production.

Determination of soil pH in the field

Two primary methods are available for the determination of field pH – electrometric and colorimetric. Both methods can be rapid, accurate and give excellent results.

Electrometric method. Many inexpensive, battery-operated, hand-held pH meters are available for accurate measurement of soil pH in the field. Measurement with a pH meter and glass electrode is based on the principle that when two solutions are separated by a thin glass electrode membrane, an electrical charge potential exists between the hydrogen ions in the solution outside the electrode and the known concentration of hydrogen ions on the inside of the electrode. The difference in electrical charge potential is proportional to the hydrogen ion concentration of the solution being measured and the dial of the meter is calibrated to give readings in pH values. The meters have manual temperature compensation and calibration capabilities and will accurately read pH values from 0–14 when properly calibrated. Accuracy is usually reported from 0.1 to 0.01 pH units. The meter is normally used with a combination (hydrogen ion/calomel) pH electrode and is calibrated in the field using buffer solutions of pH 4, 7 and 10. These meters commonly operate from a normal 9V alkaline battery with 100 plus hours of continuous use.

The representative soil sample is mixed in a plastic container with water or dilute salt solution, allowed to equilibrate, then the electrode is inserted into the mixture and the pH read directly on the dial or digital readout of the meter.

Colorimetric procedures. Colorimetric determinations are commonly less precise than electrometric determinations but the accuracy is good enough for many purposes. Colorimetric evaluation of field soil pH is based on the use of pH indicator dyes that give a specific color when in contact with solutions of varying pH. Indicator dyes form weakly colored, slightly dissociated acids and highly colored, strongly dissociated salts of metallic cations. The full color range of almost every colorimetric pH indicator is approximately ± one pH unit from mid-color for ± 90% of the color change (Jackson, 1958). The H^+ ion concentration of the solution regulates the amount of indicator, which dissociates. Indicator dyes can be in powder form, compressed into tablets, impregnated into paper strips or mixed

Table F14 Practical interpretation and implications of field pH

Field pH rating	pH	Field interpretation
Extremely acid	4.0	Free acid present, usually from oxidation of iron sulfides (FeS_2) to sulfuric acid (H_2SO_4).
Strongly acid	5.0	Soluble aluminum(Al), iron (Fe) and manganese (Mn)
	5.5	Exchangeable Al^{3+} present
Moderately acid	6.0	Common range of soil pH for crop production on non-calcareous soils.
Slightly acid	6.5	Exchangeable cations dominated by Ca^{2+}, Mg^{2+} and K^+
Neutral soil pH	7.0	
Slightly alkaline	7.6	
Moderately alkaline	8.0	Free $CaCO_3$ can be present
Strongly alkaline	8.3	Sodic soils with potential for excessive Na^+

Table F15 Common indicators used for determiing soil pH and the pH and color of their useful range (Kolthoff and Sandell, 1948; Weast, 1981)

Indicator	Intermediate color pH range	Color at end of intermediate range
Thymol blue	1.2–2.8	red–yellow
Bromophenol blue	3.0–4.6	yellow–blue
Bromocresol green	3.8–5.4	yellow–blue
Methyl red	4.8–6.0	red–yellow
Chlorophenyl red	5.2–6.8	yellow–red
Bromocresol purple	5.2–6.8	yellow–purple
Bromothymol blue	6.0–7.6	yellow–blue
Cresol red	7.0–8.8	yellow–red
Thymol blue	8.0–9.6	yellow–blue
Phenolphthalein	8.2–10.0	colorless–pink

Table F16 pH range and color change of a mixed indicator. The mixture consists of 5 mg thymol blue, 25 mg methyl red, 60 mg bromothymol blue and 60 mg phenolphthalein dissolved in 100 mL of 75% ethanol and neutralized to a green color with 0.01 M NaOH

pH		4	5	6	7	8	9
Color	red	orange	yellow	green	blue	indigo	violet

as solutions. Mixtures of indicators can be prepared to determine pH from about 2 to 9 with accuracy to the nearest pH unit. More accurate results can be obtained with indicators or combinations of indicators that are sensitive to smaller pH changes and can give pH values to 0.1 or 0.2 pH unit. Individual indicators that are commonly used in soil pH determination and their useable pH ranges are shown in Table F15. The ranges for the individual dyes overlap, and in many cases a sample of soil can be tested with two dyes, which result in a more accurate determination. Mixtures of indicators can be used to produce a single solution that covers a broader range in soil pH. One mixture is given in Table F16, which will cover the pH range from 4 to 9. Other multicomponent indicators have been described by Jackson (1958) for field-testing purposes.

Small subsamples of soil are commonly mixed in a small porcelain spot plate with the indicator solution. Indicator solutions give approximate but satisfactory results when properly used. When an indicator contacts the soil in suitable amounts, the unbuffered indicator assumes the pH of the highly buffered soil. After equilibrium is reached the color of the indicator is compared with a standard chart that relates the color of the indicator to pH. An inert white powder (commonly $BaSO_4$) is sometimes used to cover the soil sample, mask the soil color, and provide a more accurate pH indicator color determination. The powder draws the pH indicator solution from the soil for comparison to a color chart.

Paper strips impregnated with indicator dyes have also been successfully used to estimate soil pH to within half a pH unit of laboratory values (Thomas, 1996).

L. R. Hossner

Bibliography

Bache, B.W., 1970. Determination of pH, lime potential and aluminum hydroxide potential of acid soils. *J. Soil Sci.*, **21**: 28–37.

Chesworth, W., 1992. Weathering systems, Chapter2. In Martini, I.P., and Chesworth, W., eds., *Weathering, Soils and Paleosols.* New York: Elsevier, pp. 19–40.

Davies, B.E., 1971. A statistical comparison of pH values of some English soils after measurement in both water and 0.01 M $CaCl_2$. *Soil Sci. Soc. Am. Proc.*, **35**: 551–552.

Jackson, M.L., 1958. *Soil Chemical Analysis.* Englewood Cliffs, NJ: Prentice-Hall, pp. 49–55.

Kolthoff, I.M., and Sandell, E.B., 1948. *Textbook of Quantitative Inorganic Analysis.* New York: The Macmillan Company, pp. 448–450.

Magdoff, F.R., and Bartlett, R.J., 1985. Soil pH buffering revisited. *Agron. J.*, **49**: 145–148.

McBride, M.B., 1994. *Environmental Chemistry of Soils.* New York: Oxford University Press, 406 pp.

Mubarak, A., and Olsen, R.A., 1976. An improved technique for measuring soil pH. *Soil Sci. Soc. Am. J.*, **40**: 880–882.

Seatz, L.F., and Peterson, H.B., 1964. Acid, alkaline, saline and sodic soils. In Bear, F.E., ed., *Chemistry of the Soil. Am. Chem. Soc. Monogr. 16.* New York: ACM, pp. 296–297.

Thomas, G.W., 1996. Soil pH and soil acidity: p475–490. In Sparks, D.L., ed., *Methods of Soil Analysis. Part 3: Chemical Methods.* Madison, WI: Soil Science Society of America, 1390 pp.

Thomas, G.W., 2002. pH. In Rattan Lal, ed., *Encyclopedia of Soil Science.* New York: Marcel Dekker, pp. 980–984.

Van Lierop, W., 1981. Conversion of organic soil pH values measured in water, 0.01 M $CaCl_2$ or 1 M KCl. *Can. J. Soil Sci.*, **61**: 577–579.

Weast, R.C., 1981. *Handbook of Chemistry and Physics.* Boca Raton, FL: CRC Press, pp. D150–D151

Cross-references

Acid Soils
Acidity
Acids, Alkalis, Bases and pH
Alkaline soils
Calcareous Soils
Near Neutral Soils
Soil
Thionic or Sulfidic Soils

FIELD WATER CYCLE

Various sub-cycles of the total *hydrologic cycle* can be defined. One of these describes the dynamics of water movement on, into, out of, and below the surface of the Earth. This subcomponent is called the field water cycle. It is often separated from the full hydrologic cycle, because many believe that this is the environment where some of the most important physical, chemical and biological processes occur (Hillel, 1971). The continued functioning of these processes and the quantity and quality of water associated with them, are critical to the health and survival of plants and animals (including us).

The water balance

The full hydrologic cycle addresses the movement of water in its various states through the Earth-atmosphere system. The major components of the cycle are *precipitation*, *infiltration*, and *evapotranspiration*, runoff, and change in *storage*. It can be quantified through the use of an input-output model called the water balance or *water budget*. It is a form of the hydrologic continuity equation and is given by

$$I = O + dS \qquad (1)$$

where I = input, O = output, and dS = change in storage.

The designation of a process as an input or output depends on the location where the water balance equation is considered. In the subsurface region, the input for the field water cycle in

Equation (1) is infiltration while outputs are evapotranspiration and *drainage*. The sub-surface movement of water, in addition to drainage, can be described as input or output depending on the direction of flow across the boundary defining the region of interest. The change in storage term addresses primarily the water stored in the soil. Depending on the boundaries of the region of study and the detail of analysis, a number of other processes, as well as sites of water storage, can be added to Equation (1). These range from ground water flow, to water intercepted by vegetation, water intercepted by surface depressions, capillary water rise in the soil, and water stored in the tissue of plants to name a few. A more comprehensive accounting of the processes involved in water movement and storage in the subsurface, and on the surface, results in Equation (1) being expanded to include a number of these terms (Marshall et al., 1996; Hillel, 1971; Jury and Horton, 2004).

While Equation (1) is linear, the actual processes involved in the movement of water are in general non-linear. Examined in more detail, the terms are also often interrelated. This results in rather complicated relationships needed to describe the movement of water above, into, out of, and through the subsurface. A number of empirical or simplified equations have been developed to describe the movement of water in these regions (Marshall et al., 1996). These are often used in the routine analysis of everyday water movement problems. With the availability and power of newer mathematical techniques and computers, the detailed or full differential equations are now slowly being solved for real world settings with a range of heterogeneity in physical characteristics and non-linearity in relationships (Bear and Verruijt, 1991). There are still large problems to be overcome in order to be able to describe the full range of conditions found in the real world (Greminger et al., 1985). It will be some time before readily usable full predictive equations, or other quantitative techniques, for describing water movement in all situations are available.

Infiltration

This component of the field water cycle addresses the movement of water into the soil. This may be from water falling on the surface from precipitation, water moving across the surface in runoff or irrigation, the melting of snow on the surface, or from surface water bodies such as ponds.

The infiltration rate of water into the soil during a rain precipitation event, when the precipitation rate is greater than the infiltration rate, is seen to vary with time. In cases where the soil was initially relatively dry the infiltration rate begins at a relatively high rate. It then decreases with time. In cases where the water is continually applied to the surface the infiltration rate approaches a constant value. In a well-drained soil this final rate is the permeability of the soil.

Norton's empirical infiltration equation (Horton, 1940) is often used to describe the approximately exponential water infiltration rate into a particular soil. This equation is given by

$$I = i_c + (i_0 - i_c)e^{-kt} \tag{2}$$

where: i = infiltration rate, k = empirical constant, i_0 = initial infiltration rate, i_c = final infiltration rate approached as soil becomes saturated, and t = time.

A convenient approximate cumulative infiltration equation (Philip, 1957) is given by

$$I = St^{1/2} + Kt \tag{3}$$

where I = cumulative infiltration, S = sorptivity, K = saturated permeability of soil profile, and t = time.

The sorptivity is proportional to the difference between the initial and final water contents and to the square root of the field water diffusivity. This equation is the first two terms of an infinite series solution of the water-flow differential equation.

During the initial stages of infiltration, when there is a relatively high infiltration rate, both the water entering the soil and the air contained in the soil move downward. Later, as the infiltration rate decreases, air starts to flow upward. The effects of air compression and its flow counter to that of water are sometimes included in the water transport equations (Morel-Seytoux and Khanji, 1975).

As water infiltrates into a relatively dry soil, a *soil moisture front* is formed between the increased soil moisture from the applied water and the existing soil moisture. When water is applied to a well-drained soil this wetting front moves generally downward, with some lateral movement. The lateral movement depends on the physical characteristics of the soil as well as vegetative root distributions, cracks in the soil and other factors. In many cases the wetting front is found to not be a smooth surface but to exhibit preferential flow channels or regions where the water enters and moves through the subsurface faster than in surrounding regions. This preferential flow adds to the complexity required for the mathematical description of water moving into and through the subsurface.

Runoff

Water that leaves a site by surface flow is called runoff. It occurs when there is a greater input rate of water to a surface site than can leave by the sum of infiltration, evapotranspiration, and rate of storage. Runoff usually results when the precipitation rate, or water application rate, exceeds the infiltration rate. Many chemicals (e.g., those from fertilization of vegetation or pesticides for insect management) can be dissolved in runoff water or transported on detached soil particles moving with it. As a result many non-point source pollution analyses are closely linked with runoff analyses. The amount of runoff and its timing are important to analyses ranging from flood and erosion prediction on watersheds to predicting the rate of advance of irrigation water over a surface irrigated field.

Redistribution

Water in the subsurface moves in response to a number of gradients, including those due to gravity, water-content, and temperature. The potential concept is often used to simplify the analysis of the various forces acting on water. The water responds to the *total potential* it experiences (Marshall et al., 1996). The total potential is comprised of the matric, osmotic, gravity, pneumatic, and overburden potentials. For soil beneath the water table, the matric potential is replaced by a submergence potential. Water content and matric potential are often related by water characteristic curves. These curves are not unique but depend on the soil's wetting and drying history. The curves exhibit hysteresis loops referred to as scanning curves.

A number of equations have been developed to describe the movement of water in the unsaturated and in the saturated regions of the soil. Historically, soil physicists performed much of the earlier unsaturated flow analysis while ground-water hydrologists and drainage engineers largely addressed saturated flow. This is changing as each group learns more of the others activities. The result is a blending of the analytical tools and techniques into a more comprehensive analysis of water movement. The basic conservation equations of physics are the foundation for the analysis. Darcy's Equation relates velocity of water to permeability of the soil and the hydraulic gradient (Hillel, 1971). For vertical water entry into the soil, what is often measured rather than velocity is the change in volumetric moisture content with respect to time at various depths.

In a sufficiently deep soil with no ground water near the surface, the typical moisture profile after infiltration has ceased consists of a wetted region in the upper part of the profile and a relatively dry zone beneath. The post infiltration movement of water from the more moist to less moist regions is called *redistribution*. The downward movement of the water becomes increasingly slower with time. When the redistribution rate becomes negligibly small, the soil *field capacity* is reached. This is often taken to represent the upper limit of moisture available to plants. It is not a constant, for while the redistribution rate becomes relatively slow after two to three days it still has a non zero value after days, weeks, or even months in some cases. Soils vary considerable in their ability to hold water at any given time after cessation of infiltration. Field capacity can range from 4% in sands to 45% in heavy clay soils.

Evapotranspiration

This component of the field water cycle contains both the evaporation of water from the surface of the soil and the *transpiration* of water by plants. The combination of processes is called evapotranspiration. These processes describe water moving into the atmosphere from the Earth (Taiz and Zeiger, 2002). In the input-output model of Equation (1) this is an output from the field water system.

The rate at which water is taken from the soil by vegetation and passed to the atmosphere depends on the gradients of potential and the conductivities. These depend on a number of factors, the moisture content of the soil, the texture, the relative humidity of the atmosphere, the temperature of the atmosphere as well as the type of plant, the physiological condition of the plant and its stage of development.

As water evaporates from the soil surface, gradients are set up that move soil water to the surface. The rate of movement decreases as water content decreases. Where there is a water table within 2 m of the surface, this movement can continue. Capillary rise will continue to move water from the water table to the surface for evaporation.

The introduction of vegetation on the surface adds another process (transpiration) to move water from the subsurface to the atmosphere. The roots of plants reach out into the soil and allow transpiration to remove more water from the soil, and at greater depths, than from evaporation alone. The addition of vegetation to a surface area does not mean the resultant water transfer rate to the atmosphere will be the existing evaporation rate plus the transpiration. Plants cause shading of the soil and an accumulation of vegetative debris on the surface, both of which reduce the amount of water that is evaporated from the soil surface. Available energy for evapotranspiration determines the rate of maximum water loss.

As the soil water content decreases the energy with which water is held in the soil increases; the work required increases; the plant cannot obtain the water needed and begins to show stress signs such as a loss of turgor pressure in the leaves. With minor water stressing, the plant will recover if water is added to the root zone. If the plant water stress continues a point will be reached for many plants where the addition of water to the root zone will not allow the plant to recover. This is the water content at the permanent wilting point for that soil.

Drainage

Some of the water that infiltrates, or has arrived in the subsurface by other paths such as subsurface flow, leaves the region by movement in natural drainage to another lateral region, by movement to artificial drains installed to remove water, and/or by deep percolation to deeper regions of the subsurface. In all cases, drainage water is considered to be moving away from the near surface region of the subsurface and is thus an output in Equation (1).

The *capillary rise* of water toward the soil surface is considered a negative drainage. For a water table near the surface, the capillary rise of water will continue to transfer water from the water table to the surface where it is evaporated or taken up by plant roots.

The movement of water from the saturated regions of the subsurface (aquifer) to the surface (e.g., springs) is also regarded as negative drainage. These situations range from water flowing to the surface from a confined aquifer that is under pressure to the gravitational flow of water out the side of a hill slope.

Storage

Water in the near surface region is stored primarily in the pores of the soil. Other, smaller storage sites are surface depressions and the tissue of vegetative material. The interception of precipitation can also be thought of as a storage as can the accumulation of snow, even though their average residence time may be less than that associated with other forms of storage.

The *porosity* of the subsurface material indicates how much water can be contained per unit volume of saturated material (Todd, 1980). A gravel aquifer can hold 0.20 m of water per meter depth of the aquifer while a clay aquifer can hold 0.45 m of water per meter depth. The *specific yield* of these aquifers suggest about 88% of the water held in the gravel aquifer will drain out (can be pumped out) while only 7% of the clay water will drain. The saturated hydraulic conductivity values for these materials indicate how fast water moves in the aquifer in response to a given gradient. Since hydraulic conductivity values for these two materials differ by roughly five orders of magnitude, a similar difference exists for water flow velocity in these aquifers, and the extraction time for a selected volume of water.

William O. Rasmussen

Bibliography

Bear, J., and Verruijt, A., 1991. *Modeling Groundwater Flow and Pollution.* Dordrecht: Reidel, 414 pp.

Greminger, P.J., Sud, Y.K., and Nielsen, D.R., 1985. Spatial variability of field-measured soil–water characteristics. *Soil. Sci. Soc. Am. J.*, **49**: 1075–1082.

Hillel, D., 1971. *Soil and Water.* New York: Academic, 288 pp.

Horton, R.E., 1940. An approach towards a physical interpretation of infiltration capacity. *Soil Sci. Soc. Am. Proc.*, **5**: 399–417.

Jury, W., and Horton, R., 2004. *Soil Physics*, 6th edn. Hoboken, NJ: Wiley, 370 pp.

Marshall, T.J., Holmes, J.W., and Rose, C.W., 1996. *Soil Physics.* Cambridge: Cambridge University Press, 453 pp.

Morel-Seytoux, H.J., and Khanji, J., 1975. Equation of infiltration with compression and counterflow effects. *Bull. Int. Assoc. Hydrol. Sci.*, **20**(4): 505–517.

Philip, J.R., 1957. The theory of infiltration. 1. The infiltration equation and its solution. *Soil Sci.*, **83**: 345–357.

Taiz, L., and Zeiger, E., 2002. *Plant Physiology.* Sunderland, MA: Sinauer Associates, 690 pp.
Todd, D.K., 1980. *Groundwater Hydrology.* New York: Wiley, 539 pp.

Cross-references

Flow Theory
Hydrological Cycle
Water Budget in Soil

FLOCCULATION

This is the aggregation of a discontinuous (disperse) phase in a continuous one, commonly of solid particles in a liquid. The resulting aggregates are *flocs*, from the Latin "floccus" (a lock of wool). The late Latin diminutive "flocculus" gave "flocculate" and "floccule." "Floccule" usually implies a small floc or some kind of smaller unit in a floc. The term *flocculation* has tended to displace "coagulation," which is sometimes preferred when the process is at least partially reversible.

In general, this discussion concerns the flocculation of crystalline particles (the discontinuous phase) in aqueous electrolyte solutions (the continuous phase) and thus with the flocculation of lyophobic (here "hydrophobic") colloidal systems. The terms "lyophobic" and "hydrophobic" are misleading because the discontinuous phase does not "fear" the ambient liquid and is solvated, although less markedly than in lyophilic systems where interaction with the continuous phase helps to maintain the dispersed state, the reverse of the flocculated condition. Even a lyophobic discontinuous phase is partially stabilized by adsorption of the continuous phase because its aggregation involves a positive change in desolvation free energy (Shaw, 1970). Its stability, however, depends mainly on the ability of interparticle electrical repulsion to overcome the interparticle attraction at the closest mutual approach attainable by the particles during their thermal kinetic (Brownian) movement.

The relative effectiveness of the repulsive and attractive forces at particular interparticle distances changes with the nature and/or concentration of the electrolytes in the continuous phase, and thus the tendency to dispersion or flocculation varies concomitantly. Hydrophobic colloidal particles, with which clay minerals have affinities, can be flocculated by small concentrations of electrolytes. For instance, if the particles have negative surface charges, the cations, rather than the anions, of the ambient electrolyte solutions are more significant in causing flocculation. Flocculating power increases rapidly with their charge number, but their chemical nature is less significant (van Olphen, 1963, 1977; Giese and van Oss, 2002).

The stability of hydrophilic colloids is little affected by electrolytes, although precipitation ("salting out") can occur at high electrolyte concentrations, presumably because the ions introduced compete with the disperse phase by virtue of their own hydration for the solvating liquid that promotes its stability.

Flocculation and its consequences

Because the tendency to dispersion or flocculation is controlled by interfacial forces, it becomes more apparent as the interfacial area between the discontinuous and continuous phases increases in a unit volume of the system. The tendency is usually obvious when the particles in a liquid are ca 1.0 μm to 1.0 nm (10^{-6}–10^{-9} m) equivalent spherical diameter (esd). These limits are arbitrary, and 1.0 nm, for instance, supposedly approximates to the diameters of large molecules. However, macromolecules and association colloids (micelles) have effective diameters well above 1.0 μm, yet both disperse spontaneously in appropriate continuous phases (*solvents*) and can be classed as *lyophilic colloids.*

Particles ca 1.0 μm esd are usually dense enough to settle slowly in water. Those with diameters near 1.0 nm esd stay in suspension indefinitely as long as they remain dispersed rather than flocculated because they are small enough to share markedly in the thermal kinetic energy of the system.

The effects of repulsive or attractive interfacial forces can be nullified, wholly or in part, by those of inertial forces. This tendency develops at smaller particle sizes as the density of the particle becomes increasingly greater than that of the ambient liquid. Nevertheless, clean, unwetted polystyrene spheres, slightly denser than water and 1.0 μm diameter, flocculate spontaneously on the surface of the liquid because inertial forces remain ineffective until a wetting agent is added. The spheres then disperse (deflocculate or become peptized) and subsequently sink (Sennett and Olivier, 1965).

Flocculation increases the size of the largest kinetic units in a system. The enlarged units may remain suspended (dispersed) if they still share sufficiently in the thermal kinetic energy of the system, but commonly they soon become big enough to sink and form a sediment. This sediment is markedly porous because interparticle attraction persists and causes both bridging by particles and the adhesion of floc to floc. Thus many particles cannot assume the positions of lower potential energy, which would be appropriate to a system predominantly influenced by gravitational forces. If the particle concentration is sufficient, the flocs may become linked throughout the entire volume of the system, which thus changes to a gelatinous mass (*gel*). This is exemplified by some systems of montmorillonite and aqueous electrolytes. Some gelled materials (*q.v.* in Vol. IVA: *Colloids; Mineraloids*) often develop lower apparent viscosities when disturbed because redispersion, usually incomplete, is producible mechanically. The resulting dispersion (*sol*) reverts to a gel when mechanical disturbance ceases. This cyclic behavior characterizes thixotropy (see *Thixotropy, thixotropism*).

Sediments from flocculated systems often show plastic, pseudoplastic, or thixotropic behavior if the supernatant liquid is first removed. Those from dispersed systems, when freed from the supernatant liquid, are commonly "dilatant" in the sense defined by Osborne Reynolds. Modern usage of this term does not always accord with the original definition (Roscoe, 1953).

Particles settling from dispersed systems, because they are mutually repulsive and unlikely to adhere, are sufficiently affected by gravitational forces to take up positions of relatively low potential energy and thus acquire some measure of close packing. Shearing of the resulting sediment produces regions in which the particles "come out of mesh" and the system expands (dilates) in consequence. However, dilatancy can be shown by aggregates of relatively coarse flocculated particles because here inertial forces suffice to produce relatively close packing. Cleavage fragments of feldspar exemplify the phenomenon (Williamson, 1946).

Flocculated, clay-rich, subaqueous sediments, especially if they contain montmorillonite, can crack beneath their supernatant liquid if, for instance, its salinity is changed (Burst, 1965). Thus ancient mudcracks in sedimentary rocks need not imply an earlier exposure to atmospheric drying.

Fundamental approaches to the flocculation of lyophobic colloids

These approaches are discussed by Sennett and Olivier (1965), Shaw (1970), van Olphen (1963) and Giese and van Oss (2002). If a particle in an electrolyte solution has a negative surface charge – and a negative charge is common and arises by several mechanisms – this charge is partially screened by positive counterions (cations), which are components of a diffuse electrical double layer. The cations necessary to screen the remaining charge are close to the particle surface as components of the *Stern layer*. The anions, which necessarily accompany the cations in an electrolyte solution, constitute the coions or simili-ions and concentrate away from, rather than towards, the negatively charged particle surface.

Flocculation, thermodynamically considered, implies a state energetically lower than that of the corresponding dispersed system, yet it is not always rapid, and some systems remain dispersed for years. Although the thermal kinetic energy of the particles promotes mutual collisions, the collision frequency is manifestly not the sole factor controlling flocculation rate.

Flocculation results from the predominance of attractive forces at attainable interparticle distances. Such forces include those categorized as van der Waals, but especially their London components, which become increasingly effective as mass increases; the masses of colloidal particles suffice to make these forces significant. However, coulombic attractions are involved, for instance, in the flocculation of clay minerals.

If only the most thermokinetically energetic particles achieve the interparticle distances at which attractive forces predominate, flocculation is slow. If none achieves them, the system remains dispersed, or if very many, it flocculates rapidly. Opposition to flocculation results from interaction between the electrical double layers that surround each particle, and mutual approach of the particles causes an increasing repulsive force that may or may not be overcome by the attractive forces that promote flocculation. In essence, the situation can be represented by energy barriers of various heights that must be surmounted by virtue of an activation energy supplied thermokinetically by the mutually approaching particles. Appropriate calculations yield a family of curves (Figure F22).

Extensions of the mathematical arguments that lead to Figure F22, and to cognate representations, explain the *Schulze-Hardy rule* (Sennett and Olivier, 1965), and in addition, the compression of the electrical double layers that may result in an interparticle attraction effective enough to cause flocculation. Such compression can develop, for instance, in the presence of a sufficiently concentrated electrolyte, although smaller concentrations might favor dispersion rather than flocculation.

Chemical reaction between particles and their surrounding electrolyte solution complicates flocculation behavior. Clay minerals, in water or in aqueous electrolyte solutions, commonly behave in this way, and elements that were originally constituents of their crystal structures become ions, usually complex, in the ambient solution. Thus a clay mineral particle can contribute, by continued chemical reaction, to its own counterions and coions, with corresponding alterations in the flocculation state of the system, sometimes made apparent by simultaneous

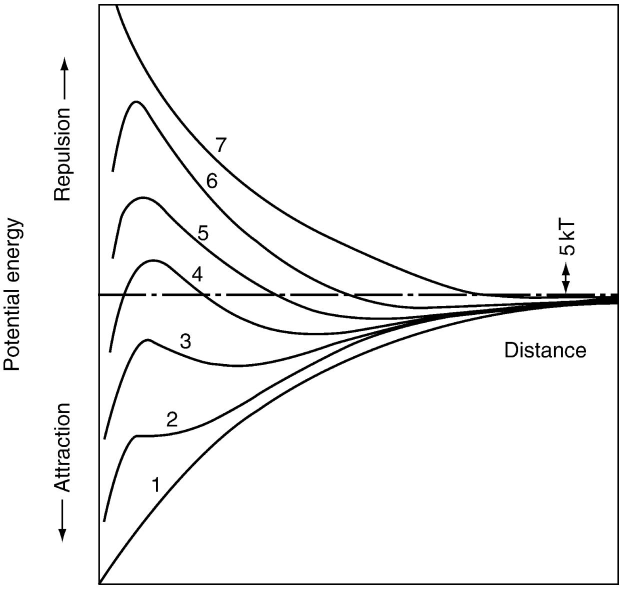


Figure F22 Net potential energy of interaction between particles in a colloidal suspension. *Curve 1:* attraction in the absence of effective repulsion, implying high electrolyte concentration and rapid flocculation. *Curves 2–7:* effects of decreasing electrolyte concentration and hence increasing double-layer thickness and longer ranging repulsive forces. *Curve 5:* the ca. 15 kT barrier imparts considerable stability to the dispersion. *Curves 3–4:* rapid and slow flocculation, respectively. Some curves have a secondary minimum at ca. 200 Å interparticle separation that may be deep enough (*curve 4*) to cause reversible flocculation (coagulation) of a considerable number of particles, especially if these are rod- or plate-like.

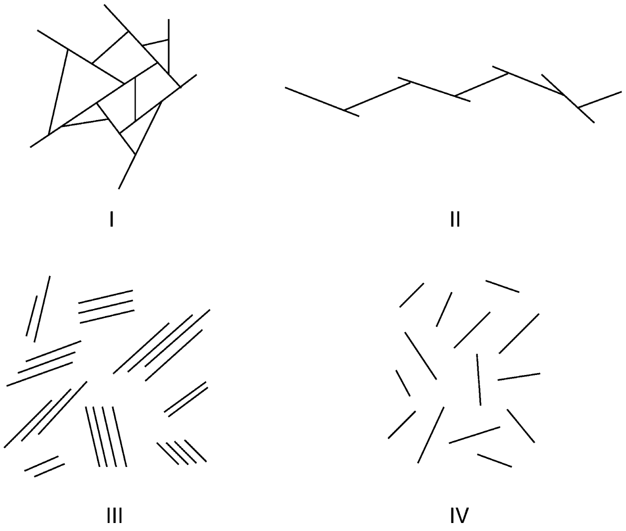


Figure F23 Schematic of kaolinite platelets associated in: *I* card-house floc formed under condition *a* of Figure F24; *II* adlineated floccule, presumably related to a card-house floc but with fewer edge-to-face contacts; *III* card-pack flocs. In *IV* the platelets are dispersed as suggested by condition *c* and perhaps *b* of Figure F24.

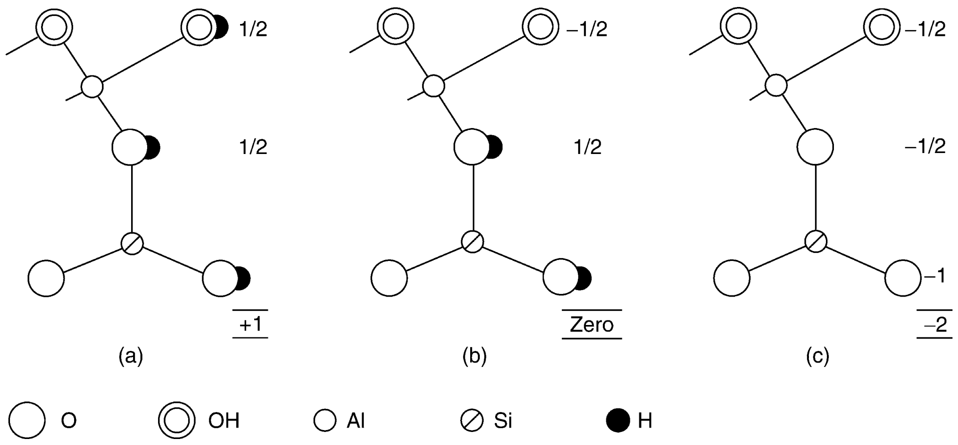


Figure F24 Hydrions attached, if at all, to oxygens at the edge faces of kaolinite when the ambient solution is (**a**) acid, (**b**) slightly alkaline, and (**c**) strongly alkaline.

changes in the apparent viscosity. The apparent viscosity commonly increases as flocculation progresses.

Flocculation of kaolinite

Kaolinite platelets can associate in card-house, card-pack (Figure F23), or other types of floc. The type of floc varies with the nature and concentration of the electrolytes present and with the corresponding pH values. Okuda and Williamson (cited in Williamson, 1974) photographed both card-house and card-pack flocs existing undisturbed in suspensions. The reality of such flocs cannot be doubted, but it is now realized that several types of open- or close-textured floc can be postulated, and electron microscopical techniques have confirmed the existence of some of them (Smart, 1971; Williamson, 1974), although the mechanisms for their production are not altogether clear. The viscometric, sedimentation volume, or optical data thought to imply the presence of the cardhouse flocs postulated by Schofield and Samson (cited in Williamson, 1974) could be interpreted equally well in terms of other types of open-textured floc. Okuda and Williamson showed that card-house flocs became attached to negatively charged air bubbles by the edge faces of their constituent crystals; demonstrably, these faces were positively charged. A possible mechanism for the origin of the positive charge, implied by Schofield and Samson but not universally accepted, is indicated in Figure F24.

As the positive edge faces of kaolinite visibly adhered also to the basal surfaces of adjacent crystals (Okuda, cited in Williamson, 1974), the latter surfaces are negatively charged. It had long been postulated that such a negative charge existed and was independent of pH. It could arise because of very minor substitutions in the kaolinite structure, such as Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+}. This concept is not easily correlated with recent analytical data (Jepson and Rowse, 1975; see Ferris and Jepson, 1975; and Rand and Melton, 1975). Card-pack flocs tend to develop in the presence of multivalent cations or when monovalent cations are present in excess – even sodium ions, which at low concentrations usually favor dispersion rather than flocculation. Okuda and Williamson photographed such flocs, which had formed in approximately neutral systems containing calcium or lead cations.

Clay pastes, because of their high concentration of solids, are unlikely to contain open-textured flocs. Moreover, shearing of the paste could collapse such flocs if they existed. For instance, extruded plastic clay, whether dispersed or flocculated, tends to contain clay mineral platelets arranged as if in card-pack flocs. Even so, the structural arrangement in the dried flocculated clay may be somewhat more porous and mechanically weaker.

W. O. Williamson

Bibliography

Burst, J.F., 1965. Subaqueously formed shrinkage cracks in clay. *J. Sediment. Petrol.*, **35**: 348–353.
Ferris, A.P., and Jepson, W.B., 1975. The exchange capacities of kaolinite and the preparation of homoionic clays. *J. Colloid. Interface Sci.*, **51**: 245–259.
Giese, R.F., and van Oss, C.J., 2002. *Colloid and Surface Properties of Clays and Related Minerals.* New York: Marcel Dekker, 295 pp.
Jepson, W.B., and Rowse, J.B. 1975. The composition of kaolinite – an electron microscope microprobe study. *Clays Clay Min.*, **23**: 310–317.
van Olphen, H., 1963. *Clay Colloid Chemistry.* New York: Interscience, 301 pp.
van Olphen, H., 1991. *An Introduction to Clay Colloid Chemistry: for Clay Technologists, and Soil Scientists*, 2nd edn. Malabar, FL: Krieger Pub. Co., 318 pp.
Rand, B., and Melton, I.E., 1975. Isoelectric point of the edge surface of kaolinite. *Nature*, **257**: 214–216.
Roscoe, R., 1953. Suspensions. In Hermans, J.J., ed., *Flow Properties of Disperse Systems.* Amsterdam: North Holland, pp. 10–12.
Sennett, P., and Olivier, J.P., 1965. Colloidal dispersions, electrokinetic effects and the concept of zeta potential. *Ind. Eng. Chem.*, **57**: 32–50.
Shaw, D.J., 1992. *Introduction to Colloid and Surface Chemistry.* London: Butterworth-Heinemann, 306 pp.
Smart, P., 1971. Soil structures in the electron microscope, structure, solid mechanics and engineering design, Part I. *Proc. Southampton 1969 Civil Eng. Mater. Conf.*, 249–255.
Williamson, W.O., 1946. Rheology of aqueous feldspar pastes. *Nature*, **157**: 341–342.
Williamson, W.O., 1974. The strength of clays at small moisture contents. *Minerals Sci. Eng.*, **6**: 3–18.

Cross-references

Aggregate Stability to Drying and Wetting
Dispersion
Hydrophility, Hydrophobicity
Physical Chemistry
Thixotropy, Thixotropism

FLOOD PLAIN

The level tracts over which a river spreads in flood, and deposits its alluvium. Also called bottomland. A typical environment of Fluvisols, Geysols and buried soils.

FLOW THEORY

When the pore space of the soil matrix is completely filled with water, the soil is referred to as *water saturated*. Thus *saturated flow* may be defined as the movement of water through water-saturated soils. The theory governing saturated water flow in soils was first formulated by Darcy (1856). He discovered that water flow in vertical columns of water-saturated, sand filter beds is proportional to the head loss (or potential difference) between the ends of the column and to a factor known as the *hydraulic conductivity* (*q.v.*), K. Darcy's apparatus is illustrated in Figure F25, where L is the length of the sand column, A is the cross-sectional area, H_1 and H_2 refer to the height of standing water (or hydraulic heads) for the upper and lower ends of the column, respectively. Darcy found that the volume of water flow through the column per unit time can be expressed as

$$Q = KA\frac{H_1 - H_2}{L} = KAi \tag{1}$$

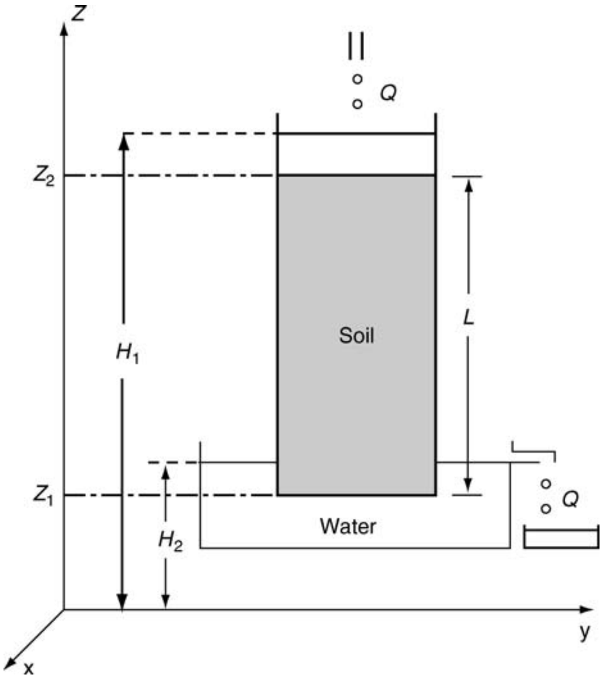


Figure F25 Diagram of soil column illustrating water flow in the vertical direction.

where i (dimensionless) is called the *hydraulic gradient*. Rearranging Equation (1), *Darcy's law* may be written in the form,

$$v = \frac{Q}{A} = Ki \tag{2}$$

where v is the water flow velocity that represents the volume of water flow per unit area of soil per unit time. It is clear from Equation (2) that the hydraulic conductivity K (the proportionality factor) has the dimensions of water velocity v. Furthermore; K is characteristic of the soil or the porous media, which indicates the ability of the soil to conduct water. In fact, from Equation (2) the hydraulic conductivity K is the water flow velocity in the soil (or porous media) when the hydraulic gradient i is unity.

It is convenient to express Darcy's law (Equations (1) or (2)) in differential forms, which is achieved by rewriting Equation (1) as

$$v = K\frac{H_1 - H_2}{z_2 - z_1} = -K\frac{H_2 - H_1}{z_2 - z_1} = -K\frac{\partial H}{\partial z} \tag{3}$$

where the partial derivative represents the change of H with respect to soil depth. Since Equation (3) represents water flow velocity in the z direction, i.e., vertically downward in the soil column (Figure F25), we can write Equation (3) as

$$v_z = -K_z\frac{\partial H}{\partial z} \tag{4}$$

where v_z and K_z are the water flow velocity and hydraulic conductivity of the soil in the z direction. Note that the negative signs in Equations (3) and (4) indicate that the water flow is in the negative z direction. Similarly, for water flow in the x direction and y direction, Darcy's Equation can be written, respectively, as

$$v_x = -K_x\frac{\partial H}{\partial x} \tag{5}$$

and

$$v_y = -K_y\frac{\partial H}{\partial y} \tag{6}$$

When the hydraulic conductivity of the soil is uniform, that is,

$$K_x = K_y = K_z \tag{7}$$

the soil is referred to as *isotropic*; otherwise, the soil is *anisotropic*.

The continuity equation

Darcy's law (Equations (4), (5), and (6)) is useful in describing flow patterns in the soil when the *water movement* (*q.v.*) is one dimensional, i.e., when water flow is in one direction only. Although Darcy's law is still valid, it is often difficult to apply directly to general soil-drainage problems in which water flow is predominantly in two or three dimensions.

The continuity equation is a general representation of water flow in the soil system and accounts for hydraulic head and soil water content changes with time at any location in the soil. To derive the continuity equation, let us examine the flow of water through a small volume element of a saturated soil. For simplicity, we consider the volume element to be a small rectangular paralle-piped with dimensions Δx, Δy, and Δz as shown in Figure F26. Assume that v_x is the water flow in the x direction (i.e., volume of water flow per unit area and time) entering the face ABCD of the volume element. Therefore the *inflow rate*, or the total volume of water flowing into ABCD per unit time, is

$$\text{inflow rate} = v_x \Delta y \Delta z \tag{8}$$

Similarly, if $v_x + \Delta x$ is the water flux in the x direction for water flow leaving the face EFGH, the total volume of water leaving EFGH per unit time, i.e., the *outflow rate*, is

$$\text{outflow rate} = v_{x+\Delta x} \Delta y \Delta z \tag{9}$$

From elementary calculus $v_x + \Delta x$ can be evaluated (approximately) from

$$v_{x+\Delta x} = v_x + \frac{\partial v_x}{\partial x}\Delta x \tag{10}$$

where $\partial v_x/\partial x$ is the rate of change of v_x in the x direction. From Equations (8), (9), and (10), the net volume of water flow (inflow-outflow) per unit time in the volume element from flow in the x direction is

$$\begin{aligned}\text{inflow rate-outflow rate} &= (v_x - v_{x+\Delta x})\,\Delta y\,\Delta z \\ &= \left(v_x - v_x - \frac{\partial v_x}{\partial x}\Delta x\right)\Delta y\,\Delta z \\ &= -\frac{\partial v_x}{\partial x}\Delta x\,\Delta y\,\Delta z \end{aligned} \tag{11}$$

Similarly, the net volume of flow per unit time from flow in the y direction is

$$-\frac{\partial v_y}{\partial y}\Delta x \Delta y \Delta z \tag{12}$$

and from flow in the z direction is

$$-\frac{\partial v_z}{\partial z}\Delta x \Delta y \Delta z \tag{13}$$

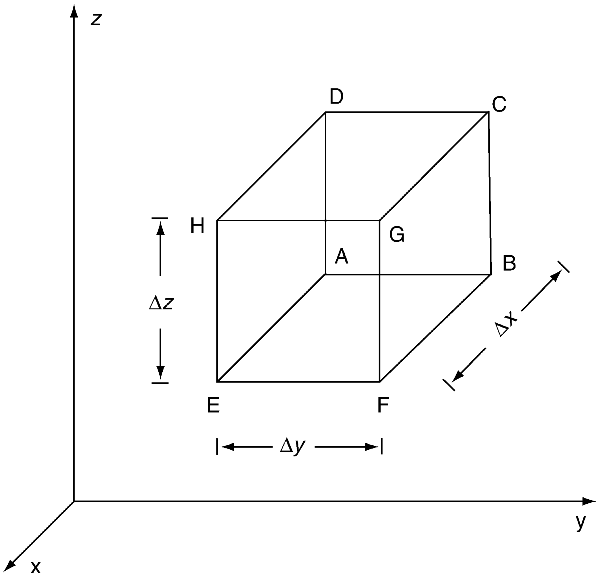


Figure F26 Rectangular volume element in water-saturated soil.

Adding Equations (11), (12), and (13) yields the net volume of water (inflow-outflow) per unit time for the entire volume element from water flow in the x, y, and z directions.

$$\text{net rate of flow} = -\left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}\right)\Delta x\,\Delta y\,\Delta z \tag{14}$$

This net rate of water flow is the volume of water gained or lost within the volume element per unit time. It is often called the *rate of water accumulation*. If θ is the volumetric water content, i.e., volume of water per unit volume of bulk soil, then, $\theta\,\Delta x\,\Delta y\,\Delta z$ is the total volume of water in the volume element. The net flow rate or the rate of water accumulation is $(\partial\theta/\partial t)\Delta x\,\Delta y\,\Delta z$, which represents the change with time of the total volume of water in the volume element. Equation (14) may then be rewritten as

$$\frac{\partial\theta}{\partial t}\Delta x\,\Delta y\,\Delta z = -\left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}\right)\Delta x\,\Delta y\,\Delta z \tag{15}$$

By dividing both sides of Equation (15) by $\Delta x\ \Delta y\ \Delta z$, we have

$$\frac{\partial q}{\partial t} = -\left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}\right)\Delta x\,\Delta y\,\Delta z \tag{16}$$

which is called the *continuity equation*. Substituting the differential forms of Darcy's law for v_x, v_y, and v_z (Equations (4), (5), and (6)) into the continuity Equation (16), we have

$$\frac{\partial\theta}{\partial t} = -\left(\frac{\partial}{\partial x}K_x\frac{\partial H}{\partial x} + \frac{\partial}{\partial y}K_y\frac{\partial H}{\partial y} + \frac{\partial}{\partial z}K\frac{\partial H}{\partial z}\right) \tag{17}$$

If the soil is isotropic, that is, $K_x = K_y = K_z = K$, and K_x is constant, Equation (17) becomes

$$\frac{\partial\theta}{\partial t} = -K\left(\frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2} + \frac{\partial^2 H}{\partial z^2}\right) \tag{18}$$

Furthermore, if the soil is water saturated, that is, if θ does not change with time, then

$$\frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2} + \frac{\partial^2 H}{\partial z^2} = 0 \tag{19}$$

which is known as *Laplace's Equation* (see Childs, 1969).

Soil drainage

Soil drainage (*q.v.*) may be defined as the removal of excess water from the soil root zone (cf. *Rhizosphere*). The drainage problems encountered under field conditions are unlimited. This discussion concerns describing the water flow pattern (*hydraulic head distribution*) and water-discharge rate for a given soil-drainage condition. These conditions are referred to as the "boundary conditions," which include, for example, rainfall or irrigation intensity, height of the water table, depth and spacings of drains, depth to an impervious layer. For a given soil-drainage problem, the boundary conditions are first outlined. A solution of the problem is then attempted by solving the water flow equation ((16) or (19)) for the outlined conditions. For simplification purposes, several assumptions are frequently made to arrive at a solution for a drainage problem. Therefore it is essential to use judgment in applying the drainage theory.

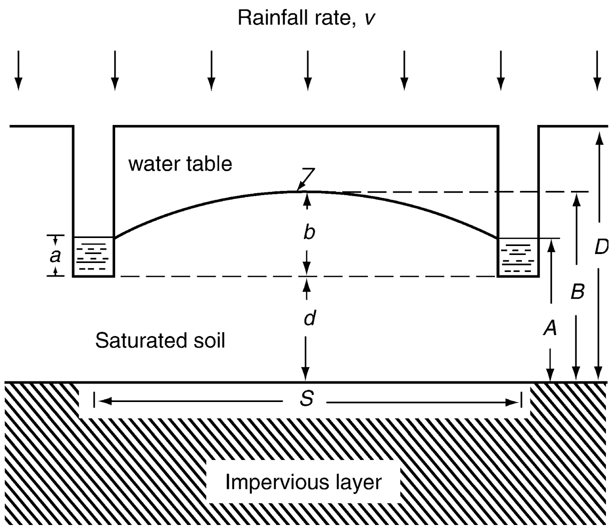


Figure F27 Schematic of surface drainage in a uniform soil underlain by an impervious layer. A water table between the open drain is maintained by a steady rainfall rate *v*.

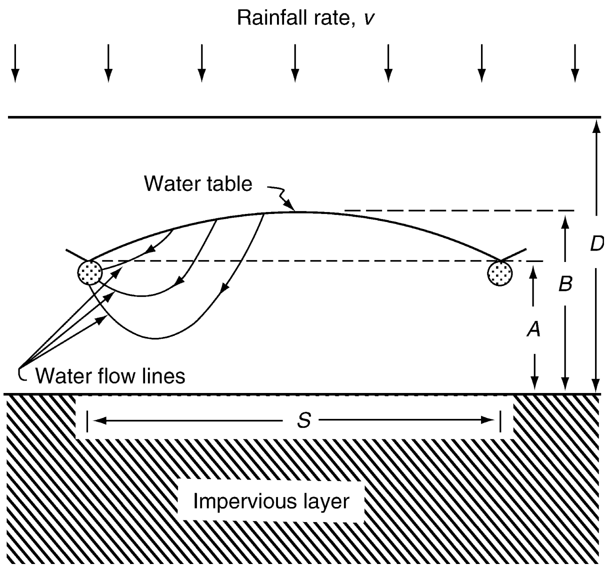


Figure F28 Schematic of subsurface draining in a uniform soil. A water table between the subsurface drains is maintained by a steady rainfall rate *v*.

To illustrate common drainage problems, Figure F27 shows a schematic of a uniform soil of a hydraulic conductivity K, having open or surface drains at spacings S. The soil is underlain by an impervious layer at depth D from the soil surface. Furthermore, the soil is receiving steady rainfall or irrigation with intensity v, where v is the volume of water per unit soil surface area per unit time. This water intensity maintains a water table with maximum height B midway between the drains and a water level A in the open drain. The corresponding drainage problem for soils having subsurface drains is illustrated in Figure F28. As shown in Figures F27 and F28, the water table may be regarded as the boundary separating the saturated soil region (below) and the unsaturated soil region (above). Therefore, below the water table, water flow is under saturated conditions, whereas water flow is under unsaturated conditions in the soil region bounded by the soil surface and the water table. Note also that in the saturated soil region, the flow path or water flow lines, which indicate the direction of water flow to the open or surface drains, are curvilinear in nature.

A simple formula, often used to determine the drain spacing S for soils having surface drains, Figure F27, is

$$S^2 = \frac{4K}{v}(b^2 - a^2 + 2bd - 2ad) \tag{20}$$

This formula clearly shows the dependence of S on the hydraulic conductivity of the soil K and the irrigation or rainfall intensity v. A similar formula for soils having subsurface drains (Figure F28) is

$$S^2 = \frac{4K}{v}(B^2 - A^2) \tag{21}$$

The above drain-spacing formulas (Equations (20) and (21)) are obtained on the basis of a certain simplification generally known as the *Dupuit-Forchheimer assumptions* (see Kirkham and Powers, 1972). Although these formulas do not provide an accurate description of the flow patterns, they are commonly used and generally yield adequate results (especially where B/S is small). More accurate drain-spacing formulas for the drainage problems shown in Figures (3) and (4) and many others can be found in Harr (1962), Luthin (1957), and Kirkham and Powers (1972).

H. M. Selim

Bibliography

Childs, E.C., 1969, *An Introduction to the Physical Basis of Soil Water Phenomena.* New York: Wiley-Interscience, 493 p.

Darcy, H., 1856. *Les fontaines publiques de la ville de Dijon.* Paris: Dalmont.

Harr, M.E., 1962. *Groundwater and Seepage.* New York: McGraw-Hill 315 p.

Kirkham, D., and Powers, W.L., 1972. *Advanced Soil Physics.* New York: Wiley-Interscience, 534 p.

Luthin, J.N., ed. 1957. *Drainage of Agricultural Lands, Monograph 7.* Madison: American Society of Agronomy, 620 p.

Cross-references

Capillary Pressure
Conductivity, Hydraulic
Field Water Cycle
Imbibition
Infiltration
Percolation
Permeability
Water Budget in Soil

FLUVIAL

Of or pertaining to a river or rivers; found or living in a river or riparian zone. The fluvial regime is dynamic and changeable in both space and time. Throughout, there is a changing relationship between erosion and deposition. In the upper reaches soil erosion by energetic waters tends to be dominant, while in the lower reaches, where the water flow is less energetic, sediments are deposited that have the potential to become soil parent materials. The sediments themselves may vary from gravel to sand, silt and clay, in any proportion or degree of sorting. The main determining factors controlling all physical features of the system are gradient, discharge and sediment supply. Characteristic soil types are Fluvisol, Gleysol and Histosol. On floodplains, sequences of buried soils (paleosols) are common.

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FLUVIOLACUSTRINE

Pertaining to or produced by the action of both rivers and lakes particularly at the interface of the two. Soil parent materials and derived soils do not in general differ markedly from those of the fluvial environment, though since the lake will act as the effective, local base level, water-saturated and wetland environments may be more common. Consequently, Gleysols and Histosols (with associated peat deposits) may be more prominent than in the fluvial regime.

FLUVISOLS

Fluvisols are weakly developed soils, commonly with A directly over C, formed predominantly on the water borne sediments associated with the flood plains rivers, and the shorelines of lakes and seas. Sedimentary stratification is usually present. This article is based on the descriptions in FAO (2001).

Connotation. Soils developed on alluvial deposits; from L. *fluvius*, river. The etymology is misleading in that Fluvisols are not confined to river sediments but also develop on lacustrine and marine deposits.

Synonyms. ‘Alluvial soils’ (Russia, Australia), ‘Fluvents’ (USDA Soil Taxonomy), Auenböden (Germany) and ‘Sols minéraux bruts d’apport alluvial ou colluvial’ or ‘Sols peu évolués non climatiques d’apport alluvial ou colluvial’ (France).

Definition. Fluvisols are defined by FAO (2001) as soils that are

1. 25 cm or more thick, and
2. with *fluvic* soil material starting within 50 cm from the soil surface and continuing downwards at least 50 cm from the soil surface; and
3. with only histic, mollic, ochric, takyric, umbric, yermic, salic or sulfuric horizons as possible diagnostic horizons.

Parent material. (Predominantly) recent, fluvial, lacustrine or marine deposits.

Environment. Periodically flooded areas (unless empoldered) of alluvial plains, river fans, valleys and (tidal) marshes, on all continents and in all climate zones.

Distribution. Fluvisols are found on all continents and in all climatic zones, with more than half of the total global extent of 350 million ha occurring in the tropics. There are major occurrences along rivers and lakes, in wetlands, deltaic regions and in coastal lowlands. In the coastal lowlands of the tropics, Thionic Luvisols (which are treated in the article *Thionic or Sulfidic Soils*) are found. Figure F29 shows the global distribution.

Characteristics. Fluvisols are young soils, formed on recent sediments, and showing evidence of stratification. Texture ranges from coarse sand to heavy clay. Horizon differentiation is weak (A/C profiles are common) but a distinct Ah-horizon may be present. *Redoximorphic* features may be present, especially in the lower part of the profile. Color depends on redox state, tending to brownish where oxidation prevails, and grayish in reduced localities. pH is normally near neutral except for Thionic Fluvisols affected by oxidation of pyrite and rendered extremely acid (pH 3 for example). Alkaline conditions may be found in some coastal Fluvisols.

Origin. These are young soils formed in environments prone to the addition of sediment during flooding events. They are therefore commonly stratified, and the distribution of organic matter in the solum may be irregular. Where the soil material

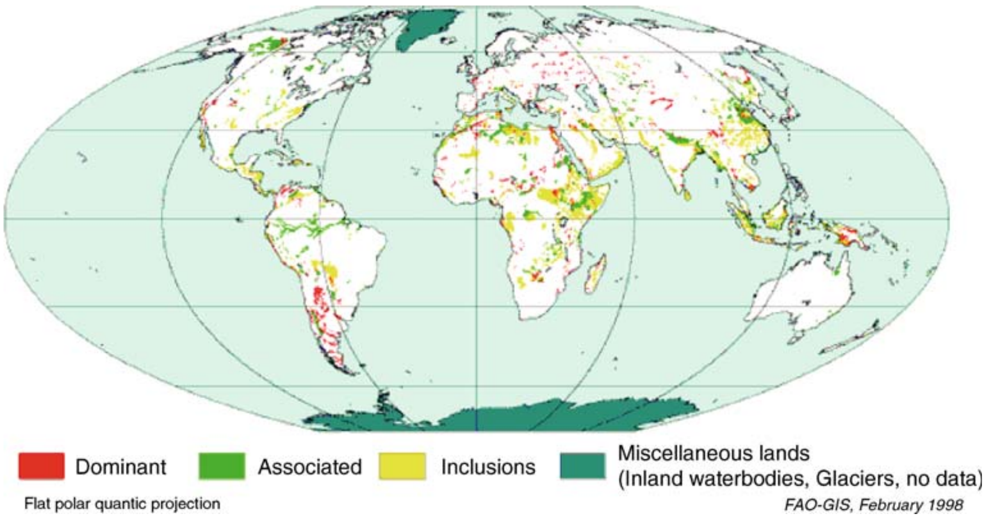


Figure F29 Distribution of Fluvisols.

has the texture of sandy loam or finer, a cambic subsurface horizon will form and the Fluvisol will grade into a Cambisol, provided that the solum is not water saturated. In the latter case, redox reactions will convert the Fluvisol into a Gleysol.

Use. Fluvisols are planted to annual crops and orchards and many are used for grazing. Flood control, drainage and/or irrigation are normally required. Thionic Fluvisols suffer from severe soil acidity and toxic levels of Al^{3+}.

Profile development. AC-profiles with evidence of stratification; weak horizon differentiation but a distinct Ah-horizon may be present. *Redoximorphic* features are common, in particular in the lower part of the profile.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

Fitz Patrick, E.A., 1986. *An Introduction to Soil Science*, 2nd edn. Essex, England/ New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag. 130 pp.

Cross-references

Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Thionic or Sulfidic Soils

FOLIC

Organic materials formed primarily by the decomposition of forest litter. In the WRB system of classification a folic horizon needs more than 20 weight percent organic carbon (35 percent organic matter), must not be water-saturated for more than one month in most years, and must have a thickness greater than 10 cm. If a folic horizon is less than 20 cm thick, the upper 20 cm of the soil must contain 20 percent or more organic carbon, after mixing.

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FRAGIPAN

From the Latin *fragere,* to break. A brittle subsurface horizon uncemented but sufficiently compacted to appear to be lightly cemented. A horizon through which roots and percolating water can pass only along preferential paths, along ped faces for example. Fragipan is recognized as a diagnostic subsurface soil horizon by the WRB and Soil Taxonomy systems of classification. World Reference Base for Soil Resources. Several hypotheses have been proposed to explain the characteristic interlocking pattern of grains in a fragipan. Where periglacial processes were once active, compression exerted by the growth of ice lenses or by the superincumbent load of above-ground ice, has been invoked. Elsewhere, repeated wetting–drying cycles or the collapse of liquefied water-saturated deposits have been suggested as responsible for the compaction. In active seismic zones, earth tremors may have caused the liquefaction.

The qualifier Fragic is used in the WRB system to indicate soils containing a fragipan horizon (e.g., Fragic Andosol, Fragic Albeluvisol, Fragic Podzol).

Bibliography

Certini, G., Ugolini, F.C., Taina, I., Bolla, G., Corti, G., and Tescari, F., 2007. Clues to the genesis of a discontinuously distributed fragipan in the northern Apennines, Italy. *Catena*, **69**: 161–169.

FRIGID

Intensely cold, devoid of heat or warmth, of a very low temperature. In soil science, applied to soil with a mean annual temperature of 8° C. Geographically, the frigid zones are the two regions of the globe, which lie within the north and south polar circles respectively.

FROST ACTION

Alternating cycles of freeze and thaw in water contained in pores, voids and fissures, and traditionally thought to be capable over the long term of causing the mechanical breakup of rock and soil. Recent work casts doubt on this belief (Birkeland, 1999, p. 54–55). Soils and other porous materials are susceptible to the heave and collapse of more or less circular patches of the surface (frost boils) as included water freezes and accumulates in lenses, then thaws under warmer conditions.

Bibliography

Birkeland, P.W., 1999. *Soils and Geomorphology*, 3rd edn. New York: Oxford University Press, 430 pp.

FULVIC ACID

The fraction of organic material that is soluble in alkaline solution, and remains in solution when the solution is acidified. The average composition worldwide is given by Sposito (1989, p. 9) as $C_{135}H_{182}O_{95}N_5S_2$.

Bibliography

Sposito, G., 1989. *The Chemistry of Soils.* New York: Oxford University Press, 277 pp.

Cross-reference

Humic Substances

FURROW

A channel cut into soil by plow, disk or hand implement, for the purposes of cultivation or drainage.

G

GABION

A wire-mesh container filled with stones. They are used in modular fashion to build retaining walls to fortify slopes and minimize erosion there on. Being porous, they allow the fortified slope to drain, thus preventing the buildup of hydrostatic pressure. A further advantage is their flexibility, which allows them to adjust to minor earth movements.

GELIFLUCTION

The creep of a surface layer of thawed, water-saturated soil downhill over frozen ground. A characteristic type of mass movement in periglacial (permafrost) environments.

Cross-references

Cryosols
Ice Erosion

GEOCHEMISTRY IN SOIL SCIENCE

Geochemistry in soil science differs from the classical geochemistry of rock formations because soil differs fundamentally from weathered rock (Singer and Munns, 1991). Soils are open, multicomponent biogeochemical systems that undergo biological, chemical, and physical transformations leading to a characteristic morphological feature – the soil horizons – which reflect the unique influences of percolating waters and living organisms acting over millennia. These transformations also serve to link soils with the atmosphere and hydrosphere, as illustrated for the element nitrogen (N) in Figure G1, a flow diagram which applies to natural soils at spatial scales ranging from pedon to landscape. Soil N flows are similar to those for soil C, in that humus ("soil organic matter") is the dominant storage component and emissions to the atmosphere are an important pathway of loss. The emissions send mainly N_2 along with N_2O and NH_3 to the atmosphere, the N_2O, like CO_2 and CH_4, being of environmental concern because of its very strong absorption of terrestrial infrared radiation (greenhouse gas). The source of these gases is dissolved inorganic N, whose transformation is termed denitrification when N_2 and N_2O are the products and ammonia volatilization when NH_3 is the product. Denitrification is typically mediated by respiring microorganisms, whereas ammonia volatilization results from the deprotonation of aqueous NH_4^+ (which itself may be bacterially produced) under alkaline conditions. Dissolved inorganic N comprises the highly soluble, "free-ion" chemical species, NO_3^-, NO_2^-, and NH_4^+, which can transform among themselves by electron transfer processes (redox reactions), be complexed by other dissolved solutes, react with particle surfaces, or be absorbed by living organisms, as illustrated in Figure G1. Natural soils tend to cycle N without significant loss through leaching (as NO_3^-), but denitrification losses can be large if soluble humus, which is readily decomposed by microorganisms, is abundant and a flooding event induces anaerobic conditions, thereby eliminating O as a competitor with N for the electrons made available when humus is degraded. Cultivated soils, on the other hand, often show excessive leaching and runoff losses of N, as well as significant emissions – both being of major environmental concern – because of high inputs of nitrate or ammonium fertilizers that artificially and suddenly increase inorganic N content. A similar problem occurs when organic wastes with low C/N ratios are applied to these soils as fertilizers, since rapid microbial mineralization of such materials is favored.

This example illustrates the typical way in which geochemistry in soil science includes within its purview the transformations and cycling of chemical elements as affected by atmospheric, biological and hydrological agents.

Geochemical patterns in soils

The major elements in soils are those whose concentrations exceed 100 mg kg^{-1}, all others being termed trace elements.

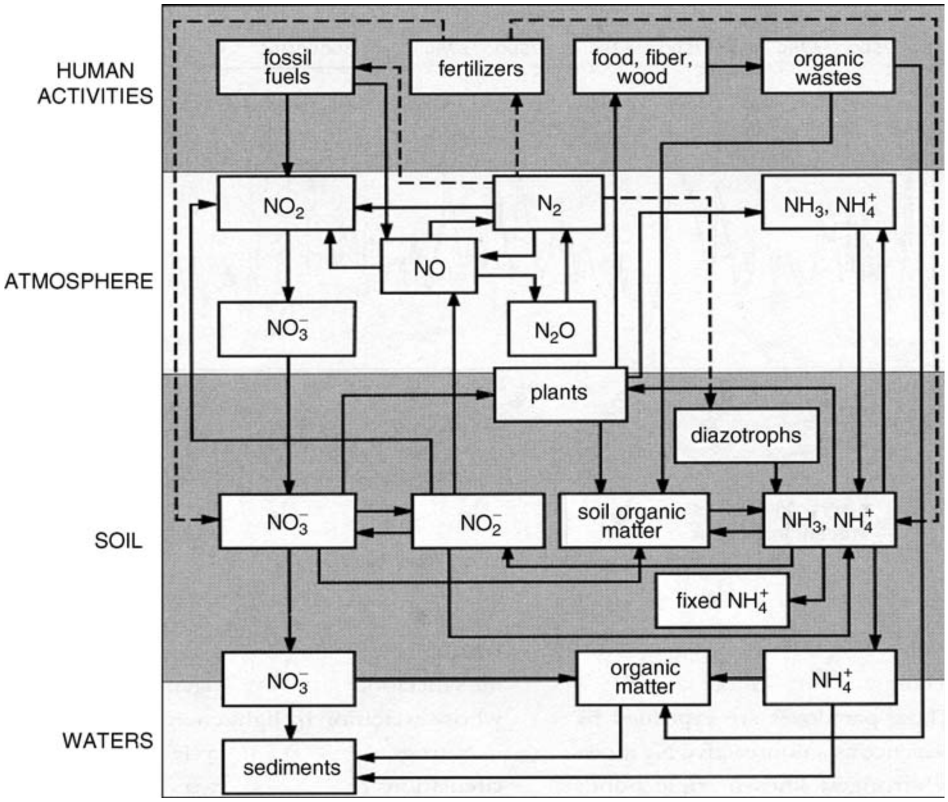


Figure G1 Main reservoirs and flows in the biogeochemical cycle of nitrogen (Smil, 2000).

The major elements include O, Si, Al, Fe, C, K, Ca, Na, Mg, Ti, N, S, Ba, Mn, P, and perhaps Sr and Zr, in decreasing order of concentration (Schacklette and Boerngen, 1984). Notable among the major elements is the strong enrichment of C and N in soils relative to crustal rocks, whereas Ca, Na, and Mg show significant depletion. The strong enrichment of C and N is a result of the principal chemical forms these elements assume in soils, namely those associated with organic matter. The average C/N, C/P, and C/S ratios, 8, 61, and 13, respectively, in soils are very low and, therefore, conducive to microbial mineralization processes, further reflecting the active biological milieu that distinguishes soil from crustal rock.

The major elements C, N, P, and S also are macronutrients, meaning they are essential to the life cycles of organisms and are absorbed by them in significant amounts. The global biogeochemical cycles of these elements are therefore of major interest, especially because of the large anthropogenic influence they experience. Mining operations and fossil fuel production, for example, combine to release annually more than one thousand times as much C and N, one hundred times as much S, and ten times as much P as is released annually worldwide from crustal weathering processes. In soils, these four elements undergo biological and chemical transformations that release them to the vicinal atmosphere, biosphere, and hydrosphere, as was illustrated for N in Figure G1.

A simple geochemical parameter with global environmental significance is the anthropogenic mobilization factor (AMF), calculated as the mass of an element extracted annually, through mining operations and fossil fuel production, divided by the mass released annually through crustal weathering processes and volcanic activity. If AMF is well above 10, an element is said to have significant anthropogenic perturbation of its global biogeochemical cycle (Klee and Graedel, 2004). According to this criterion, the transition metals Cr, Ni, Cu, Zn, Mo, and Sn; the "heavy metals" Ag, Cd, Hg, and Pb; and the metalloids As and Sb have significantly-perturbed biogeochemical cycles. Not surprisingly, these 12 elements also figure importantly in environmental regulations.

The chemical elements essential to plant growth in soil are: H, B, C, N, O, Mg, P, S, CI, K, Ca, Mn, Fe, Cu, Zn, and Mo (Singer and Munns, 1991). Of these elements, B, CI, Mn, Fe, Cu, Zn, and Mo are micronutrients (absorbed in trace amounts) and Mg, S, and Ca are secondary nutrients (absorbed in small, but not trace, amounts). The remaining six elements are macronutrients. The 16 essential elements – with the exception of Mo – have the distinguishing property that their atomic number ≤ 30 (Frausto da Silva and Williams, 1991). Thus, they are among the "light elements" that have relatively small crystallographic ionic radii. The biological significance of this property can be appreciated by reference to two important geochemical parameters that are applied to the metal elements (Fraústo da Silva and Williams, 2001).

The first is the ionic potential (*IP*), which is the valence of a metal cation divided by its crystallographic ionic radius expressed in units of nanometers. Metal cations with $IP < 30\ \text{nm}^{-1}$ tend to be found in circumneutral waters without significant concentrations of complexing ligands as solvated chemical species ("free cations"); those with $30 > IP < 100\ \text{nm}^{-1}$ tend to hydrolyze readily in circumneutral waters; and those with $IP > 100\ \text{nm}^{-1}$ tend to be found as oxyanions. Examples of these three classes are: Na^+ ($IP = 9.8\ \text{nm}^{-1}$), Al^{3+} ($IP = 56\ \text{nm}^{-1}$), and Cr^{6+} ($IP = 231\ \text{nm}^{-1}$). If a metal element has different valence states, it may fall into different classes: Cr^{3+} ($IP = 49\ \text{nm}^{-1}$) hydrolyzes, whereas hexavalent Cr forms an oxyanion species in aqueous solution. Thus alkali and alkaline earth metals, with the notable exception of Be, will be free cations in circumneutral aqueous solutions. The same is true for the monovalent "heavy metals" (e.g., Ag^+) and the bivalent transition metals and "heavy metals" (e.g., Mn^{2+} and Hg^{2+}), although the bivalent transition metals come perilously close to the IP hydrolysis threshold. Trivalent metals, on the other hand, tend always to be hydrolyzed (e.g., Al^{3+}, Cr^{3+}, and Mn^{3+} ($IP = 46\ \text{nm}^{-1}$)), and quadrivalent or higher-valent metals tend to be oxyanions. The soluble metal species in circumneutral waters are either free cations or free oxyanions, whereas hydrolyzing metals tend to precipitate as insoluble oxides or hydroxides. Thus, falling into the middle IP range (30 to $100\ \text{nm}^{-1}$) is the signature of metal elements that are not expected to be soluble at circumneutral pH in the absence of complexing ligands.

The second important geochemical property of metal elements is their Class A or Class B behavior. A metal cation is Class A if it (1) has low polarizability (the ease with which the electrons in an ion can be drawn away from its nucleus) and (2) it tends to form stronger complexes with oxygen-containing ligands (e.g., carboxylate (COO^-), phosphate, or a water molecule) than with N- or S-containing ligands. A metal is Class B if it has the opposite characteristics. If a metal is neither Class A nor Class B, it is termed Borderline. The Class B metals are the "heavy metals" Ag, Cd, Hg, and Pb, while the Borderline metals are the transition metals, Ti to Zn, along with Zr, Mo, and Sn, each of which can behave as Class A or Class B depending on their valence and local bonding environment.

The description of metals according to these two parameters can be applied not only to understand the behavior of metals in terms of solubility and complex formation, but also to predict their status as plant and microbial toxicants. For a given metal cation, if $IP < 30\ \text{nm}^{-1}$ and the metal is Class A, then it is unlikely to be toxic (e.g., Ca^{2+}), except possibly at very high concentrations (e.g., Li^+, Na^+). If $IP > 100\ \text{nm}^{-1}$, or if $IP < 30\ \text{nm}^{-1}$ and the metal is Borderline, then it is quite possibly toxic, examples being Cr^{6+} in the first case and bivalent transition metal cations in the second case. If instead, $30 < IP < 100\ \text{nm}^{-1}$, or the metal cation is Class B, then it is very likely to be toxic, examples being Be^{2+} and Al^{3+} in the first case, and Ag^+, Hg^+, along with the bivalent "heavy metals," in the second case. The chemistry underlying these conclusions is simple: If a metal tends to hydrolyze in aqueous solution or has covalent binding characteristics, it is very likely to be toxic, whereas if it tends to be solvated in aqueous solution and has ionic or electrostatic binding characteristics, it is not as likely to be toxic. Toxicity is thus associated with insoluble metal cations and with those that tend to form covalent bonds in complexes with ligands. The first property evidently reflects low abundance in aquatic systems and, therefore, the non-availability of a metal element as life evolved, whereas the second property is inimical to the relatively labile metal cation binding that characterizes most biochemical processes. Indeed, Borderline metals become toxicants when they displace Class A metals from essential binding sites in biomolecules, bonding to these sites more strongly, and Class B metals are always toxicants, simply because they can displace either Borderline metals (which often serve as cofactors in enzymes) or Class A metals from essential binding sites through much more tenacious bonding mechanisms. Large AMF values are associated with Borderline and Class B metals, implying, unfortunately, that human perturbations of metal biogeochemical cycles have enhanced the concentrations of toxicant metals in soil and water environments.

One of the most important geochemical properties of soils is their content of trace elements (Adriano, 2001). Soil minerals containing trace elements serve as reservoirs for the elements, releasing them slowly into the soil solution as weathering continues. If a trace element is also a micronutrient, then the rate of mineral weathering becomes a critical factor in soil fertility. For example, the ability of soils to provide Co to plants depends on the rate at which this element is transformed from an Mn oxide constituent to a soluble chemical form. Soil chemical properties, like pH, electrode potential, and water activity, will affect the rate of this transformation and thus control Co solubility. Similarly, the weathering rate of soil minerals containing Cd as a trace element will determine in part the potential hazard of this toxic element to plants.

The ways in which trace elements occur in primary and secondary soil minerals are summarized in Tables G1 and G2. (Table G2 also indicates trace elements found typically in

Table G1 Occurrence of trace elements in primary minerals

Element	Principal modes of occurrence in primary minerals
B	Tourmaline, borate minerals; isomorphic substitution for Si in micas
Ti	Rutile and ilmenite (FeTiO_3); oxide inclusions in silicates
V	Isomorphic substitution for Fe in pyroxenes and amphiboles and for Al in micas; substitution for Fe in oxides
Cr	Chromite (FeCr_2O_4); isomorphic substitution for Fe or Al in other minerals of the spinel group
Co	Isomorphic substitution for Mn in oxides and for Fe in pyroxenes, amphiboles, and micas
Ni	Sulfide inclusions in silicates; isomorphic substitution for Fe in olivines, pyroxenes, amphiboles, micas, and spinels
Cu	Sulfide inclusions in silicates; isomorphic substitution for Fe and Mg in olivines, pyroxenes, amphiboles, and micas, and for Ca, K, or Na in feldspars
Zn	Sulfide inclusions in silicates; isomorphic substitution for Mg and Fe in olivines, pyroxenes, and amphiboles, and for Fe or Mn in oxides
As	Arsenopyrite (FeAsS) and other arsenate minerals
Se	Selenide minerals; isomorphic substitution for S in sulfides; iron selenite
Mo	Molybdenite (MoS_2); isomorphic substitution for Fe in oxides
Cd	Sulfide inclusions and isomorphic substitution for Cu, Zn, Hg, and Pb in sulfides
Pb	Sulfide, phosphate, and carbonate inclusions; isomorphic substitution for K in feldspars and micas, for Ca in feldspars, pyroxenes, and phosphates, and for Fe and Mn in oxides

association with soil humus.) The chemical process governing the trace element common also in primary silicates (Table G1); but, in this case, trace element occurrences described in these tables is coprecipitation, the simultaneous precipitation of a chemical element with other elements by any mechanism at any rate. The three broad types of coprecipitation are inclusion, adsorption and solid solution formation (Sposito, 1989).

If a pure solid phase that would be formed by a trace element has a very different atomic structure from that of a host mineral which coprecipiatates with the trace element, then the host mineral and the trace element will occur together only as morphologically distinct solids. This kind of association is termed inclusion. For example CuS often occurs as a separate phase in primary silicates (Table G1). If there is some structural compatibility between a trace element and the corresponding major element in a host mineral, then coprecipitation can produce a mixture of the two elements at the mineral/soil solution interface. This mechanism is termed adsorption because the mixed solid phase is restricted to the interfacial region and its composition varies as the host mineral continues to precipitate from the soil solution (Stumm, 1992). Examples of adsorption are the surface accumulation of oxyanions, like borate, phosphate or molybdate, on secondary metal oxides (Table G2) and of transition metals, like Fe or Ni, on soil organic matter.

Table G2 Trace elements coprecipitated with secondary soil minerals and soil humus

Solid	Coprecipitated trace elements
Fe and Al oxides	B, P, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Mo, As, Se, Cd, Pb
Mn oxides	P, Fe, Co, Ni, Cu, Zn, Mo, As, Se, Cd, Pb
Ca carbonates	P, V, Mn, Fe, Co, Cd, Pb
Illites	B, V, Ni, Co, Cr, Cu, Zn, Mo, As, Se, Pb
Smectites	B, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb
Vermiculites	Ti, Mn, Fe
Humus	B, Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Cd, Pb

Finally, if structural compatibility is high, and free diffusion of a trace element within a host mineral is possible, a major element in the host mineral can be replaced uniformly throughout by the trace element. This kind of homogeneous coprecipitation is solid solution formation. It is likely if the ionic size and valence of the substituting element are comparable to those of the element replaced. Solid solution formation occurs when secondary aluminosilicates precipitate and incorporate metals like Ni, Cu, and Zn to substitute for Al in their structures (Table G2), or when Ca carbonate precipitates with Cd substituting for Ca. "Isomorphous substitution" of this kind is common also in primary silicates (Table G1); but in this case, trace element substitution occurs as minerals crystallize from a silicate melt. As noted above, trace elements, even those that are micronutrients (e.g., Cu and Zn), can produce toxicity in plants (phytotoxicitv) at sufficiently high concentrations in the soil solution.

Geochemical transformations in soils

The continual input and output of percolating water, biomass, and solar energy in soils makes them change with the passage of time. These changes are reflected in the morphological development of soil horizons, but they are also apparent in the mineralogy of the soil clay fraction as it changes from weathering.

Table G3 provides a summary of typical changes in mineralogy observed in the clay fraction during soil profile development. These changes are known collectively as the Jackson-Sherman weathering stages, and they can be classified as "early stage," "intermediate stage," or "advanced stage," (Jackson and Sherman, 1953; Jackson, 1965). Early-stage weathering exhibits sulfates, carbonates, and primary silicates, other than quartz and muscovite, in the soil clay fraction. These minerals survive only if soils remain very dry, or very cold, or very wet, for most of the time; i.e., for reasons of age or if they lack, the throughputs of water, air, and thermal energy that usually characterize open systems in nature (entisols, inceptisols, gelisols, and andisols). Intermediate-stage weathering features quartz, muscovite, and secondary aluminosilicates

Table G3 Jackson-Sherman soil weathering stages

Characteristic minerals in soil clay fraction	Characteristic soil chemical and physical conditions	Characteristic soil properties
Early stage		
Gypsum	Low water and humus content, very limited leaching	Minimally-weathered soils: arid or very cold regions, waterlogging, recent deposition
Carbonates	Reducing environments, cold environments	
Olivine/pyroxene/amphibole	Limited amount of time for weathering	
Fe(II)-bearing micas		
Feldspars		
Intermediate stage		
Quartz	Retention of Na, K, Ca, Mg, Fe(II), and silica: Moderate leaching, alkalinity	Soils in temperate regions: forest or grass cover, well-developed A and B horizons, accumulation of humus and clay minerals
Dioctahedral mica/illite	Parent material rich in Ca, Mg, and Fe(II), but not Fe(II) oxides	
Dioctahedral vermiculite/chlorite	Silicates easily weathered	
Smectite		
Advanced stage		
Kaolinite	Removal of Na, K, Ca, Mg, Fe(II), and silica:	Soils under forest cover with high temperature and precipitation: accumulation of Fe(III) and Al oxides, absence of alkaline earth metals
Gibbsite	Intensive leaching by fresh water	
Iron oxides	Oxidation of Fe(II)	
Titanium oxides	Low pH and humus content	

prominently in the clay fraction. These minerals survive under conditions that do not deplete soluble silica [$Si(OH)_4^0$] and the macroelements, and that do not result in the complete oxidation of Fe^{II} incorporated into illite or smectite (aridisols, vertisols, mollisols, and alfisols). Advanced-stage weathering, on the other hand, is associated with intensive leaching and strongly oxidizing conditions, such that only hydrous oxides of Al, Fe^{III}, and Ti persist ultimately (ultisols and oxisols). Kaolinite will be an important clay mineral only if the removal of silica by leaching is not complete or if there is an invasion of silica-rich waters, as can occur, for example, when leachate from the upper part of a soil toposequence moves laterally into the profile of a lower part.

The order of increasing persistence of the soil minerals listed in Table G3 is downward, both among and within the three stages of weathering. Primary minerals, therefore, tend to occur higher in the list than secondary minerals, and the former can be linked with the latter by five key geochemical transformations (Sposito, 1989). Of these, the most important is hydrolysis (reaction with water), illustrated by the chemical reactions:

$$\overset{\text{albite}}{NaAlSi_3O_8(s)} + 8H_2O = Na^+(aq) + Al(OH)_2^+(aq) + 3Si(OH)_4^0(aq) + 2OH^-(aq) \tag{4}$$

$$\overset{\text{albite}}{NaAlSi_3O_8(s)} + 8H_2O = \overset{\text{gibbsite}}{Al(OH)_3(s)} + Na^+(aq) + 3Si(OH)_4^0(aq) + OH^-(aq) \tag{5}$$

In these reactions, the dissolution of the feldspar, albite, occurs through chemical reaction with water to form dissolved species (denoted by "aq"). Equation (4) describes a congruent dissolution process because only dissolved species make up the products, whereas Equation (5) describes an incongruent dissolution process because a solid-phase product-gibbsite is formed as well.

A convenient pictorial representation of congruent dissolution reactions can be developed through the construction of activitv-ratio diagrams (Lindsay, 2001; Sposito, 1989). An activity-ratio diagram for three secondary minerals in an acidic soil is shown in Figure G2. The Jackson-Sherman weathering scenario (Table G3) indicates that, when soil profiles are leached free of silica with fresh water, 2:1 layer-type clay minerals (smectite, vermiculite, illite) are replaced by 1:1 layer-type clay minerals (kaolinite) and, ultimately, these are replaced by metal oxyhydroxides (e.g., gibbsite). This sequence of mineral transformations can be represented by the successive dissolution reactions of smectite, kaolinite, and gibbsite (Sposito, 1989):

$$\overset{\text{smectite}}{Mg_{0.208}[Si_{3.82}Al_{0.18}](Al_{1.29}Fe^{III}_{0.335}Mg_{0.445})O_{10}(OH)_2(s)} + 3.28H_2O + 6.72H^+(aq) = 1.47Al^{3+}(aq) + 0.335Fe^{3+}(aq) + 0.653Mg^{2+}(aq) + 3.82Si(OH)_4^0(aq) \qquad \log K = 3.2 \tag{6}$$

$$\overset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4(s)} + 6H^+(aq) = 2Al^{3+}(aq) + Si(OH)_4^0(aq) = H_2O \quad \log K = 7.43 \tag{7}$$

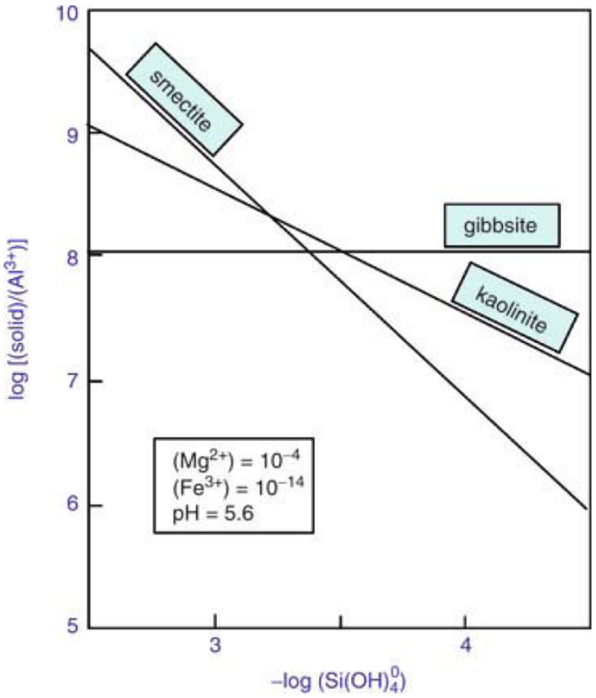


Figure G2 Activity ratio diagram for control of Al solubility by clay minerals and gibbsite (Sposito, 1989).

$$\overset{\text{gibbsite}}{Al(OH)_3(s)} + 3H^+(aq) = Al^{3+}(aq) + 3H_2O \qquad \log K = 8.11 \tag{8}$$

The solid-phase reactant in Equation (6) is montmorillonite, with Mg^{2+} as the interlayer exchangeable cation. Its dissolution reaction (at 298.15 K) is characterized by the equilibrium constant, K. The value of K for the dissolution of kaolinite (Equation (7)) reflects a well-crystallized solid phase. Poorly crystallized kaolinite – typical of intensive soil weathering conditions – would yield $\log K \approx 10.5$. In Equation (8), gibbsite also is assumed to be well crystallized; poorly crystallized gibbsite would yield $\log K \approx 9.35$.

Equations (6) to (8) can be used to construct an activity-ratio diagram in respect to $Al^{3+}(aq)$ activity in the soil solution, shown conventionally between curved brackets, that is (Al^{3+}), as influenced by the leaching of silicic acid (Sposito, 1989). At a given value of the soil-solution activity of silicic acid [$Si(OH)_4^0$], which is the independent variable (and under the assumption that all solid phases are in their Standard States), the solid that produces the largest value of the activity ratio, [(solid)/(Al^{3+})] is the one that is most stable and, therefore, the one that will be present at equilibrium. This conclusion follows because a solid phase that produces the smallest soil solution activity of a free ionic species will also control the solubility of that species. The effect of soil profile leaching at pH 5 is represented in the activity-ratio diagram by moving from left to right along its x-axis. Amorphous silica supports ($Si(OH)_4^0$) $\approx 10^{-2.7}$. This condition, which reflects the intensive weathering of primary silicates in an acidic soil, leads to the prediction that smectite is the most stable solid phase with respect to solubility control of Al. As leaching and the loss of silica proceed, the silicic acid activity will decrease, and when $(\mathrm{Si(OH)_4^0}) \ll 10^{-4}$ (the silicic acid activity supported by the dissolution of quartz, gibbsite becomes the most stable Al-bearing solid phase. This progression of minerals agrees with field observations as summarized in the Jackson-Sherman intermediate-to-advanced weathering stages (Table G3).

The geochemical interpretation of activity-ratio diagrams is influenced by the existence of varying degrees of crystallinity of soil minerals, with a corresponding variation in their solubility (Sposito, 1985). For example, in the case of Figure G2, poorly crystallized forms of gibbsite and kaolinite, alluded to above, would require replacing K by larger values, such that the gibbsite line would be plotted 1.24 units lower and the kaolinite line would be shifted downward by 1.53 units (Figure G3). The effect of these changes is to create "windows" of gibbsite and kaolinite stability, instead of single lines in the diagram, and thus to enlarge the range of silicic acid activity over which smectite can remain the most stable solid phase. This kind of variability and the typical value, $(\mathrm{Si(OH)_4^0}) \approx 8 \times 10^{-4}$, in acid soils suggests that smectite, kaolinite, and gibbsite commonly will coexist in these soil weathering environments.

Another important geochemical transformation is complexation (often inappropriately called "chelation"), the reaction of complexing anions with metals in soil minerals (Sposito, 1989):

$$\overset{\text{Muscovite}}{\mathrm{K_2[Si_6Al_2]Al_4O_{20}(OH)_4(s)}} + 6\mathrm{C_2O_4H_2(aq)} + 4\mathrm{H_2O}$$
$$= 2\mathrm{K^+(aq)} + 6\mathrm{C_2O_4Al^+(aq)} + 6\mathrm{Si(OH)_4^0(aq)} + 8\mathrm{OH^-(aq)} \tag{9}$$

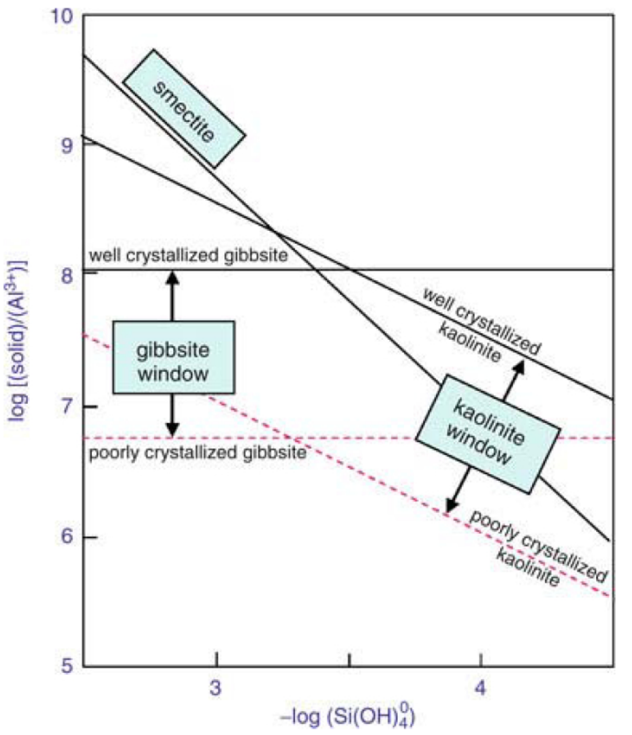


Figure G3 Gibbsite and kaolinite windows for the same conditions as Figure G2.

The second compound on the left side of Equation (9), oxalic acid (ethanedioic acid), dissociates and releases its anion, $\mathrm{C_2O_4^{2-}}$, to form a soluble complex with $\mathrm{Al^{3+}}$. This complex formation, in turn enhances the possibility of congruent dissolution for muscovite, since the soluble complex, $\mathrm{C_2O_4Al^+(aq)}$, helps to prevent the hydrolysis of Al that otherwise could lead to gibbsite precipitation, as in Equation (5).

Cation exchange, on the other hand, is a geochemical transformation associated with the incongruent dissolution of muscovite to form vermiculite in soils that retain both $\mathrm{Ca^{2+}}$ and $\mathrm{Si(OH)_4^0}$ (Sposito, 1989):

$$\overset{\text{Muscovite}}{\mathrm{K_2[Si_6Al_2]Al_4O_{20}(OH)_4(s)}} + 0.8\mathrm{Ca^{2+}(aq)} + 1.3\mathrm{Si(OH)_4^0(aq)}$$
$$= \overset{\text{vermiculite}}{1.1\mathrm{Ca_{0.7}[Si_{6.6}Al_{1.4}]Al_4O_{20}(OH)_4(s)}} + 2\mathrm{K^+(aq)}$$
$$+ 0.4\mathrm{OH^-(aq)} + 1.6\mathrm{H_2O} \tag{10}$$

The $\mathrm{Ca^{2+}}$ ion exchanges with $\mathrm{K^+}$ to occupy an interlayer position in vermiculite. This kind of reaction is favored for example, in an aridisol having abundant dissolved Ca (and silicic acid) in the soil solution. Incongruent dissolution is accompanied often by oxidation-reduction reactions, if Fe or some other "redox element" is involved in weathering. An example is the incongruent dissolution of biotite, which contains $\mathrm{Fe^{II}}$, to form vermiculite, which contains both $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$, as well as goethite, which contains only $\mathrm{Fe^{III}}$. Finally, hydration-dehydration can be added to complete this listing of significant geochemical transformations. An example of dehydration is the transformation of ferrihydrite to hematite:

$$\mathrm{Fe_{10}O_{15} \cdot 9H_2O(s) = 5Fe_2O_3(s) + 9H_2O} \tag{11}$$

Mineral dehydration reactions are favored as the relative humidity of soil water drops below 100%.

The geochemical transformations surveyed very briefly in this article provide a chemical basis for the cycling of elements through the weathering of soil minerals both within and between the Jackson-Sherman stages. In respect to silicates one "master variable" controlling these transformations is the activity of silicic acid in the soil solution. As the activity and therefore the concentration of $\mathrm{Si(OH)_4^0}$ decreases through leaching, the mineralogy of the soil clay fraction passes from the primary minerals of the early stage to the secondary minerals of the intermediate and advanced stages. Should the $\mathrm{Si(OH)_4^0}$ concentration increase through an influx of silica, on the other hand, as chemical principles would indicate, the mineralogy can be expected to shift upward in Table G3.

Finally, to restate a point stressed at the beginning of this article, the geochemistry of soils is largely distinguished from the geochemistry of rocks by the role played by organisms and humus. The integration of biology – particularly microbiology – into aqueous geochemistry has been one of the significant advances in the science in recent years (see e.g., Drever, 2004 page xvii).

Garrison Sposito

Bibliography

Adriano, D., 2001. *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals*, 2nd edn. New York: Springer, 867 pp.

Drever, J.I. (ed.), 2004. *Surface and Ground Water, Weathering and Soils: Treatise on Geochemistry*, Vol. 5. New York: Elsevier, 626 pp.

Fraústo da Silva, J.J.R., and Williams, R.J.P., 2001. *The Biological Chemistry of the Elements: The Inorganic Chemistry of Life.* 2nd edn. New York: Oxford University Press, 575 pp.

Jackson, M.L., 1965. Clay transformations in soil genesis during the quaternary. *Soil Sci.*, **99**: 15–22.

Jackson, M.L., and Sherman, G.D., 1953. Chemical weathering of minerals in soils. *Adv. Agron.* **5**: 219–318.

Klee, R.J., and Graedel, T.E., 2004. Elemental cycles: a status report on human or natural dominance. *Annu. Rev. Environ. Resour.*, **29**: 69–107.

Lindsay, W.L., 2001. *Chemical Equilibria in Soils.* Caldwell, NJ: Blackburn Press, 449 pp.

Schacklette, H.T., and Boemgen, J.G., 1984. Element concentrations in soils and other surficial materials of the conterminous United States: an account of the concentrations of 50 chemical elements in samples of soils and other regoliths. U.S.G.S. Prof. Paper 1270. Washington, DC: USGC, 105 pp.

Singer, M.J., and Munns, D.N., 2002. *Soils: An Introduction*, 5th edn. Upper Saddle River, NJ: Prentice-Hall, 429 pp.

Smil, V., 2000. *Feeding the World: A Challenge for the Twenty-First Century.* Cambridge, MA: MIT Press, 360 pp.

Sposito, G., 1985. Chemical models of weathering in soils. In Drever, J.I., ed., *The Chemistry of Weathering.* Boston, MA: D. Reidel Pub. Co., pp. 1–18.

Sposito, G., 1986. Distribution of potentially hazardous trace metals. *Met. Ions Biol. Syst.*, **18**: 1–20.

Sposito, G., 1989. *The Chemistry of Soils.* New York: Oxford University Press, 277 pp.

Stumm, W., 1992. Chapters 1, 2 and 13 of Chemistry of the Solid–Water Interface: Processes at the Mineral–Water and Particle–Water Interface in Natural Systems. With contributions by Laura Sigg (Chapter 11), Barbara Sulzberger (Chapter 10). New York: Wiley, 428 pp.

Cross-references

Biogeochemical Cycles
Geology and Soils
Macronutrients
Micronutrients
Nitrogen Cycle
Phosphorus Cycle
Plant Nutrients
Sulfur Transformations and Fluxes
Trace Elements

GEOGRAPHY OF SOILS

The geography of soil is concerned with the distribution and variability of soils on terrestrial landscapes ranging from local to global scales. Birkeland (1999, chapter 10) gives a clear exposition of the conceptual framework, but see Bunting (1967), Boulaine (1975), Cruickshank (1972) Steila and Pond (1989), and Foth and Schafer (1980) for earlier ideas. Of the soil forming factors, it is principally climate and the closely dependent variable vegetation that determine soil geography in this sense. For present purposes they are best considered as a linked variable. The remaining soil forming factors – parent material, topography and time – may be considered secondary determinants which modify the geographical regularities imposed by the linked variable climate-vegetation.

The classic 1938 Yearbook of Agriculture of the U.S. Department of Agriculture (USDA, 1938) made the concept explicit in terms of diagrams such as Figure G4, in which climatic gradients in temperature and rainfall are of primary importance in determining vegetation and hence soil variations over the land surface. Not surprisingly, considering its provenance, this model follows fairly closely the pattern of soils on the North American continent (Figure G5), with the cold-hot gradient following a north-south axis, and the wet-dry gradient an east-west one. Reverse the north-south gradient and the model fits South America almost as well, allowing for the fact that the southern tip does not reach such high latitudes. Where differences exist between model and reality, they are explainable as being due to the effects of the other soil forming factors as previously stated. For example this is most obvious in the case of topography, with the Cordillera disrupting the simple latitudinal and longitudinal variations imposed by climate-vegetation.

A different perspective on the relationship of soil and weathering conditions to climate and vegetation is shown as a pole to equator transect in Figure G6.

The time factor

Tectonic events (including volcanism) and glaciations are the principal ways by which the pedogenetic clock is reset. Where such geological activity is of recent date, new lithospheric materials have been exposed to the weathering regime, and the soils that are forming are inevitably at an immature stage of development. Where recent tectonic or glacial activity is lacking, the soils can be expected to be more mature. As such maturity evolves the geographical distribution of soil types follows ever more closely the climate-vegetation zonation of a given area. This can be seen especially on the land surfaces of Australia and Africa, both of which contain geologically undisturbed peneplains of great age (order of 10^7 years or more). It is there that you find the ferralitic soils that have had the time to be winnowed down to simple chemical and mineralogical compositions represented by the residua system of weathering (Chesworth, 1992).

The organic factor

Jackson and Sherman (1953) draw a distinction between two compartments of the weathering zone: an upper (pedochemical) compartment, with a notable organic presence to influence weathering processes, and a lower (geochemical) compartment, in which this presence is, if not absent, much attenuated. Essentially the dividing line is the transition from the solum to the parent material. Since weathering in the parent material will be the least affected by any reactions and interactions between biotic and abiotic components, it will be relatively uniform throughout the world (leaving aside any consideration of differences in rates of weathering). Hydrolysis in the zone of geochemical weathering, will therefore largely be determined by the ability of the system H_2O–CO_2 to produce protons. Only in the solum will protons from an organic source make a significant difference. Pedogeochemical weathering in the solum therefore, can be expected to vary with the linked soil-forming factor climate-vegetation. How many distinctly different variations in pedogeochemical weathering this amounts to, depends upon how fine the distinctions are that are used in defining the zones. Pedro (1979) for example recognizes five zones worldwide, based on the type of hydrolysis that takes place. Gaucher (1977), taking other factors into account, distinguishes ten different types of soil-chemical environment. Chesworth's version (1992) is the basis of Figure G7.

Along these lines, an important geographical distinction relates to the acid soils to which the weathering system evolves in regions with a humid climate. In cold and temperate zones, where coniferous forests and ericaceous heaths are found, the

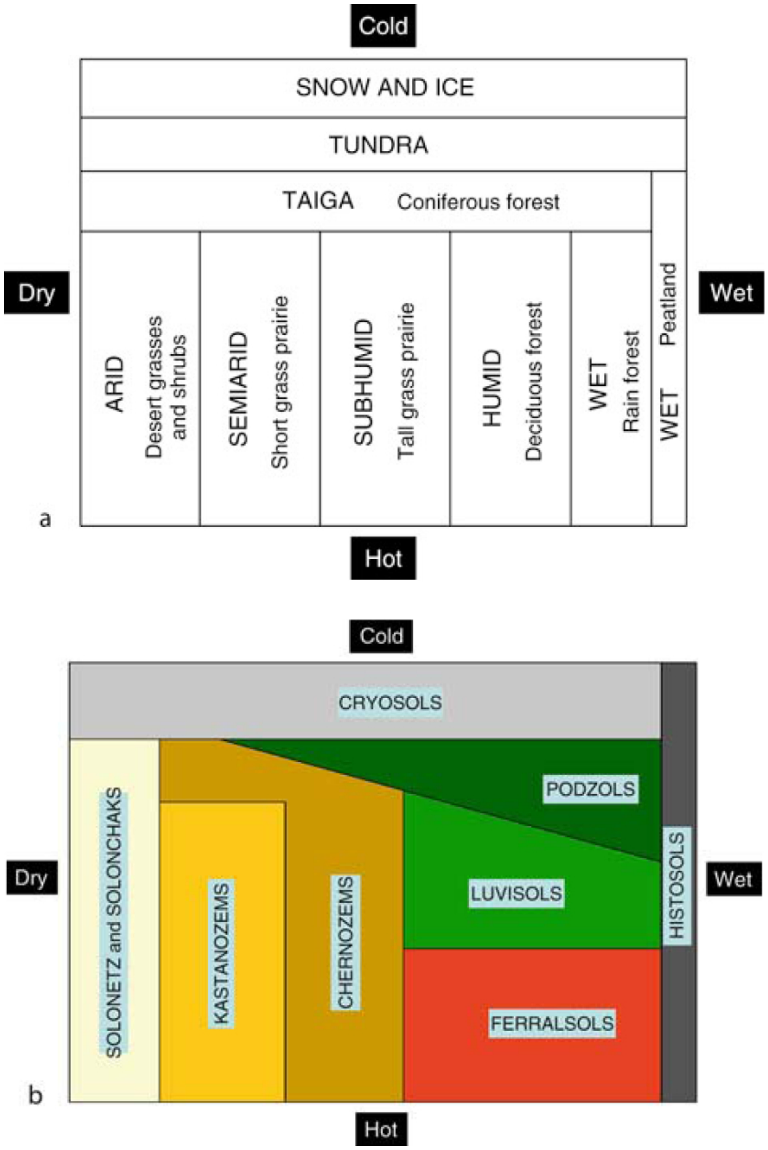


Figure G4 The classic conception of the geography of soils developed by the U.S. Department of Agriculture (USDA, 1938). (a) Climate-Vegetation zones. (b) Simplified distribution of soils (according to the WRB system), corresponding to (a).

activity of organic acids and complexants lead to the formation of organic soils. By contrast, in the tropics where the organic component in the soil is relatively quickly oxidized and destroyed, the pedochemical compartment of the weathering zone does not greatly differ from the geochemical one, both being dominated by the system $H_2O–CO_2$ as proton source. Ferralsols represent the typical end point in this situation.

Closing remarks

Two further tendencies relating to the wet-dry variable of Figures G4 and G5, are important. The first concerns redox state. So far the soil systems considered have been implicitly oxidizing i.e., well drained. If part or all of the solum becomes water saturated, reducing conditions prevail in the zone of saturation. Soils therefore develop hydromorphic characteristics, gleying being the most obvious. There is one significant geographical environment where this state of water saturation is common – the circumpolar region of continuous and discontinuous permafrost. Here, summer melting effects only the near surface, and a perched water table forms on the still frozen material deeper down. Furthermore, this region was covered by ice during the Pleistocene glaciations and is recently emergent from elevations below sea level. As a consequence it tends to be swampy and to contain areas of peat accumulation and Histosol formation. Histosols, Gleysols and peatlands form a circumpolar zone, especially in the northern hemisphere.

The second additional tendency relates to well drained and therefore oxidizing systems, under arid or semi-arid climates. Unlike the humid climate soils and conditions already considered, leaching will not take place except in regions of contrasted climate where a rainy period occurs. Otherwise, evapotranspiration exceeds atmospheric precipitation and there will be a net movement of water towards the surface. Evaporation will thereby lead to the precipitation of mineral phases in the upper part of the profile, and a common sequence, with increasing aridity is calcite, gypsum, and sodium salts. In turn, this may give a rough zonation of Calcisols, Gypsisols, solods and Solonetz around desertic regions.

Finally, the geographical zonation characteristic of a pole to equator transect of the Earth's land surface (generalized in Figure G6), is mimicked to some degree on a local scale, where variation in elevation may be sufficiently great to give a range

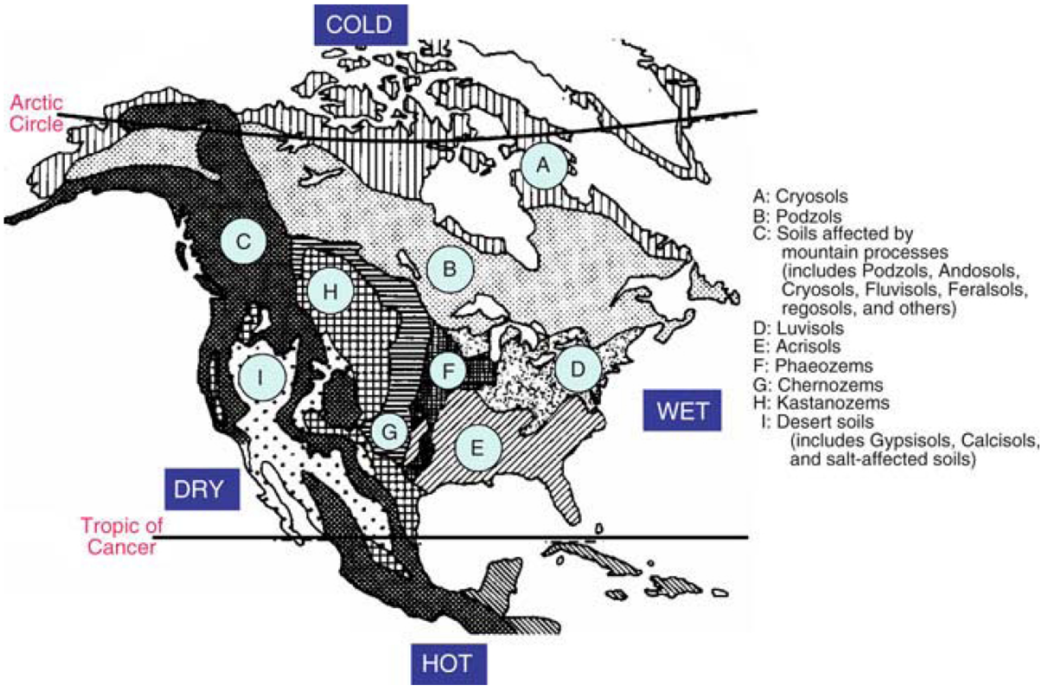


Figure G5 The real-world picture for North America, corresponding to the theoretical framework of Figure G4 (soil zones mapped according to the WRB system).

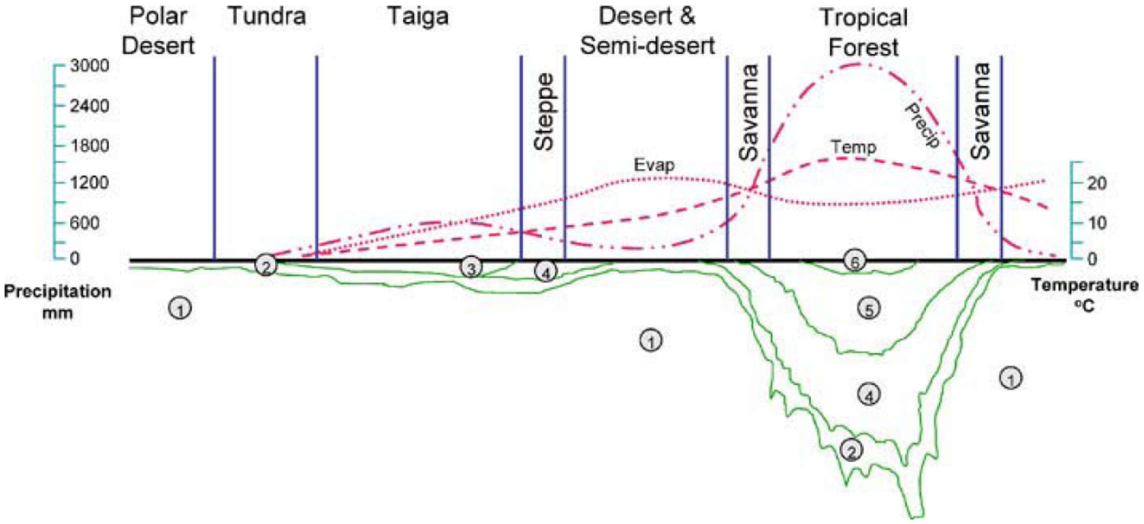


Figure G6 Polar-Equatorial transect, correlating the land ecosystems with variation in temperature and moisture conditions, and with a generalized, qualitative assessment of the related geography of the soil-forming environment under well-drained conditions: *1:* Bedrock. *2:* Incipient chemical alteration limited by cold in tundra, and lack of water in desert and semi-desert. Alkaline conditions and salt deposition under semi-desert conditions. *3:* Acidic conditions favoring podzolization. *4:* Near neutral conditions with respect to pH, bisiallitization. Calcite deposition possible under steppic vegetation. *5:* Acidic conditions favoring monosiallitisation. *6:* Acidic conditions favoring allitisation.

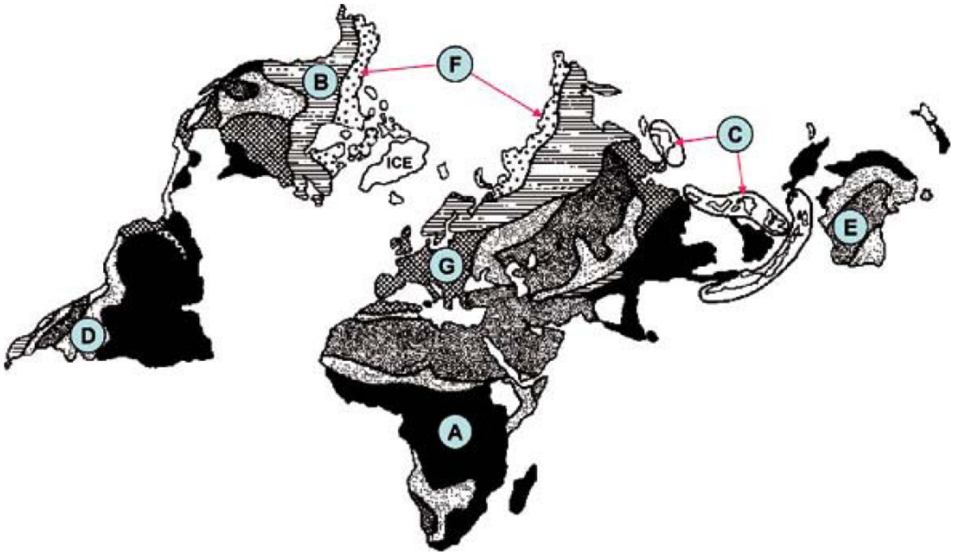


Figure G7 Geography of soil-forming processes adapted from Chesworth (1992). Acidifying processes: *A:* ferallitisation; *B:* podzolisation; *C:* andosolisation. Alkalinizing processes: *D:* deposition of Ca and Mg salts in the solum; *E:* deposition of Na salts in the solum. Hydromorphic processes are common in zone *F*, but are not excluded from other zones where soils become water-saturated. *G* denotes areas of humid, temperate to sub-tropical climate where soil processes under near-neutral conditions predominate.

of climate-vegetation conditions. At the extreme (Kilimanjaro for example) conditions range from tropical at the base, to the equivalent of polar at the summit, and soil-forming processes vary accordingly.

Ward Chesworth and L. J. Evans

Bibliography

Birkeland, P., 1999. *Soils and Geomorphology.* New York: Oxford University Press, 430 pp.
Boulaine, J., 1975. *Geographie des Sols.* Presses Universitaires de France, 200 pp.
Bunting, B.T., 1967. *The Geography of Soil.* 2nd edn. London: Hutchinson, 213 pp.
Chesworth, W., 1992. Weathering systems, Chapter 2. In Martini, P., and Chesworth, W., eds., *Weathering Soils and Paleosols.* New York: Elsevier, pp. 19–40.
Cruickshank, J.G., 1972. *Soil Geography.* Newton Abbot: David and Charles, 256 pp.
Foth, H.D., and Schafer, J.W., 1980. *Soil Geography and Land Use.* New York: Wiley, 484 pp.
Gaucher, G., 1977. Vers une classification pedologique naturelle base sur las geochimie de la pedogenese. *Catena*, **4**: 1–27.
Jackson, M.L., and Sherman, G.D., 1953. Chemical weathering of minerals in soils. *Adv. Agron.*, **5**: 219–318.
Pedro, G., 1968. Distribution des principaux types d'alteration chimique a la surface de globe. Presentation d'une esquise geographique. *Rev. Geog. Phys. Geol. Dyn.*, **10**: 457–470.
Steila, D., and Pond, T.E., 1989. *The Geography of Soils: Formation, Distribution, and Management.* 2nd edn. Savage, MD: Rowman & Littlefield, 239 pp.
USDA, 1938. *Soils and Men*. Washington, DC: U.S. Department of Agriculture, 1232 pp.

Cross-references

Biomes and their Soils
Factors of Soil Formation
Geology and Soils

GEOLOGY AND SOILS

The observation by Humphrey Davy (1813) that "there must be at least as many varieties of soil as there are species of rocks exposed at the surface of the Earth" (Davy, 1813), is conceivably the earliest recognition in modern science, of the parent rock as a significant soil-forming factor. The importance of the lithosphere to an understanding of the pedosphere is now well accepted. Consequently, the following discussion begins with the internal cycle of the Earth, the fundamental source (literally) of the lithosphere and of new materials that have been added to the soil-forming system throughout geological time.

Nature and origin of the lithosphere

The lithosphere is the outer zone of the solid Earth, made up of the crust and a part of the upper mantle welded to it. On a global scale it is fractured into a number of separate plates all of which are capable of moving relative to each other. Convection in the mantle, fueled by radiogenic heat, is the driving force that moves the plates around, and in doing so gives rise to such phenomena as earthquakes, igneous activity, metamorphism, mountain building, and, of course, continental drift. This idea, the Theory of Plate Tectonics, is the ruling paradigm in modern geology. Essentially there are three types of plate boundary (1) constructive (also referred to as spreading centers, divergent boundaries, mid-ocean ridges, and continental rifts), where plates move apart, and the gap is plugged by new additions of magma from the mantle; (2) destructive (also referred to as convergent or collisional boundaries, and subduction zones), where plates move together, metamorphism takes place, and melting in both mantle and crust produces new igneous rocks; and (3) conservative (also referred to as transform faults) where

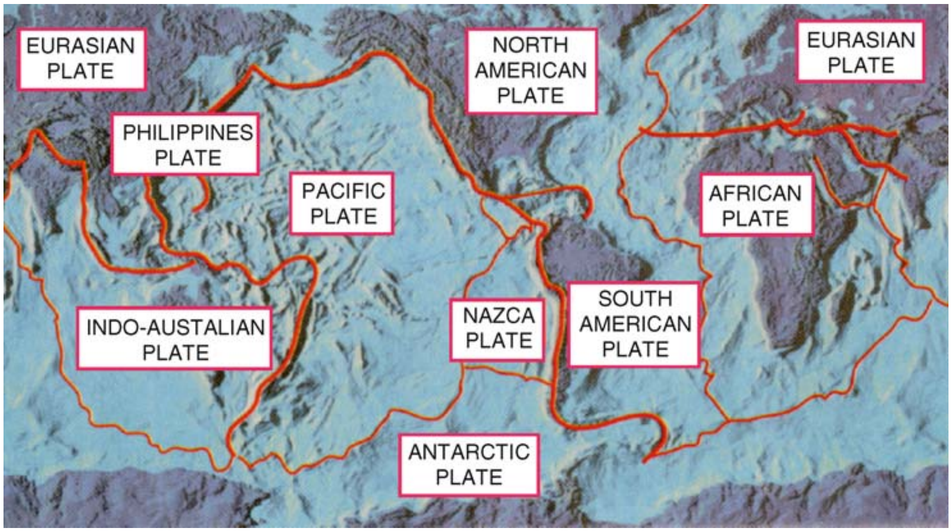


Figure G8 The plate tectonic map of the world.

plates slide past each other and no new rock material is added to the lithosphere (Figure G8). New material is added or exposed to the weathering system, and hence to the pedosphere, only along boundaries of types (1) and (2).

The crust, the upper division of the lithosphere, has also been called the oxysphere. This is because the crust and its component materials (minerals) at the atomic level have an architecture that is largely determined by the way that oxygen atoms and ions stack together – oxygen being the most abundant element in the crust, taking up more than 90% of the crustal volume. In fact, the simplest model for the crust is that of a close packed, three-dimensional array of oxygen anions (Figure G9), in which the net negative charge is balanced by cations occupying holes in the structure. In close packed structures three-, four-, six- and 12-fold coordination with respect to oxygen is permitted as shown in Figure G9. Some elements. Most notably Ca, Na and K commonly fit into spaces of 8-fold coordination. Where this occurs, the close packing is disrupted.

Minerals are the fundamental, organized units of the Earth and in the crust the most common minerals are those listed in Table G4. Again, most of the minerals named have structures that approximate close packing, with oxygen (and OH in phases such as the sheet silicates and the amphiboles) as the main structure-determining element. For example, olivine is almost perfectly close packed, though plagioclase with calcium in 8-fold coordination with oxygen is only approximately close packed. However, the main point is that oxygen plays a decisive role in the structure of the most common minerals so that the ways, in which other elements behave, largely depends on how they coordinate with oxygen. This, in turn, depends on the general chemical nature of the element to be considered.

Rocks are aggregates of minerals, and igneous rocks are commonly taken to be primary. In fact igneous rocks are as derivative (secondary) as sedimentary or metamorphic rocks, being themselves derived from pre-existing solid materials. The two most abundant types of igneous rock for example are granite (derived from the partial melting, or anatexis, of relatively acid rocks in the crust) and basalt (derived from the partial melting of ultrabasic rocks in the mantle). Granite makes up about two thirds of the continental crust, whereas basalt accounts for over 90% of the sea floor.

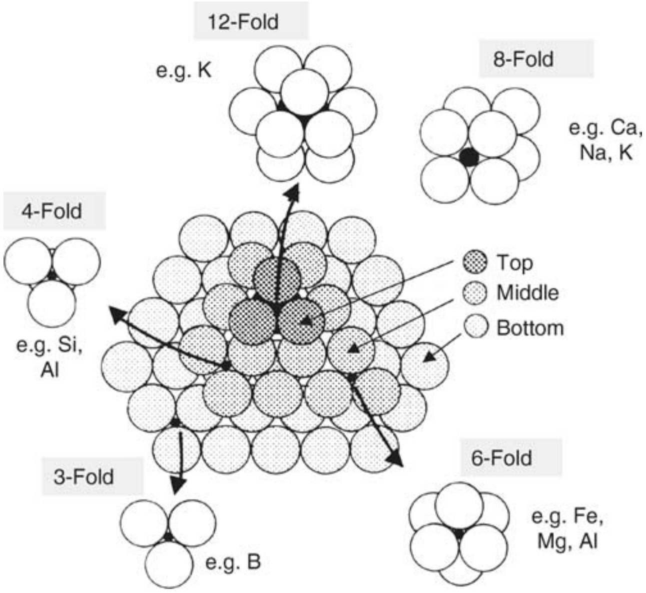


Figure G9 Close packing of oxygen atoms showing typical coordination structures for a number of characteristic elements. To a first approximation the diagram can be considered as a representation of the elemental structure of the crust of the Earth (the oxysphere) (adapted from Chesworth, 1991).

The proximate source of soil parent material of course, is the surface of the continental crust and it is the composition of this surface, rather than the bulk composition of the crust that is significant in the present context. This turns out to be andesitic on average (Table G5).

Table G4 Mineralogical composition of the upper part of the continental crust by volume, (after Ronov and Yaroshevsky, 1969)

Quartz	12
K-feldspar	12
Plagioclase	39
Mica	5
Pyroxene	11
Olivine	3
Clay minerals (and chlorite)	4.6
Calcite (and aragonite)	1.5
Dolomite	0.5
Magnetite (and titanomagnetite)	1.5
Others	4.9

Table G5 Oxide components that make up 99% of the chemical composition of the average soil parent material in continental regions. Based on the 'andesitic' average composition of the upper continental crust (Taylor and McClennan, 1985)

SiO_2	66.0
TiO_2	0.5
Al_2O_3	15.2
FeO	4.5
MgO	2.2
CaO	4.2
Na_2O	3.9
K_2O	3.4

Structural considerations

The spreading center (or oceanic ridge) and the subduction (or collision) zone, being the two types of plate boundary that contribute material from the endogenic geological cycle to the exogenic one, are the locuses of communication between the interior of the Earth and its surface. The relationship between the two is shown in cross section in Figure G10, which also shows the location of the four different tectonic units described next.

Ocean rift

The ocean rift or ridge system is the site where sub-alkali (or tholeiitic) basalt, is produced by relatively shallow melting in the mantle. The mantle itself, dominantly an ultrabasic combination of magnesian olivine and pyroxene with a minor amount of a Ca alumino-silicate, partially melts below the ridge, and magma is emplaced in the rift. Most of the sea floor is formed in this way, and over billions of years, the process has depleted the upper mantle in lithophile elements. Iceland sits on top of the mid-Atlantic ridge and constitutes the largest oceanic island composed of tholeiitic basalt. Relatively minor amounts of other volcanic rocks are produced on islands of this type by crystallization differentiation, which drives the composition of melts towards silica-oversaturated compositions (e.g., rhyolite).

Subduction zone

The oceanic lithosphere, with its veneer of sediments, is moved away from the ridge by plate tectonic forces. At an active continental margin, it travels below the continental lithosphere in the process called subduction. Some of its sedimentary load, with materials from the eroding continent, is scraped away, but some is subducted with the down-going slab of oceanic lithosphere, together with connate water. The downward slab is gradually subjected to increased pressures and temperatures, and responds by first metamorphosing and then by partially melting at a deeper level. The metamorphism drives off part of the volatile content, which is principally H_2O, with CO_2 as the next most important constituent. Melting takes place in the descending slab, in the mantle wedge trapped between the slab and the continental lithosphere, and also in the continental lithosphere itself. The melts that form depend on a number of physical and chemical factors such as temperature, total pressure, partial pressures of H_2O, CO_2, and other volatiles, and degree of melting. Basaltic melts are prominent again, but the characteristic melts are more acid, and form andesites, by explosive eruption, or crystallize in the plutonic regime predominantly into granite, granodiorite, and other rocks of the calc-alkaline suite. The whole process is associated with regional metamorphism and the deformation of the continental margin into linear mountain belts or orogens. Subduction may actually swallow up whole ocean basins and bring continents into collision. This produces the highest mountains, for example the Himalayas at the present day. The Appalachians, which were produced by continental collision in Paleozoic times, were probably comparable to the Himalayas before erosion reduced them to their present size.

The rate of subduction on average must equal the rate of sea floor spreading, and is normally 5 cm yr^{-1} or less.

The craton

The stable continental interior, that has not undergone a mountain building event since at least the late Precambrian in most cases, is called the Craton. It is exposed in areas like the Canadian Shield, and on its margins, may have been invaded during Phanerozoic times by shallow seas. Where this has happened, the Craton becomes a continental platform for shallow water deposits that eventually undergo diagenesis and become the common sedimentary rocks sandstones, shales, limestones, and, occasionally, evaporites.

The great Precambrian Shields of the world contain within them an important break at about 2.6 billion yr ago. Younger rocks than this (for example the Grenvillian rocks of the Canadian Shield) contain structures that indicate that they are the eroded roots of mountain belts, similar to those just described. Rocks older than 2.6 billion yr lack the linear features of mountain belts and appear to have formed when the Earth's lithosphere was much more generally mobile and prone to break-up. Volcanism was more common and the volcanic rocks have been metamorphosed to greenstones and punched through by more or less equi-dimensional batholiths of granite and granodiorite.

Continental rifts

The craton is not entirely quiescent, but may break open into a rift similar to an oceanic rift, but spreading at rates commonly at least two orders of magnitude slower. The process may lead to the formation of a new arm of the ocean (as in the Red Sea for example), and it is believed to have been the initial means by which the Mesozoic continents of Laurasia and Gondwanaland broke up into the continents that now exist. The volcanic rocks that are added to the crust along continental rifts, are mostly alkali rich and silica undersaturated, and range in composition from alkali basalt to phonolite. Alkali metasomatism, usually affects the country rocks. The unusual plutonic igneous

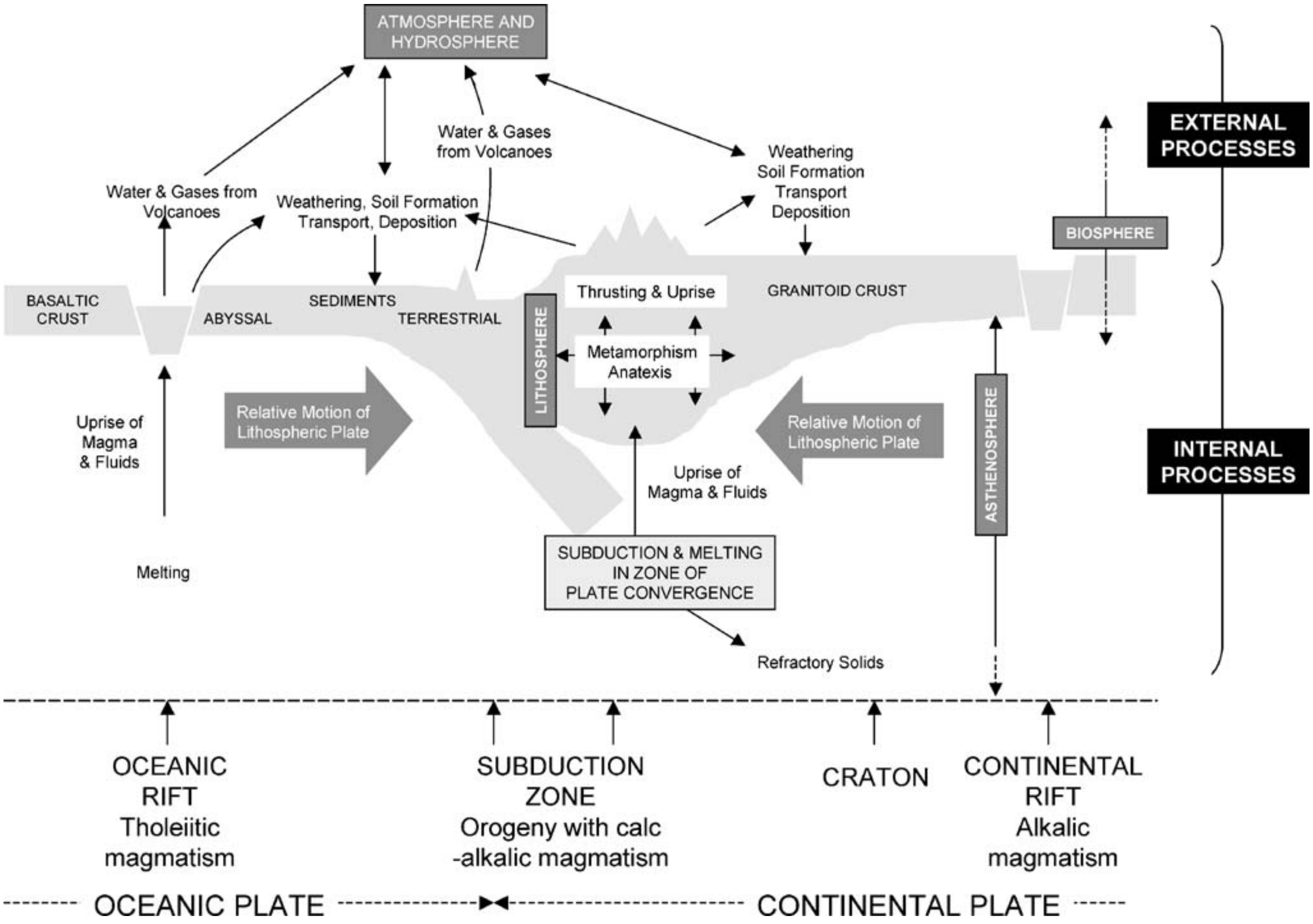


Figure G10 Interactions between internal and external processes in the plate tectonic model of the Earth.

rock carbonatite may be associated, as too may be diamondiferous kimberlite, though the latter, found emplaced in funnel like structures called pipes that extend down to the Earth's mantle, may be emplaced entirely independently of any continental rift system.

Weathering of parent materials

The processes just described produce a wide variety of materials for the formation of soils.

Igneous parent materials. Under humid conditions, weathering with accompanying leaching losses, drives the composition of soils towards end points within the four-component system SiO_2–Al_2O_3–Fe_2O_3–H_2O (which may be considered a residua system of weathering). Figure G11 shows the compositional and mineralogical changes that attend soil formation on granitoid parent materials. It also illustrates the normal sequence of secondary mineral formation. In the earliest stages of weathering the soil will tend to have small, active clay fraction dominated by amorphous phases. With continued weathering, 2 : 1 sheet silicates will form either as neoformations, or as clay minerals inheriting part of their structures from pre-existing mica. This is the stage of bisiallitisation, and is followed by the stage of monosiallitisation in which 1 : 1 sheet silicates form. Continued weathering over the very long term may leach silica from the system relative to aluminum, such that gibbsite becomes the dominant neoformation – the stage of allitisation found in certain humid tropical soils on ancient erosional surfaces. Throughout the production of new minerals in the soil, older, primary phases may persist. Breakdown of the older minerals generally follows a sequence established by Goldich (1938) and illustrated in Figure G12.

Figure G13 illustrates the convergence of soil compositions upon similar end points, no matter where the starting point is in the spectrum of igneous rock compositions. It suggests that the quotation from Davy in the first paragraph of this article requires modification and that very old soils in comparable soil-forming environments, may become at least chemically and mineralogically indistinguishable from each other no matter what the parent rock.

Rock texture is an important property in determining the rate and extension of weathering. Massive igneous rocks weather less readily than those that are fragmental. For example, granites on the Canadian Shield still show finely etched striae and chatter marks, 6–10 000 yr after the departure of Pleistocene ice sheets, whereas rhyolitic and dacitic agglomerates and tuffs (similar in composition to the Precambrian granites of the Shield) in the Western Cordillera of North America forms well developed profiles in less than a thousand years.

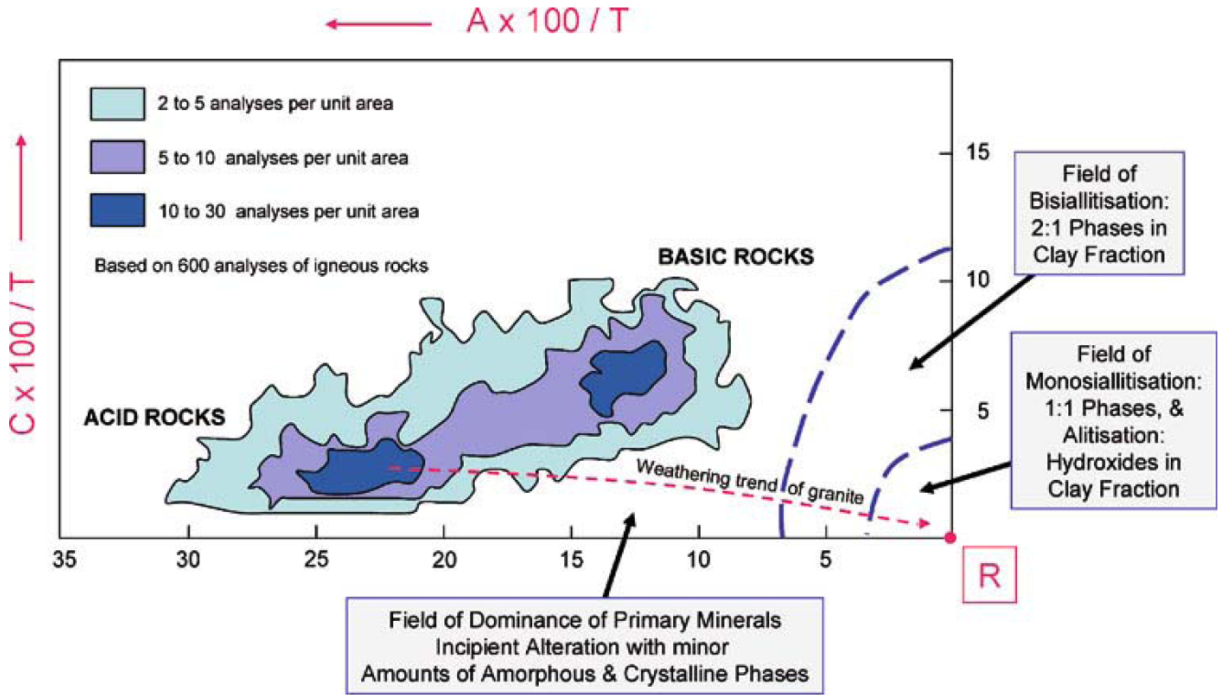


Figure G11 The normal weathering trend in the formation of soils on granitoid rocks. *R* is the sum of the weight percentages of the components SiO_2, Al_2O_3, Fe_2O_3; *A* is $Na_2O + K_2O$, *C* is CaO and *T* is the sum of SiO_2, Al_2O_3, Fe_2O_3, Na_2O, K_2O, CaO (adapted from Chesworth, 1973).

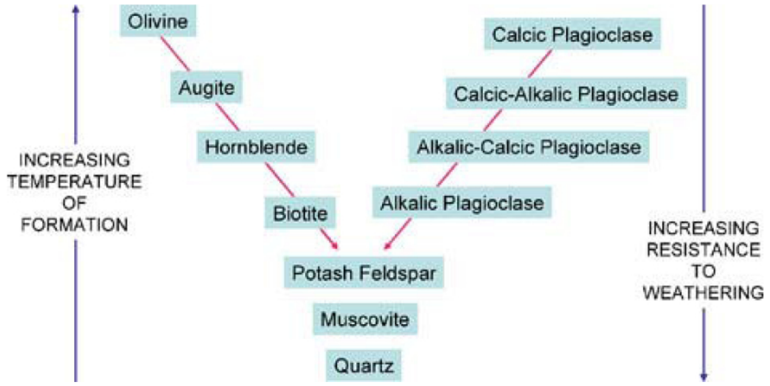


Figure G12 Mineral stability in weathering in relation to Bowen's Series of minerals forming by the crystallization of basic magma (after Goldich, 1938).

Sedimentary parent materials. The commonest sedimentary rocks are either clastic or carbonate in type. Clastic sedimentary rocks weather along similar trends to the igneous rocks just described, though they have already weathered in at least one cycle of weathering. This will have the effect of displacing the starting composition of the soil-forming system away from the igneous rock field towards the end points in the system SiO_2–Al_2O_3–Fe_2O_3–H_2O already mentioned. An earlier episode of weathering will also lower the content of primary weatherable minerals relative to igneous parent materials. It would also produce secondary phases such as clay minerals, which though weatherable, are more likely to persist throughout a soil-forming episode than primary ferromagnesian or felsic minerals.

Pettijohn (1957) devised a mineral persistence sequence (Table G6), which can be used to illustrate this point. Weathering tends to eliminate minerals higher in the sequence before those that are lower. Consequently a parent rock at stage 20 will be relatively easily weathered, while one at stage 4 will be much less readily weathered. Jackson and Sherman (1953) presents an equivalent sequence for the clay-sized fraction of soils (Table G7).

The weathering of carbonate rocks will produce soils that (at least to begin with) will be dominated chemically by carbonate reactions. While calcite persists in the solum, the soil will be alkaline in nature, and in humid regions will normally have a pH between 7 and 8. As weathering and leaching continue, calcite will be progressively destroyed in the solum, and will

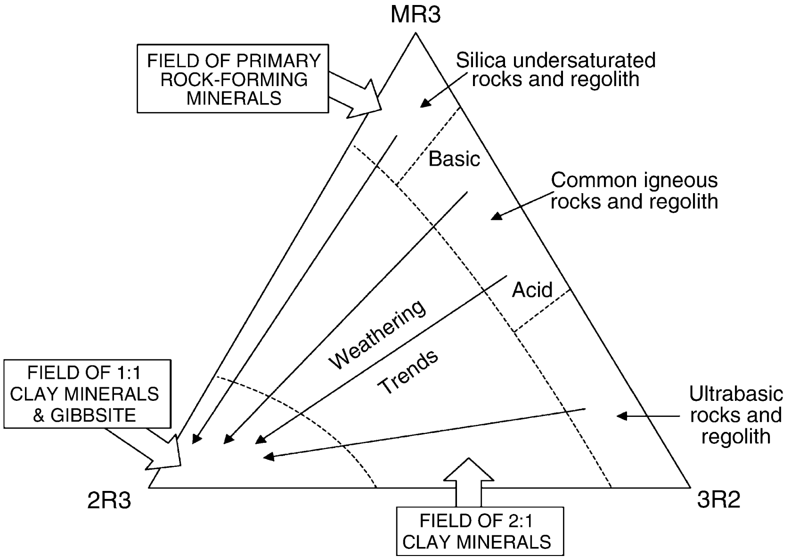


Figure G13 Chemical and mineralogical trends during weathering and soil formation. The diagram is adapted from Macias and Chesworth (1992) following Velde (1985). *R2* is $Mg^{2+} + Mn^{2+} + Fe^{2+}$; *R3* is $Fe^{3+} + Al^{3+} + Ti^{4+}$; and *M* is $Na^{+} + K^{+} + 2Ca^{2+}$. The *MR3* apex represents the bulk composition of feldspars, the *2R3* apex represents minerals such as gibbsite, kaolinite and pyrophyllite, and the *3R2* apex represents serpentine and talc. Illite solid solutions lie roughly half way between *MR3* and *2R3*, and smectites cover a zone in the bottom half of the triangle ranging from beidellite on the *2R3–MR3 sideline*, to saponite on the *3R2–MR3 sideline*.

Table G6 The order of decreasing persistence of primary minerals to weathering (Pettijohn, 1957)

−3	Anatase	11	Epidote
−2	Muscovite	12	Hornblende
−1	Rutile	13	Andalusite
1	Zircon	14	Topaz
2	Tourmaline	15	Sphene
3	Monazite	16	Zoisite
4	Garnet	17	Augite
5	Biotite	18	Sillimanite
6	Apatite	19	Hypersthene
7	Ilmenite	20	Diopside
8	Magnetite	21	Actinolite
9	Staurolite	22	Olivine
10	Kyanite		

Table G7 Weathering indices of clay-sized particles in soils and soil parent materials after Jackson and Sherman (1953)

	Index Mineral	Other mineral substance at same stage
1	Gypsum	halite, sodium sulphate
2	Calcite	dolomite, aragonite, apatite
3	Hornblende	olivine, pyroxenes, anorthite, analcite
4	Biotite	glauconite, mafic chlorite, antigorite, nontronite
5	Albite	plagioclase, microcline, volcanic glass
6	Quartz	cristobalite, tridymite
7	Dioctahedral micas	muscovite, 10 Å zones of sericite
8	Vermiculite	collapsible 14 Å interstratified zones
9	Montmorillonite	beidellite
9	Pedogenic chlorite	interstratified 2:2 zones
10	Allophane	sesquioxic, halloysitic allophanes
10	Kaolinite	halloysite
11	Gibbsite	boehmite
12	Hematite	goethite, limonite, lepidocrocite, magnetite
13	Anatase	rutile, ilmenite, leucoxene, zircon, corundum

only be found in the C horizon (as in the luvisols of Southern Ontario and adjacent parts of New York State for example). In the absence of calcite, the chemical evolution of the soil will follow the trends already discussed.

Since sedimentary rocks have a very significant zone of weakness, the bedding plane, attitude (dip and strike) of the rock will play an important role in the development of a weathering profile. A horizontal stratum for example will weather to a more even depth, than a bed dipping at a high angle. In the latter case, ease of percolation of water down the exposed bedding planes will tend to produce deeper profiles along the planes than within the body of the rock. A similar phenomenon can be observed with igneous rocks (along joints or the bedding planes of volcanic rocks), and with metamorphic rocks (with respect to foliation planes).

Metamorphic parent materials. Except for the dehydration and decarbonation that invariably accompany metamorphism, and that tend to be more complete as metamorphic grade increases, the chemical composition of a metamorphic rock will be similar to that of its unmetamorphosed precursor. Chemical weathering trends in a soil derived from a metamorphic parent rock, will therefore be similar to what would be expected from the equivalent igneous or sedimentary precursor of the metamorphic rock in question. Mineralogically however, the evolutionary pathways will differ, in that the metamorphic rock may contain minerals specific to metamorphism, such as the Al_2SiO_5 polymorphs, chlorite, garnet, staurolite, cordierite and so on. Even so the commonest sequence of changes will have the soil system passing through stages of bisiallitisation, monosiallitisation and allitisation as before, as weathering intensity proceeds (Macias and Chesworth, 1993).

As with sedimentary rocks, carbonate-bearing metamorphics such as marble will form soils that will be dominated by calcite weathering, at least in the early stages. Luvisols will commonly develop with time. Carbonate-bearing systems also react readily

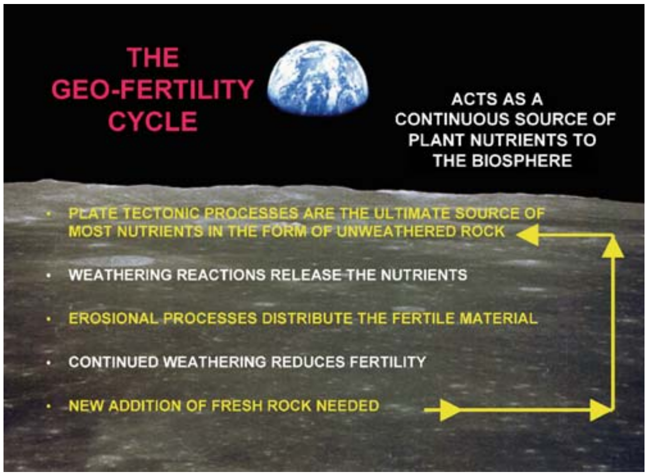


Figure G14 The geo-fertility cycle, the principal means by which the fertility of the biosphere is maintained with respect to all plant nutrients other than N, which is obtained from the atmosphere.

with emanations from intrusive igneous rocks. The latter add volatile components to the system and metasomatize the invaded rock to produce a skarn. The added volatiles show up in the presence of minerals such as fluorite (F), apatite (P), scapolite (Cl) and tourmaline (B). Again, the presence of phases of this kind will modify the weathering pathways early in the soil-forming process, but the ultimate evolution towards end points in the system SiO_2–Al_2O_3–Fe_2O_3–H_2O will remain unchanged.

Geology and soil fertility

A soil derives its fertility from atmospheric (H_2O, CO_2, N) and geological (P, K, minor and trace nutrients) sources. With time, leaching losses lead to a decreasing availability of nutrients in the soil, and geological processes are important in providing the fresh, inorganic materials that are necessary to refertilize the pedosphere. At the largest scale, a geo-fertility cycle keeps the planetary biosphere provided with nutrients (Figure G14).

The ultimate source of new, nutrient-rich materials to the pedosphere is the mantle. Over the 4.5 billion yr of Earth history, melting in the mantle, latterly beneath plate boundaries, but more generally in the earliest Precambrian, has continued to add solids, gases, and water to the lithosphere, atmosphere, and hydrosphere. This has created, and with much feedback, maintained the surface of the Earth as an abode for life. Without this contribution by the internal geological cycle, the planet Earth would be as dead as Mars or (the contrast is clear from Figure G14), the Moon (Chesworth, 1982).

Ward Chesworth

Bibliography

Chesworth, W., 1973. The Parent Rock Effect in the Genesis of Soil. *Geoderma*, **10**: 215–225.
Chesworth, W., 1982. Late Cenozoic geology and the second oldest profession. *Geosci. Canada*, **9**: 54–61.
Chesworth, W., 1991. Geochemistry of micronutrients, Chapter 1. In *Micronutrients in Agriculture. Soil Science Society of America Book Series No. 4*, pp. 1–30.
Chesworth, W., 1992. Weathering in soils, Chapter 2. In Martini and Chesworth, eds., *Weathering, Soils and Paleosols*, pp. 19–40.
Davy, H., 1813. *Elements of Agricultural Chemistry in a Course of Lectures for the Board of Agriculture.* London: Longman, Hurst, Rees, Orme, and Brown, 323 pp.
Goldich, S.A., 1938. A study in rock weathering. *J. Geol.*, **46**: 17–23.
Jackson, M.L., and Sherman, G.D., 1953. Chemical weathering of minerals in soils. *Adv. Agron.*, **5**: 219–318.
Macias, F., and Chesworth, W. 1992. In Martini and Chesworth, eds., *Weathering in Humid Regions, with Emphasis on Igneous Rocks and Their Metamorphic Equivalents*, Chapter 12, pp. 283–306.
Martini, I.P., and Chesworth, W., 1992. *Weathering, Soils and Paleosols.* New York: Elsevier, 618 pp.
Pettijohn, F.J., 1957. *Sedimentary Rocks*, 2nd edn. New York: Harper, 718 pp.
Ronov, A.B., and Yaroshevsky, A.A., 1969. Chemical composition of the Earth's crust. In Hart, P.J., ed., *The Earth's Crust and Upper Mantle.* Geophysical Monograph 13. Washington, DC: American Geophysical Union, pp. 37–57.
Taylor, S.R., and McClennan, S.N., 1985. *The Continental Crust. Its Composition and Evolution.* Oxford: Blackwell, 312 pp.
Velde, B., 1985. *Clay Minerals: A Physico-Chemical Explanation of their Occurrence.* Amsterdam: Elsevier, 427 pp.

Cross-references

Geochemistry in Soil Science
Geography of Soils

GILGAI

A type of microrelief on clay rich soils caused by expansion and contraction as the clay takes up or releases water. Adapted from an Australian aboriginal word meaning a saucer-like depression, which collects rainwater. Several types are recognized, differing in overall morphology, or in presence or absence of stones.

Bibliography

CSIRO, 1983. *Soils, An Australian Viewpoint*. Melbourne: Division of Soils, Commonwealth Scientific and Industrial Research Organization, Australia. London: Academic Press, 928 pp.

GLACIAL

Pertaining to, or produced by, sheets of ice or glaciers. A glacial landscape is one left behind when a glacier melts. A glacial epoch or ice age is a period of time when ice sheets expanded and contracted over large areas of the surface of the Earth. Glacial processes and deposits are the reason why the soils of the northern hemisphere above a latitude of about 45 degrees, are young and of high inherent fertility, by contrast with the soils of the tropical and sub-tropical zones.

Cross-reference

Ice Erosion

GLACIATION

A process by which a landscape is covered by ice sheets, commonly of continental proportions. Four major glaciations have occurred over the last two million years and account for extensive deposits of soil parent materials particularly in the northern hemisphere. Glaciation has the effect of restarting the pedological clock by (a) scraping away the products of earlier pedogeneses, and (b) depositing transported materials as moraines and other landscape forms, on which new soils can form.

Bibliography

Martini, I.P., Brookfield, M.E., and Sadura, S., 2001. *Principles of Glacial Geomorphology and Geology.* Upper Saddle River, NJ: Prentice-Hall, 381 pp.

Cross-references

Erosion
Ice Erosion

GLACIOFLUVIAL

Pertaining to a stream or river deriving its water from the melting of ice. The water reworks sedimentary material originally carried by the ice, and deposits it in valleys (often as braided stream interlayerings of gravel, sand and silt), as alluvial fans, or more extensively as outwash plains. The sediments are generally low in clay and provide the parent materials for a number of well-drained mineral soils, including Podzols in the boreal zone and Cambisols and Luvisols in temperate regions.

Cross-reference

Ice Erosion

GLACIOLACUSTRINE

Pertaining to a lake produced by the melting of ice, commonly at the end of a glaciation. The sediments deposited are commonly clay rich and are well exemplified by the clay plains that may be observed at scattered localities around the Great lakes of north America. They mark previous extensions to those lakes, and because of the high content of clay in the parent material, have become the site of Gleysol formation since deglaciation over roughly the last 12 000 to 8 000 years.

GLEY

See *Gleysols* and figure G16.

GLEYSOLS

Gleysols are wetland soils, which in the natural state are continuously water-saturated within 50 cm of the surface, for long periods of time. Reduction of Fe and Mn leads predominantly to grayish hues in the profile below the water table. This article is based on the descriptions in FAO (2001).

Connotation. Soils with clear signs of excess wetness; from R. *gley*, mucky mass.

Synonyms. Gleysols are equivalent to ‘gleyzems’ and ‘meadow soils’ (Russia), ‘aqu-’ suborders of entisols, inceptisols and mollisols (Soil Taxonomy), ‘Gley’ (Germany). ‘Groundwater soils’ and ‘hydromorphic soils’ are commonly used general terms.

Definition. Gleysols are defined by FAO (2001) as

1. having gleyic properties within 50 cm from the soil surface; and
2. having no diagnostic horizons other than an anthraquic, histic, mollic, ochric, takyric, umbric, andic, calcic, cambic, gypsic, plinthic, salic, sulfuric or vitric horizon within 100 cm from the soil surface.
3. having no abrupt textural change within 100 cm from the surface.

Parent material. Gleysols develop on a wide range of unconsolidated, geologically young materials. Fluvial, marine and lacustrine sediments of Pleistocene or Holocene age are typical, and range in mineralogy from basic to acidic.

Environment. River basins and valleys and low topographic positions and depressions, prone to high water table levels.

Distribution. Gleysols cover about 720 million ha globally in all climatic zones. The largest extent is in the sub-arctic of Russia, Siberia, Canada and Alaska, and in humid temperate and subtropical lowlands (for example in China and Bangladesh) especially where associated with large estuarine and deltaic systems. There are about 200 million ha of Gleysols in the tropics (the Amazon region, equatorial Africa and the coastal swamps of Southeast Asia, for instance). Figure G15 shows the global distribution.

Gleysols of the sub-arctic and temperate latitudes are associated with *Histosols* and with *Fluvisols* (in riverine and coastal areas). Gleysols at higher landscape positions are confined to depression areas with shallow groundwater where they occur adjacent to *Luvisols* and *Cambisols*. Gleysols in the steppe zone are found together with *Chernozems* and *Phaeozems*. Gleysols in arid regions occur predominantly in fluvial and marine lowlands, e.g., together with *Solonchaks* and *Solonetz*. A wide variety of soils (*inter alia* Calcisols, Gypsisols, Cambisols, Regosols, Arenosols and Leptosols) can be expected on adjacent uplands.

Gleysols in the humid tropics are confined to structural wetlands; *Acrisols*, *Lixisols*, *Nitisols*, *Alisols* and *Ferralsols* occur in (better-drained) adjacent uplands.

Characteristics. Water-saturation over a long period is the defining physical condition of Gleysols. Provided the dominant iron mineral is not relatively unreactive (as hematite may be in tropical examples), or the temperature is not too cold to inhibit reaction, Fe is reduced from the reds, oranges, yellows and light browns of the ferric state to the darker colors of the ferrous state grading to olive or even dark blue hues. Since ferrous iron is relatively mobile it may be removed completely from the profile, which then assumes a grayish hue. If ped surfaces are open to oxygenation, any iron present will reconvert to the ferric state so that the surfaces will assume the brighter coloration again. Typical re-oxidation products are ferrihydrite (reddish-brown) and goethite (yellowish brown). In combination the color

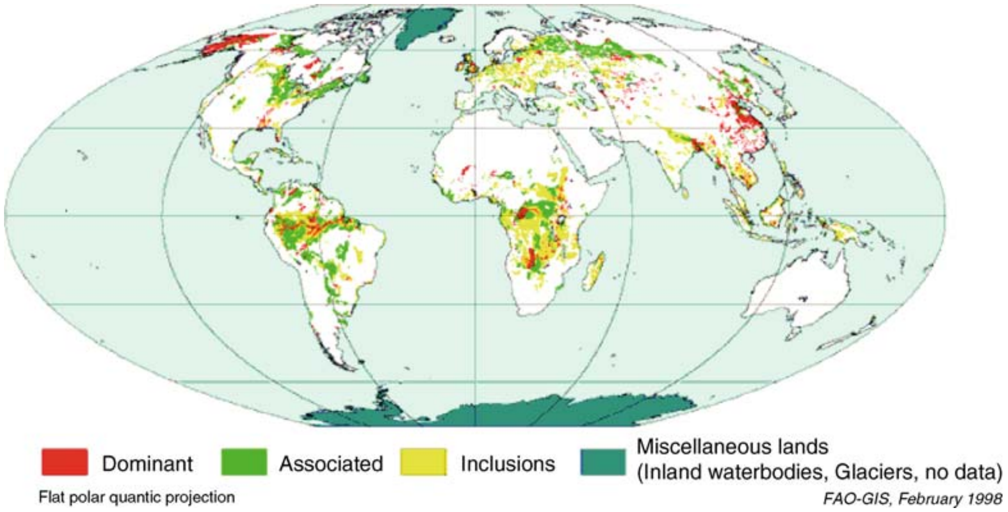


Figure G15 Global distribution of Gleysols.

patterns are clear evidence of redox activity, though in some cases the activity may be fossil in nature, and date from a former (e.g., Holocene or Pleistocene) water regime. The movement of ferrous iron and its oxidation to the ferric state may lead to the segregation of irregular masses of so-called "bog iron ore", especially in sandier soil materials.

The profiles that develop during the formation of Gleysols are mainly A(Bg)Cr or H(Bg)Cr sequences. The H horizon (a mixture of organic and mineral matter known technically as muck) appears where Gleysols are almost permanently waterlogged throughout the year.

Origin. Redox processes related to water movements and conditions, are the dominant genetic reactions in Gleysols. A constant state of water saturation within 50 cm of the soil surface and the presence of decaying organic matter as a major source of electrons, means that essentially immobile ferric iron is converted into mobile ferrous iron, which may be flushed from the system over the long term, thereby converting the soil material from predominantly brownish colors to grayish ones. Mn reacts similarly in being converted from an immobile manganic state to a mobile manganous one.

The Fe^{2+} and/or Mn^{2+} ions may then be transported to an oxidizing environment where ferric (and manganic) compounds reform, and the dominant color of ferric Fe reasserts itself. Root channels and fissures in the soil are typical localities where re-oxidation may take place. A lowering of the water table, subsequent to climate change, or to artificial drainage, can achieve the same effects on a wider scale. In essence, the position and movement of the water table is critical to the formation of gleyic properties. Similar properties are associated with stagnic conditions, the distinction between stagnic and gleyic states being made on the basis of field situation. The gleyic state is associated with the regular groundwater table, so that the zone of groundwater movement where alternate oxidations and reductions occur overlies reduced materials. The stagnic state, associated with a perched water table, leads to reduced materials overlying more oxidized ones.

Use. An excess of water is the main limitation of natural Gleysols. Untouched, and typically under swamp vegetation, they may be left idle, or used for extensive grazing. With artificial drainage Gleysols are used for arable cropping, dairy farming and horticulture. In tropical and subtropical climates rice may be cropped.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science.* 2nd edn. Essex, England/New York: Longman Scientific & Technical/Wiley. 255 pp.

Zech, W., and Hintermaier-Erhard, G. 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag 130 pp.

Cross-references

Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils
Hydric Soils
Redoximorphic Features
Redox Reactions and Diagrams in Soil

GOSSAN

The oxidized, weathered product of a sulfide-bearing rock usually of a reddish color due to the presence of ferric iron. In terms of the process of formation, gossans are analogous to Thionic Luvisols (acid sulfate soils), and like them are associated with acid drainage waters of pH 3 or less (acid rock drainage).

Cross-references

Redox Reactions and Diagrams in Soil
Thionic or Sulfidic Soils

GROUNDWATER

Water below the land-surface filling (saturating) pore spaces, fractures or other voids. The upper level of saturation is the water table. The region in a soil or surficial geological deposit below the water table is the phreatic zone. The region above the water table is the vadose zone (see Figure G16).

GUANO

The accumulated, excrement of birds, especially sea-birds, formerly (before the dominance of artificial fertilizers) used as phosphate-rich manure. The best quality imported from Peru, and used by nineteenth century farmers in Europe and the USA, contained about 15 percent each of phosphate and nitrate. It was highly prized enough to inspire a “guano rush” to Peru, and a war amongst Peru, Bolivia and Chile (Skaggs, 1994).

Bibliography

Skaggs, J.M., 1994. *The Great Guano Rush: Entrepreneurs and American Overseas Expansion.* New York: St. Martin’s Press, 334 pp.

GULLY

A channel cut by running water on sloping ground. Operationally, in agriculture, gullies are defined as “erosional channels that are too large to be removed easily with standard tillage equipment” (Hassett and Banwart, 1992, p. 143). The process of formation is referred to as gully erosion or gullying.

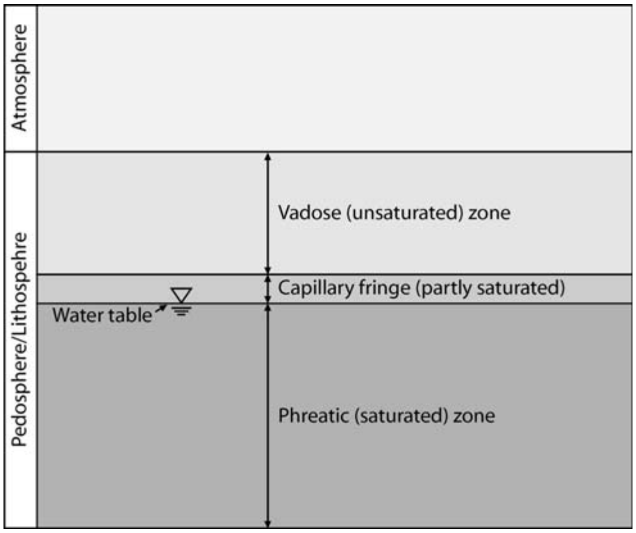


Figure G16 Vadose and phreatic zones in the near-surface hydrological environment. Where the water table is high enough to lie within the solum over an extended period of time, gleying of the soil will occur.

Bibliography

Hassett, J.J., and Banwart, W.L., 1992. *Soils and Their Environment.* Englewood Cliffs, NJ: Prentice-Hall, 424 pp.

GYPSAN

See *Cutan*.

GYPSISOLS

Gypsisols are soils with a significant accumulation of pedogenetic gypsum ($CaSO_4 \cdot 2H_2O$) in the solum. This article is based on the descriptions in FAO (2001).

Connotation. Gypsisols take their name from the characteristic mineral gypsum formed within these soils.

Synonyms. ‘Desert soils’ (USSR and in other classifications), aridisols (USDA Soil Taxonomy), yermosols or xerosols (FAO, 1974).

Definition. Defined in FAO (2001) as soils with

1. a gypsic or petrogypsic horizon within 100 cm of the surface; and
2. no diagnostic horizons other than an ochric horizon, a cambic horizon, an argic horizon permeated with gypsum or calcium carbonate, a vertic horizon, or a calcic or petrocalcic horizon underlying the gypsic or petrogypsic horizon.

Other reference soil groups (viz. Vertisols, Solonchaks, Gleysols and Kastanozems) may also have a gypsic or petrogypsic horizon, and may intergrade with Gypsisols. However the presence of other diagnostic properties determines that such soils are not themselves Gypsisols.

Parent material. Formed mostly on unconsolidated alluvial, colluvial or aeolian deposits of base-rich weathering material.

Environment. Gypsisols occur in the most arid, desertic environments with a yearly net water-deficit of atmospheric precipitation with respect to evapotranspiration losses. This is the same type of climatic environment as Calcisols, with which soils they are associated.

Distribution. Worldwide there are about 100 million ha of Gypsisols, occurring exclusively in hot, desertic regions. Major occurrences are in and around the more arid and desertic regions of the Middle East, SW Asia and adjacent central Asian republics, in the deserts of Libya and Namibia, in southeast and central Australia and in the southwestern USA. Figure G17 shows the global distribution.

Characteristics. The characteristic sequence of horizons is AB(t)C. The surface layer is a yellowish brown, ochric A, about 20 to 40 cm thick, low in organic matter. It shows evidence of strong de-gypsification, commonly contains 40% or more of clay, and has a weak, subangular blocky structure. Below is a pale brown or whitish cambic or argic (possibly relict) B. Secondary minerals in the B horizon occur as a soft,

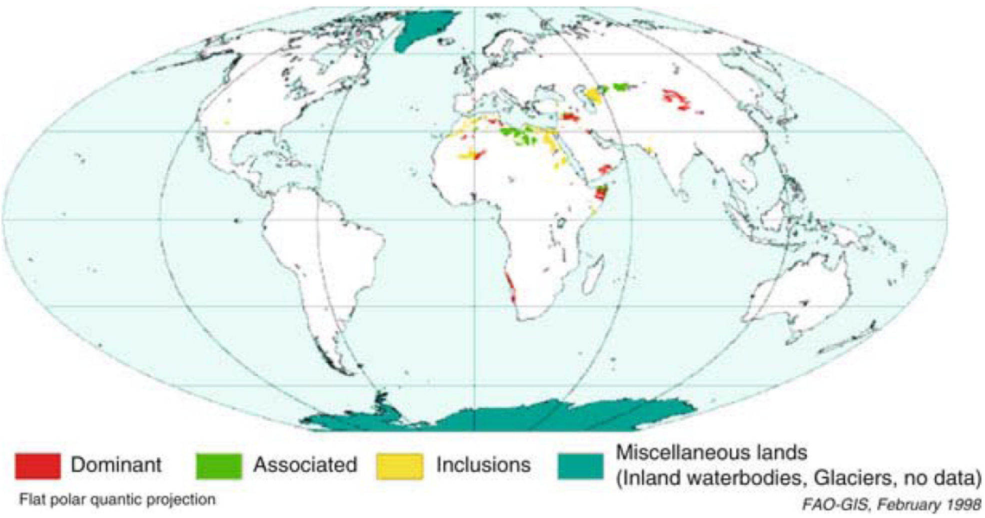


Figure G17 Global distribution of Gypsisols.

powdery and highly porous mixture of gypsum, lime and clay, as a hard, massive petrogypsic horizon of almost pure, coarse gypsum crystals, or as something in between these extremes. Where gypsum occurs in the C horizon it may be a secondary precipitation or an original component of the parent material. Hydraulic conductivity in Gypsisols varies from 5 to greater than 500 cm d^{-1}. Where the surface is more or less completely encrusted, infiltration of surface water is minimal. High percolation rates occur where dissolution has opened up and widened cracks and holes communicating with the sub-surface. Surface soil material tends to wash into these cracks and to be lost to the farmer. This wasting process produces an irregular land surface that requires a yearly leveling. The available water holding capacity of the de-gypsified surface is normally 25 to 40% by volume. If the surface layers contain more than 15% gypsum, they normally have 15% clay or less, and their retention of 'available' soil water is no more than 25% by volume. Surface soil with a loamy texture slakes easily then dries to a crust of fine flakes. This hinders the infiltration of rainwater and promotes sheet wash and gully erosion. In small quantities, gypsum is relatively harmless to plants, but in the quantities common below the surface in Gypsisols (25% of more), the availability of major plant nutrients such as phosphorus, potassium and magnesium, is impaired. The cation exchange capacity (CEC) depends on the content and type of clay. Typically it is about 20 cmol(+) kg^{-1} in the surface soil and around 10 cmol(+) kg^{-1} deeper down. Ca^{2+} is the dominant cation on the exchange complex.

Origin. Gypsisols form mainly on gypsiferous parent materials. In climatic zones where evapotranspiration exceed atmospheric addition of water, the components of calcium sulfate enter solution in the parent material and are transported upwards in the soil solution. As a result, secondary gypsum precipitates higher in the profile and a gypsic or petrogypsic horizon forms, often above an accumulation of calcite. In arid zones, the winter season is normally wet compared to the hot, dry summers. Consequently gypsum may be leached from the surface soil in winter. In summer of gypsum ($CaSO_4 \cdot 2H_2O$) may dehydrate to the hemihydrate ($CaSO_4 \cdot 0.5H_2O$) a loose, powdery, poorly crystalline compound. In winter it re-hydrates to highly irregular crystals of gypsum. These may form clusters to compact layers or surface crusts up to tens of centimeters thick. Within the body of the soil, gypsum precipitates as fine, white, powdery crystals in several habits. Filamentous accumulations form in old root channels and are referred to as "gypsum pseudomycelia". Alternatively the gypsum may precipitate in pockets, or in a more dispersed fashion as coarse crystalline 'gypsum sand', or again, as a continuous, well cemented petrogypsic horizon. In addition, rossette-shaped accumulations of gypsum known as "desert roses" occur below stones. In a few cases, the accumulations of gypsum form in situ in response to special, conditions, where sulfates have been locally supplied to a soil system from shallow groundwaters or oxidizing sulfides.

Use. Deep Gypsisols located close to water resources can be planted to a wide range of crops. Yields are severely depressed where a petrogypsic horizon occurs at shallow depth. Nutrient imbalance, stoniness, and uneven subsidence of the land surface upon dissolution of gypsum in percolating (irrigation) water are further limitations. Irrigation canals must be lined to prevent the canal walls from caving in. Large areas of Gypsisols are in use for low volume grazing.

Otto Spaargaren

Bibliography

FAO, 1974. FAO-UNESCO Soil Map of the World, 1:5,000,000. Vol. 1. Legend. Paris: UNESCO, 59 pp.

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

Fitz Patrick, E.A., 1986. *An Introduction to Soil Science*, 2nd edn. Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Alkaline Soils
Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils

H

H HORIZON

See *Horizon, Profile, Horizon Designations*.

HALOMORPHIC

Said of a soil formed under the influence of alkaline or neutral salts, particularly sodium chloride. Essentially synonymous with the groups Solonchak and Solonetz, but including salic subclasses of soils such as Fluvisols in estuarine, deltaic and marine coastal environments.

HARDENING

Hardening or induration of a soil takes place by the loss of void space by compaction or filling with fine materials. Plinthite, a diagnostic horizon for Plinthosols, is typically high in goethite, kaolinite and quartz, and low in organic matter. Fresh, t is firm but readily cut with a spade. On exposure, it dries out and hardens irreversibly. In this case, the hardening involves the dehydration of goethite to hematite which then forms a cement for the other mineral grains present.

Cross-references

Duricrusts and Induration
Durisols
Plinthosols

HARDPAN

A soil layer in which the particles have become cemented by secondary deposition of calcite, iron oxides, silica or other minerals. Addition of water does not cause slaking. Hardpans are commonly impervious and may cause a perched water table. In the WRB system, soils with hardpans within 100 cm of the surface are designated as Petric, and the horizon itself may be named in terms of the cementing agency e.g., Petrocalcic, Petrogypsic (FAO, 2001, Annex 2 and 3).

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

HARROW

A heavy frame made commonly of iron and set with tines, which is dragged over ploughed land to break and pulverize the soil, remove weeds and prepare a seedbed.

HEALTH

When applied to soil or more generally to an environment, the implication is that the system performs its ecological role in an unimpaired fashion. A metaphor that has become fashionable and in soil science has usurped to some degree, the meaning of the well established (and more precisely defined term) ‘soil quality'. Application of the metaphor in ecology (including soil science) is often referred to as the 'health paradigm'. Attempts to quantify soil health and give the term a rigorous meaning (e.g., Nunez-Reguira et al., 2006) involve estimation of physical (temperature, moisture, porosity, hydraulic conductivity, density and plasticity), chemical (pH and C/N ratio) and biological properties (most probable number of microorganisms and organic matter content), and also assessment of larger scale features of the environment such as bioclimate.

Bibliography

Núñez-Regueira, L., Proupín-Castiñeiras, J., Rodríguez-Añón, J.A., Villanueva-López, M., and Núñez-Fernández, O. 2006. Design of an experimental procedure to assess soil health state. *J. Therm. Anal. Calorim.*, **85**: 271–277.

HEALTH PROBLEMS AND SOIL

More than two thousand years ago Hippocrates and other Greeks pointed out that certain human illnesses were related to specific landscapes (see e.g., Jacobi, 1930). By degrees similar relationships were found to concern animals.

Experiments are often easier to carry out on animals than on man, and therefore it can be relatively/to discover connections between soil conditions and health situations in domestic animals. Another factor of importance is the geographic transportation of food and feed. In some regions certain animal species are dependent to a high degree on the feed material produced locally, while humans receive their food matter from different areas.

The concept of geomedicine

Geomedicine is the science dealing with the influence of ordinary environmental factors on the geographical distribution of health problems in man and animals (Lag, 1990). Definition of the subject is comparatively new, but the roots are, as mentioned, very old.

Improved methods for chemical analyses, and discovery of important physiological regularities have been the basis for a rapid growth in geomedicine.

The expression "environmental geochemistry and health" (Thornton, 1987) has been used for many of the problems covered by geomedicine. In both cases basic literature on composition of rocks, soils, food and feed is important (see e.g., Goldschmidt, 1954; Wedepohl, 1969; Schormuller, 1965–1970; Koivistoinen, 1980). The term epidenrology was originally connected to infections. In ecotoxicology, environmental toxicology and environmental chemistry many geomedical problems are discussed.

Influence of rock chemistry and chemical climate on soil properties

In the 1870s it was stated that the properties of natural soils were determined by the mineralogical parent material, the climate, the living organisms, the topography, and the length of time for soil formation. With cultivation or other interferences the properties change as result of activities of mankind.

Complicated chemical processes are always going on in the soils. For a long time it was supposed that original mineralogical composition had a decisive influence on the chemical properties of the soil. In later years it has been stated that chemical climatology can be of importance too. Chemical differences in the soil connected to the chemical climate, can have interesting geomedical consequences. For instance occurrences of dangerous illnesses due to very low concentrations of iodine and selenium can be explained in this way. Where the bedrock is low in selenium, young soils, as a rule, have low selenium and iodine contents (see e.g., Lag, 1990).

Pollution of the soil and exhausting of nutrients

In many countries industrializing of societies has resulted in soil pollution. Dangerous matter has in this way been brought into circulation systems. From the soils the matter is transported to plants and further to animals and man, and by waste products back to the soils again.

One of the most notorious cases of soil pollution may be the cadmium supply, which caused the itai-itai-disease in Japan (Kitagishi and Yamane, 1981). Harmful effects of acid precipitation are being discussed with concern in many countries.

Intensified agricultural management has led to increases in some special pollution. Along with commercial fertilizers containing phosphorus, small amounts of cadmium are brought to the soils. Nitrogen fertilizers can, under unfavorable circumstances, cause toxic effects in man and animals. Heavy application of certain nutrients may be followed by the exhaustion of others in the soils. Infection matter and parasites can be spread by manure and sewage sludge.

Some deficiencies causing geomedical problems

A classical geomedical example is goiter caused by insufficient iodine supply. Interesting historical surveys on this and other geomedical questions are presented e.g., by Underwood (1977) and Kovalskij (1977).

A connection between osteomalacia in domestic animals and very low contents of phosphorus in rocks and soils was stated unequivocally more than l00 years ago (Dircks, 1879; Vogt, 1888). Dental caries is in some instances due to lack of fluorine. Deficiencies of iron have often caused anemia. The content of copper, cobalt and zinc in soils is in some districts so low that this brings about health problems.

In 1957 it was clarified that selenium is a necessary element for animals. Later it has been stated that selenium deficiency is often connected with particular soil conditions. Owing to influence of the chemical climate the selenium contents of the Norwegian soils decrease with increasing distance from the ocean and decreasing amounts of precipitation. Long before it was proved that selenium is essential, serious toxic effects of this element had been discovered in USA.

Examples of special toxic effects

Fluorine can cause dangerous, harmful effects. This is partly related to volcanic eruptions and partly to industrial pollution. For instance in Africa and Iceland serious fluorine damages have been found close to volcanoes. Detrimental fluorine pollution occurs in the neighborhood of Norwegian aluminum factories (see Jag, 1990).

Mining has resulted in pollution by a great number of elements. Damages by arsenic, lead, mercury, cadmium, copper, zinc and nickel have been reported frequently. When sulfide ores are exploited, pH will often decrease in the environment. The pH can be lower than 3.0 when sulfide-containing wastes are mixed in the soil, and in such acid surroundings no vascular plants can develop. Even at a somewhat higher pH, where the hydrogen ions do not directly kill the plants, the sulfuric acid may set free other toxic elements. Aluminum and manganese are examples.

Pollutants, harmful for the surroundings, were spread from many other types of industry. A great number of local polluted soil areas exist, each with consequences for health.

Global air currents transport acids, radioactive substances and other pollutants. The Chernobyl disaster is a drastic example. In many places radon is a dangerous matter.

Along the roads the soils receive lead from motorized traffic.

Interrelationships and future development

Many different factors have often to be considered when geomedical problems are to be evaluated. When concentrations of a certain element are extremely high or low, a conclusion may be drawn easily. However, the effect of one element will frequently depend on others.

Antagonism and synergism between different elements have been known for a long time. In such complicated systems as relationships between soil conditions and health situations, the regularities are often difficult to discover, however. A few examples may be mentioned.

Interrelationships between copper and molybdenum are well known in animal nutrition. A high content of molybdenum can result in copper deficiency, and a low molybden content in a toxic effect of copper.

The trace elements selenium and cadmium interfere mutually in many biological processes. Selenium often reduces the toxicity of cadmium. These elements also interfere in processes where other elements are involved (Lag, 1991).

Calcium acts antagonistically towards many other elements. Magnesium and potassium have mutual relationships both in soil reactions and in plant and animal nutrition.

Large numbers of relationships exist between important organic compounds and single nutrients and toxic elements.

It is likely that attention will, gradually, be drawn much more in the direction of prevention of diseases. Relations between soil conditions and health problems in man and animals must then come into sharper focus. So far a huge number of questions are not yet answered. We can expect comprehensive research activities in geomedicine in the future.

J. Lag

Bibliography

Dircks, W., 1879. Einige Untersuchungen Uber Hew. Forschungen auf dem Gebite der Viehaltung, 6. *Heft*, **1879**: 274–282.

Goldschmidt, V.M., 1954. *Geochemistry.* Oxford: Clarendon Press, 730 pp.

Jacobi, G., 1930. Das goldene Buch des Hippocrates. Eine medizinische Geographic aus dem Altertum. *Schriftreihe des Natura*, Vol. 5, 75 pp.

Kitagishi, K., and Yamane, J., ed., 1981. *Heavy Metal Pollution in Soils of Japan.* Tokyo: Japan Scientific Society Press, 302 pp.

Koivistoinen, P., ed., 1980. Mineral element composition of Finnish food: N, K, Ca, Mg, P, S, Fe, Cu, Mn, Zn, Mo, Co, Ni, Cr, F, Se, Si, Rb, Al, B, Br, Hg, As, Cd, Pb and ash. *Acta Agric. Scand. Suppl.,* **22**: 171 pp.

Kovalskij, V.V., 1977. Geochemische Skologie. *Biochemie*, 353 pp.

Lag, J., ed., 1990. *Geomedicine.* Boca Raton, FL: CRC Press, 278 pp.

Lag, J., ed., 1991. *Human and Animal Health in Relation to Circulation Processes of Selenium and Cadmium.* Oslo: The Norwegian Academy of Science and Letters, 224 pp.

Schormtiller, J., ed., 1965–1970. *Handbuch der Lebensmittelchemie.* 9 Vols. Berlin: Springer-Verlag.

Thornton, I., ed., 1987. Proceedings of the 1st international symposium on geochemistry and health, Oxford, 264 pp.

Underwood, E.J., 1977. *Trace Elements in Human and Animal Nutrion.* New York: Academic Press, 545 pp.

Vogt, J.H.L., 1888. Norske ertsforekomster. V. Titanjern-forekomsterne i noritfeltet ved Ekersund-Soggendal. *Archiv Mathematik og Naturvidenskab*, **12**: 1–101.

Wedepohl, K.H., ed., 1969. *Handbook of Geochemistry*, Vol. I. Berlin: Springer-Verlag, 442 pp.

Cross-references

Bioremediation
Chemical Composition
Diffusion Processes
Edaphic Constraints on Food Production
Environment
Irrigation
Leaching
Pollution
Sludge Disposal
Soil Water and Its Management
Trace Elements

HEAT CAPACITY

Soil temperature affects the rates of the physical, chemical and biological reactions and processes in the soil, thereby influencing plant growth and the soil's biological activity. A change in soil temperature, caused by a gain or a loss of heat from the soil, depends on the specific heat and heat capacity of the soil, and the range of temperature change for a given heat gain or loss is governed by the heat capacity (McInnes, 2002).

Heat capacity of a soil depends on its constituents – solids, water content and in frozen soils, ice content – that are spatially time- and temperature-dependent. Soil heat capacity can be either measured or calculated, provided the specific heat mass and volume fraction of each soil constituent under consideration is known (de Vries, 1963; Kluitenberg, 2002).

Concepts and definitions

Heat capacity, C, is commonly defined as the amount of heat, AQ, needed to be added to a material or a system to cause an increase in its temperature from T to $T + \Delta T$.

This definition is stated in a specific form in Equation (1):

$$C = Time_{\Delta T=0}(\Delta Q/\Delta T) \rightarrow \delta Q/\delta T \qquad (1)$$

In thermodynamic terms, we distinguish between the volumetric and mass heat capacities. The volumetric heat capacity, C_V, given by Equation (2):

$$C_V(\delta U/\delta T)_{V=\text{const.}} \qquad (2)$$

where U is the total internal energy of the system or the mass of the material under consideration; heat content, C, is related to U by $Q = \Delta U + W$ where $W = \Delta PV$ is the work performed by the system (increase in pressure by ΔPV at constant volume). If one maintains constant pressure, then $W = P\Delta V$ where under constant pressure, the system will change its volume when work is performed. Under these conditions, heat capacity of a system at constant pressure is given by Equation (3), where H is the system's heat content:

$$C_P = (\delta H/\delta T)_{P=\text{const.}} = [\delta(U + PV)/\delta \mathrm{T}]_{P=\text{const.}} \qquad (3)$$

The heat capacity term, C, is the most commonly used term in soil applications as it varies with the amount of mass in the system. If expressed on a unit mass basis, it is independent of the size of the system and is termed the "specific heat" of the system. In other words, specific heat is the ratio of the heat capacity of a system or material equal to that of mass water, under the same temperature and pressure conditions.

Methods of heat capacity determination

As stated above, the heat capacity of a soil system can be calculated from its constituents. A commonly used unit is the heat capacity on a volume basis of the soil system. For a mixture of materials, such as soil, C, the heat capacity on a volume basis is given by the sum of heat capacities of the mixture's constituents, $P_j C_j$, weighted by their volume fraction x_j, where P_j is the density of constituent j (de Vries, 1963). Specific heat capacities of various soil constituents or the soil mixture can either be empirically determined by a calorimetric method, as described by Taylor and Jackson (1986), or using published measured values (see Table H1) and calculating C using Equation (4):

$$C = \sum_{j=1}^{n} P_j C_j x_j \tag{4}$$

Observed and calculated heat capacities

Values of specific heat and heat capacities of various soil constituents given in Table H1 show that Equation (4) can be simplified by using a single averaged value for several respective soil constituents, e.g., some of the solid fraction such as clay minerals and quartz. These will be represented by $\rho C_i = 2.45$ (M Jm^{-3} K^{0-1}). Using for the soil's solids, water, and organic matter fraction, the values of 2.35, 4.186, and 2.45 (M Jm^{-3} K$^{0-1}$) respectively, and ignoring the contribution of air content to the soil's volumetric heat capacity due to its very low specific heat value, Equation (4) can be simplified and rewritten as given in Equation (5):

$$C = 2.45x_{\text{solids}} + 4.186x_{\text{W}} + 2.45x_{\text{organic matter}} \tag{5}$$

provided dolomite, basalt, $CaCO_3$, Fe, and Al oxides do not constitute an appreciable volume fraction in most of the soils under consideration. One should note that for a rigid soil, the only volume fraction that is time-dependent is water content. Thus, the volumetric soil heat capacity can be expressed as a linear function of its volumetric water content, soil texture, and bulk density.

Equations (4) and (5) hold as long as the soil matrix remains invariant to changes in water and air contents, but should be modified when a) swelling-shrinking soils are considered, and b) if a state of phase changes takes place, e.g., freezing or thawing.

When water is added or lost from a swelling-shrinking clay soil, total soil volume changes are observed, and the ratio between the volume fractions of the solids and water varies. Consequently, the heat capacity varies and the changes are non-linear with changes in water content as long as the soil volume changes but tends to become linear as soil shrinkage ceases and water content still varies in the soil, usually at low to very low volumetric water content.

When a phase change takes place, as in a freezing-thawing soil, and latent heat of fusion 333 (MJ Mg) is either absorbed or released from the soil without a change in temperature and a slight or no change in soil volume occurs (Miller, 1980), Equation (4) is then replaced by Equation (6):

$$C = \sum \rho_j C_j x_j + \rho_{\text{ice}} L_{\text{fus}} x_{\text{ice}} \tag{6}$$

Similar changes are required when the soil under consideration is at elevated temperatures, and a slight temperature change will cause a relatively appreciable increase in soil vapor content, requiring a correction for latent heat of vaporization, in a similar way to Equation (6).

In the case where salt concentrations in the soil solutions become very large, as in soils moistened with brine, the volumetric heat capacities relative to that of pure water of brines may diminish by a small percentage to almost 24% (Noborio and Mclnnes, 1993), and if Equation (5) is to be used,

Table H1 Specific and volumetric heat capacities of selected soil constituents

Material	C (MJ · Mg · K$^{0-1}$)	P (Mg · m^{-3})	C (MJ · m^{-3} · K$^{0-1}$)	Source
Quartz	0.795–0.875	2.65	2.107–2.319	1,2,4
Granite	0.804	2.60	2.090	1
Dolomite	0.92–0.96	2.90	2.668–2.784	1
Basalt	0.89	3.00	2.670	1
$CaCO_3$	0.8	2.71	2.358	1
$CaSO_4$	0.816	2.45	2.000	1
Fe_2O_3	0.682–0.691	5.24	3.574–3.621	1
Al_2O_3	0.908	3.70	3.360	4
Kaoline	0.975–1.021	2.60	2.535–2.655	1,4
Clay minerals	0.757–1.13	2.65	2.006–2.995	1,5
Calcareous sandy soil	1.04	–		4
Humic calcareous sandy soil	1.076	–		4
Garden soil	1.042	2.65	2.761	4
Water	4.186	1.00	4.186	4
Ice	1.883	0.917	1.726	5
Air	0.963	0.00125	0.0012	5
Humus	1.854–1.996	1.3	2.410–2.480	1,4,5

1. Ulrich (1894), taken from de Vries (1963).
2. Kersten (1949).
3. Bower and Hanks (1962).
4. Land (1878), taken from de Vries (1963).
5. de Vries (1963).

the proper value of the volumetric heat capacity of the soil solution should be used instead of 4.186 ($MJm^{-3}\ K^{0-1}$).

Amos Hadas

Bibliography

Bowers, S.A., and Hanks, R.J., 1962. Specific heat capacities of soils and minerals as determined with a radiation calorimeter. *Soil Sci.*, **94**: 392–396.

Kersten, M.S., 1949. Thermal properties of soils. *Bull. Univ. Minn. Inst. Tech. Eng. Exp. Stn.*, **28**: 1–228.

Kluitenberg, G.J., 2002. Heat capacity and specific heat. Chapter 5.2. In Dane, J.H., and Topp, G.C., eds., *Methods of Soil Analysis, Part 4, Physical Methods.* Soil Science Society of America Book Series Number 5. Madison, WI: Soil Science Society of America, pp. 1201–1208.

McInnes, K.J., 2002. Temperature. Chapter 5.1. In Dane, J.H., and Topp, G.C., eds., *Methods of Soil Analysis, Part 4, Physical Methods.* Soil Science Society of America Book Series Number 5. Madison, WI: Soil Science Society of America, pp. 1183–1199.

Miller, R.D., 1980. Freezing phenomena in soils. In Hillel, D., ed., *Application of Soils Physics.* New York: Academic Press, pp. 254–299.

Noborio, K., and McInnes, K.J., 1993. Thermal conductivity of salt-affected soils. *Soil Sci. Soc. Am. J.*, **57**: 329–334.

Taylor, S.A., and Jackson, R.D., 1986. Heat capacity and specific heat. In Klute, A., ed., *Methods of Soil Analysis. P. I, Physical and Mineralogical Methods*. Agronomy Monograph #9, 2nd edn., Madison, WI: American Society of Agronomy: Soil Science Society of America. (2 vols.).

de Vries, D.A., 1963. Thermal properties of soils. In van Wijk, W.R., ed., *Physics of Plant Environment.* Amsterdam: North Holland, pp. 210–235.

Cross-references

Bulk Density
Thermal Regime
Thermodynamics of Soil Water
Water Content and Retention

HEATH

An extensive, uncultivated tract of wilderness or waste land with a vegetation dominated by low bushes and ericaceous plants. Under a humid, temperate climate the characteristic soils are Podzols.

It is now generally accepted that some of the heathland areas of western Europe are anthropic in nature - the result of deforestation by fire by Neolithic and older populations.

Bibliography

Dimbleby, G.W., 1962. *The development of British heathlands and their soils.* Oxford: Clarendon Press, 120 pp.

Cross-reference

Neolithic

HISTORY OF SOIL SCIENCE

The history of the growth of soil science briefly presented here, receives a comprehensive treatment in Warkentin (2006). Hillel (2005) contains a great deal of valuable historical material, scattered and disseminated under many headings. A single-volume work on soil scientists and their field, from a western European viewpoint, is that of Jean Boulaine (1989). A Russian perspective is given by L. A. Krupenikov (1981). There are also brief, expert, historical sketches in the entries “Soil Conservation” and “Soil Science” in G. A. Good (1998).

Ancient writings and cultural forcings

Possibly the oldest written observations on soils and agronomy are to be found in Jewish culture – the Old Testament of the Bible and the Talmud – much of which were evidently passed down in the folklore of a largely agricultural population (Hillel, 1991). The ongoing labors of archaeologists focus geographic attention on three not-entirely independent areas. All appear to have been linked by the late Stone Age cultural transitions from hunting and gathering, to the seasonal exploitation of seed-bearing grasses (Struever, 1971). Also, during the globally significant transition from ice age to interglacial climatic conditions there were very remarkable and extreme environmental fluctuations. Following the migrations of climatic belts from latitude to latitude, early humankind naturally had to adjust. Seasonally adjustable campsites eventually became stabilized into year-round villages. Basket- and pottery-making became essential for seed storage and seasonal plantings. The selection of the best soils followed naturally.

The three geographic regions noted above are *(a)* The Mesopotamian plains between the Tigris and Euphrates, their headwaters, and their nearby grass lands (e.g., in present-day Syria); *(b)* the Nile Valley, specifically the Blue Nile from the foothills of Ethiopia to the junction with the White Nile, and from there downstream to the delta; and *(c)* the Indo-Gangetic plains of present-day India and Pakistan (although this case is much more speculative because the archaeological foundations are weak). In each use there was a pre-existing culture of a nomadic, pastoral nature (Mesolithic to Neolithic), in which there would appear to be no awareness of the existence of soil as a sine-qua-non of any cultural tradition. In each case the great river valleys and their giant alluvial tracts are oriented more or less north-south. The rivers in each case are said to be allogenic, that is, their headwaters are located in climatic and environmental setting that differs from the setting downstream.

Climatically, all three regions are subject to very dramatic fluctuations of seasonality (Oliver, 2005). That is to say, the rainy seasons fluctuate, over century scales, so that one region for example receives winter rains for a few centuries and then, after a period of indecisive nature or extended droughts, begins a phase of summer, monsoonal rains. A classical review of the erosion/sedimentation alternation and its mechanisms is that of Vita-Finzi (1969) with respect to Mediterranean valleys. This sort of seasonal switching forced profound cultural changes (Sandar et al., in Warkentin, 2006). Warkentin (2006) also contains the following source material: soil care and land use in ancient Israel (A. Hutterman); similar details for classical Greece (J. Bech); for the Romans (V. Winiwater); and from the New World, materials on soil from Aztec sources (B. Williams).

During the cultural vacuum that marked the triumph of faith-based, anti-scientific cultures in the Western World, enlightenment came from the Arabic and Persian speaking peoples, notably in what is now Uzbekistan and Iran. This hiatus lasted until the cultural revival of the 15th to 18th centuries (Feller and Yaalon in Warkentin, 2006).

Curiously enough, it was the economic incentives that spurred the feudal owners of Russia’s great landed estates and opened the door to the age of Dokuchaev and the introduction of science into soil studies (Evtuhov in Warkentin, 2006) and the development of soil classification The latter was always within the framework of Dokuchaev's ideas, but without his environmental requirements (Gerasimova, Konyuskov, in Hillel et al., 2005).

In America, again it was the economic incentive that triggered scientific studies, but from a totally distinctive starting point, the chemistry and structure of soils, in contrast to the more philosophic, genetic and regional approach of the Russian workers. Government agencies, federal and state, were empowered with the systematization of soil studies. Genesis in the Russian sense was regarded rather as a curiosity. Eugene Hilgard and Milton Whitney were early leaders (Amundson in Warkentin, 2006). C. F. Marbut from 1913–1935 steered the U.S. Soil Survey along a biological or Darwinian, evolutionary course (Brown, in Hillel et al., 2005, p. 235). With the 20th century came the idea of soil cover patterns and the catena (Gennadiyev and Bockheim in Warkentin, 2006).

With the discoveries and exploration of the semiarid American West came the birth of a new science, geomorphology. Previously it was known as "physiography" or "physical geography" and there emerged a schism that still persists to this day, particularly in Europe. There physical geography was often regarded as a "soft science". In contrast, geomorphology was locked into geology and the "hard sciences".

In a volume of the Earth Science series it is natural that geological links should be sought between the soil classifications, climate, topography and the parent materials. With respect to the last of these within the northern hemisphere there is a single overreaching factor: the last glaciation (Wisconsinan or Würm), which underwent its closing phases about 9 000–15 000 years ago (Birkeland, 1974). In the mid-latitudes of the United States and Russia, as well as China, those phases were dominated by cold, dry climates, quite unlike the present, featuring immense dust storms and depositing vast layers of loess. Weathering of that loess blanket has been a constantly fluctuating, intermittent process since then (Ruhe, 1965; he called the process "Paleopedology"; see also Yaalon, 1971).

The linking factor, of geological and paleoclimatic origin, was that both regions, U.S. and Russian, are straddled by the loess belt, the periglacial blanket of dust and silt that dates from not one but multiple late glaciation stages of repeated "ice age" cycles. Under postglacial warmth and precipitation these yellow loess deposits usually weather to a reddish or brown "loam" that fell into the U.S. soil order mollisols and its suborders. Often it is accompanied by "krotovinas", a collective term for earthworm products, snails, infilled rabbit and prairie-dog burrows. This "loam" (a common geological term - see the article Texture) constitutes the major source of the agricultural wealth of both countries, as well as its extension in Western Europe and eastwards into China (Kukla et al., 1990). Its development in the southern hemisphere is similar but of minor extent.

Despite the powerful role of the geological linkage, the U.S. and Russia have long been separated by traditional, ideological and political differences that have served to direct their scientists into wholly disparate tracks. In Russia the tradition evolved from the tsarist monolithic form of government where the agricultural land was distributed among the ranks of a feudal hierarchy. This compartmentalization was perpetuated during the seventy years of soviet rule, which reduced the small holdings of the "kulaks" and larger units of the aristocracy to giant collective farms.

Nothing could be more different in the American agricultural system, which was based on the independent small holdings of family oriented units following the English and German traditions of the Middle Ages. Late 20th century mechanization and conglomeration has converted the American scene to something approaching the Soviet collectives, but in a highly mechanized and rationalist way, dictated by private agribusiness monopolies. American experience of soil degradation, the infamous "dustbowl" disaster, and so on, can be traced back to forest-cutting even in the early 19th century (Bennett, 1939; Helms, p. 767, in Good, 1998).

First scientists

The first and unquestionable "father of soil science" (Warkentin, 2006) was V. V. Dokuchaev who was linked to the Russian Academy of Science (originally in St. Petersburg), but who was first approached by the big landowners who wanted to improve the economic viability of their territories. In this way he traveled widely with a background knowledge derived from the German schools of geochemistry.

The year 1899 marked *(a)* the first textbook of soil science (*Pochvovedenie* by N. M. Sibirtzev), which contained a synthesis of Dokuchaev's ideas about classification of soils and their genetic history; and also *(b)* the first appearance of a soil science journal, with the same name *Pochvovedenie* (edited by P. V. Ototski, followed later by A. A. Yarilov). This journal played a major role in the beginnings of soil science, although this leading role was lost during the secretive and xenophobic conditions of Soviet hegemony. Nevertheless more than 20% of the world's soil science material appeared in the Soviet Union. During the last half-century this journal has (in part, or in whole) been translated into English. According to Yaalon (1999) over 5000 soil science publications now appear annually. Dokuchaev was responsible for the introduction of many of the basic terms. A mineralogist by training, he created the genetic and zonal approach, as well as the concept of the soil profile. He had been commissioned to start regional mapping by the Economic Society of St. Petersburg and by 1883 had published the *Russian Chernozem*, the principal soil of the steppe. It was presented as his doctoral thesis and contained the foundations of scientific pedology. It defined the five genetic factors: parent material, climate, biota, relief and age. The first textbook, by N. M. Siburtzev (1890–1900), as noted above, expanded the terminology, introducing what were originally folk terms such as Podzol and Solonetz. Siburtzev became the first professor of pedology. The year 1899 also marks a milestone for soil science in the United States when through its Department of Agriculture it initiated the systematic mapping of soils (later to become the Soil Survey Division). The standard map sheet was the 1-inch to the mile (about 1 : 63000) quadrangle sheet provided by the U.S. Geological Survey, following the old British duodecimal scales used by the first colonists. Initially the "soil types" were to become "soil series" differentiated by texture and geological substrate, and refined to take in the full soil profile.

Eventually all aspects were included in "Soil Taxonomy: Seventh Approximation" and progressively improved through the 20th century, which was designed to fit the needs of management soil users (Soil Survey Staff, 1960, through several iterations to currently Soil Survey Staff, 1997).

To begin with, the American soils specialists were not in the least interested in genesis, but in what the soil could grow. In fact, an early definition of soil was "any medium on which plants would grow" (Jenny, 1941), which incidentally would include wet blotting paper. Gradually the development of the U.S. Soil Taxonomy was expanded to embrace more genetic and landscape concepts (for example, the "andisols" and their volcanic connections). Robert V. Ruhe (1919–1993) pioneered the idea of soil geomorphology (Ruhe, 1965).

The Russian approach had at first little influence in America, although in 1901 the Siburtzev classification was translated into English by the USDA. In contrast, it spread rapidly into central Europe where E. Ramann (1851–1926) became the first university professor of soil science in a German institution. He contributed the term *braunerde* (chestnut soil) to the vocabulary. The Russian textbook by K. D. Glinka (1867–1927) was translated into German as *Die Typen der Bodenbildung* (1914), and had a widespread influence (although apparently none at all at first in the United States; an English translation came much later).

A turning point in the United States was reached when C. F. Marbut (1863–1935) read Glinka's book and was impressed by the Dokuchaev approach. This led to an expansion of the U.S. Taxonomy (Jenny, 1961; Simonson, 1968, 1969), which allowed some reconnection between the two extremes. The German penchant for organization reached its zenith in 1930 with the publication of the massive *Handbuch der Bodenlehre* (edited by E. Blanck, 1877–1953). After this, according to Yaalon (1997), "modern soil research took off at an accelerated rate". Yaalon submitted that there have been essentially three paradigm leaps in the history of soil science:

a. Liebig's *mineral theory* of plant nutrition in the 1840s.
b. Dokuchaev's recognition of the *soil profile* (later to be called the *pedon*), with its multiple and independent soil-forming causative factors (see the Siburtzev textbook in 1899).
c. The general acceptance in the 1960s and 1970s of the deterministic process-response model for soil reconstruction.

Experimental science

A fundamental aspect of modem experimental science is reproducibility, a singularly difficult problem for the study of soils and geology. In England, an independently wealthy English gentleman, Sir John Bennet Lawes and his assistant Henry Gilbert, established the Rothamsted Experimental Station at Harpenden, some 50 km N of London in 1843. Their objective was to try out all sorts of crops, fertilizers and synthetic "weather" conditions, so that they could positively recommend certain procedures and materials of benefit for agriculture in general. Top-level scientists were hired and very quickly an enviable reputation for rigorously tested procedures was established. R. K. Schofield (1901–1960) developed quantitative methods for measuring water movement in soils.

Rothamsted investigated at a "hands-on" scale the science of soil physics, soil chemistry and soil biology. It had more in common with the Germanic centers of soil investigation, and less with the mapping programs of Russia and the U.S. One of their distinguished researchers was H. L. Penman (1909–1976) who presented to the Royal Society of London, a paper on "Natural evaporation from open water, bare soil, and grass" with an equation that was later adopted by the Food and Agricultural Organization of the United Nations. In America, the concept of "evapotranspiration" was developed by C. W. Thornthwaite, a statistical procedure, useful on a broad scale but less satisfactory for actual crops.

In the U.S. an agricultural experimental station was established at the New Jersey State University of Rutgers in 1887, under its first director George Hammell Cook. Jacob Lipman, who had come originally as a migrant from the Ukraine, developed the role of soil bacteria developed. He initiated the journal *Soil Science* and was its first editor. He was responsible to a large extent for the internationalization of soil science (Tedrow, in Hillel, et al., 2005).

The concept of soil chemistry is one of the oldest in soil science, founded by Justus van Liebig (1803–1873). He was one of the "most versatile German chemists of all times" (van der Ploeg, et al. in Hillel et al., 2005). He took the moral high ground in soil chemistry, railing against the industrial exploitation of the soil, which at that time was simply starved of its normal nutrients. His son Hermann von Liebig worked at the Agricultural Experiment and Research Station in Munich. Fertilization, he argued, should aim to replace in the soil what was removed by cropping.

Rock weathering, laterite and the tropics

In the 19th century the idea of "parent material" was more or less taken for granted. The transition from fresh bedrock to progressively altered mantle was inherent in the C horizon of Dokuchaev's ideal profile. In 1890 the U.S. Geological Survey issued a professional volume on the "*Origin and Nature of Soils*", prepared by a professor of geology at Harvard, N. S. Shaler (1841–1906) who was also state geologist for Massachusetts. Then in 1897 followed an epoch-making book "*Rocks, Rock-weathering, and Soils*" by G. P. Merrill, which still stands today as a standard work on this subject.

Rock weathering became an archaeological topic in the comparison of different lithological rock types used in the making of tombstones. Limestone or marble proved to be exceptionally susceptible to the acidity of rainwater, a condition exacerbated particularly during the 20th century with its rising atmospheric pollution by CO_2, SO_2 and NO_x. Other rock types developed a *weathering rind* (Birkeland, 1974) e.g., of yellow-brown color around the dark gray to bluish-black of an epidiorite, gabbro, slate or mudstone. The relative ages of boulders in glacial tills could be gauged by depth and degree of this weathering.

In the tropics, the pioneer work of F. H. Buchanan as early as 1807 showed that igneous rocks, notably the granitic Precambrian varieties from the Indian peninsula were susceptible to deep weathering which created a soft, glutinous clay, often dozens of meters thick. He observed how Indian artisans molded these clays in blocks, which were exposed in the sun and thus to dehydration. This led to the creation of building bricks, and hence his name *laterite* (from "*later*" the Latin for brick). A UNESCO review of laterites is provided by Maignien (1966). The lithified form is called "plinthite" in the U.S. Taxonomy.

Since the first description of laterite by Buchanan (1807), which was little more than a traveler's notes, there have been many attempts at an accepted definition. An idealized separation, into *(a)* "true" laterites where the added iron (or alumina) is autochthonous, that is enrichment takes place by translocations within the weathering profile, and *(b)* with allochthonous elements typical of "ferricretes". The distinction is not always readily apparent (Thomas, 1994), but in favorable situations the distinctions have long been recognized, such as on the edge of the Western Australian shield, where the "high-level" plateau surfaces are clearly autochthonous, in contrast to the valley-fills which are typical ferricretes (sometimes called "low-level laterites"). In places, the latter contain thick accumulations of pisolitic gravels. The French literature is presented in Tardy (1992) and Tardy and Roquin (1998). The term laterite is avoided in the two most extensively used modern soil classifications. Most laterites fall into the categories oxisol (U.S. Soil Taxonomy) and Ferralsol (WRB).

As explained by Finkl (2005), the Ferralsols are characterized by a colloidal fraction, which gradually dehydrates when exposed on old geomorphic surfaces. Worldwide they cover more than 900 million ha. Duricrusts of ferruginous or siliceous nature, evolve progressively on a multi-million-year time-table. The typical development is seen in northern and western Australia (see, for example, John Hays, in Jennings and Mabbutt, 1967).

In the 20th century the study of *paleosols* ("ancient soils"), particularly in Australia, but also in Africa mainly by British and French scientists, showed that enormously wide landscapes were covered by hard laterites that could eventually be dated either by igneous intrusives or by paleontologically identified stratigraphic overlaps. These laterites are not universal, as some people thought (Yaalon, 1997), but the message was slow to disseminate since the two key references were in Dutch (by Mohr 1874–1970), and in German, by P. Vageler. According to Lester King (1967), a New Zealand trained geologist who later shifted to Africa, these laterite-crusted landscapes were initiated in a succession following the retreat of the Permo-Carboniferous ice sheets that once covered Gondwanaland. With each extended paleoclimatic cycle of warm-wet weathering, there followed a relatively brief cool cycle of lowered sea level, general desiccation and "lateritization" (in places; also "bauxitization"). Thus the present-day soils and landscapes of the former Gondwanaland are very different from those of North America, Europe and Asia.

These differences became apparent to Australian soil scientists in particular when they attempted to create soil classification systems that were closely compatible with either the Russian system (Dokuchaev basis), or the American (Seventh Approximation) Taxonomy. A history of these endeavors is summarized by Fitzpatrick (in Hillel, 2005, vol. 1, p. 211). The first proposal was set forth by Prescott in 1931 with emphasis on soil genesis and by the *Handbook of Australian Soils* in 1968, which incorporated many of the American Taxonomic features. A fundamentally new scheme was presented by Isbell (1996), and summarized by Fitzpatrick (in Hillel, 2005). Fitzpatrick emphasizes the Australian continent's absence of recent glaciation. In the small-scale mapping on 1 : 1 million scale, the importance of landscape types became apparent. On detailed scales, the user-demands were given priority e.g., viticultural soil surveys, or engineering considerations in fiber-optic cable routing.

In East Africa geologists from Britain and Germany (Büdel, 1982) developed the concept of weathering by "etchplanation", the deep-seated weathering front corresponding to the depth of penetration by ground water which led to the idea of "rotted rock" (Saprolite) in situ. This is a process that had been pioneered by Merrill in the United States, notably in the Appalachian piedmont belt, although it was not on the vast scale seen in Gondwanaland. It may be noted that weathering in the Appalachian piedmont was mainly of Tertiary age and was only superficially modified by Quaternary periglacial modeling.

In the stable cratons of Gondwanaland, the depth of the weathering fronts, often exceeding 100 m, may be observed by descending mining shafts. The landscape surfaces display a progressive alternation between "stacked veneers" left by transgressive marine phases and cut into by regressive continental phases with their associated paleosols, an overall process called the "cratonic regime" by Fairbridge and Finkl (1980). The key to its understanding is the extreme slowness of development of the overall system. In his revolutionary studies of the paleosols in the SW of Western Australia, Finkl found the oldest of them contained Permian ice-age erratics and progressively younger ones were dated by paleontologically-dated overlap relationships. The mean rate of lowering of the cratons as a whole was 10 cm per million years (Finkl and Fairbridge, 1979).

The slowness of the whole cratonic process is reflected in the long-term stabilization of the continental cratons, but the preservation of the paleosols depends upon a combination of lateritization, bauxitization and silicification. Under the low solubility range of silica, typical of rainwater and the aqueous phase in common soils, a silicified paleosol becomes a quasi-permanent feature of the landscape.

In North America the effects of the Quaternary glaciation, and of periglacial modifications in the non-glaciated part of the country, together with complex tectonism, combine to expunge much of the earlier record – but not quite. The pre-Paleozoic paleosol is visible at the cratonic margin in Minnesota, for example, and across certain sectors of the Canadian Shield traces of stripped planation surfaces can be observed. Ambrose (1964) called these exhumed surfaces "paleoplains". Comparable surfaces are seen in Europe and Asia. Particularly around the margins of the Fennoscandian Shield as in central Sweden, the pre-Paleozoic paleosols are becoming widely recognized.

One could say that the ticking clock of weathering for many northern hemisphere soils began about 10 000 yr ago, but in Gondwanaland the same process began more than 200 million yr earlier. The cyclical alternations that are so strikingly displayed in the Gondwanaland countries are brought out particularly by the paleopedological indicators, which are exceptionally well preserved with ages going back in some cases 100–200 million yr (Fairbridge and Finkl, 1980). From the historical point of view, it is interesting that much of the literature is in French, the explanation perhaps lying in the fact that the former French colonies once extended over vast areas in Africa, the core regions of Gondwanaland. The transgressive phases were identified as "thalassocratic", the regressive as "epeirocratic" (Haug, 1907), respectively ocean-dominated and continent-dominated. These phases were linked to soil regimes by Erhart (1956) in his theory of "biorhexistasy", in which the biostatic soil-building phase (long, humid and stable) alternated with "rhexistatic" interruptions (short, mainly arid, and disturbed). Erhart (1971, 1973a,b) also traced the "itineraries" respectively of aluminum and silicon.

Paradoxically it is the formerly soft and often water-saturated soils, the latosols, that tend to be destroyed, while their lithified derivatives (representing only brief episodes of geologic history) remain as prominent mesa-capping geomorphological features of extensive landscapes.

Gondwanaland and continental drift

Whereas the beginnings of soil science had their foundations in the northern hemisphere, concepts of ancient paleosols developed and flourished particularly in the southern hemisphere, notably in Australia. The idea of a former "super-continent" (Laurasia) in the north, required no great stretch of the imagination once the concept of continental drift and eventually the plate tectonic paradigm was accepted in the 20th century. However, the southern "super-continent", while created as "Gondwanaland" by a Viennese professor, Edward Suess (1885), generated far more opposition in the north than it did, curiously enough, in the southern hemisphere. In academic circles it was opposed by the conservatives, but favored by the more adventurous. The clinching factor was the discovery and dating of Permian-Carboniferous glaciations in all point of Gondwanaland.

An additional factor in this acceptance came with the growing strength of a new brand of science, paleoclimatology. Soil science played a role in this new discipline, because certain soils are simply unknown in particular latitudes. The oxisols and latosols are totally unkown poleward of about 45° (except as paleosols). Lester King (l967) discovered distinctive paleosols of tropical origin associated with particular erosional surfaces throughout Gondwanaland. Systematically dated, these corresponded closely to formerly warm periods in Earth history (but only since the last glaciation there, i.e., the Permian). The progressive taphrogenetic break-up of the old continent (Fairbridge, 1982) led to the epeirogenic uplifts of the old weathering surfaces that had been identified by King.

In SW Australia today the old landscapes are covered by thick oxisols, which would have acquired immensely long exposure to climates with high precipitation, yet the present annual average is less than 500 mm (Mulcahy, 1960; also in Jennings and Mabbutt, 1967). Coastal valleys were invaded by marine rias and carbonate-rich soils reflect this distinctive history. It is a widespread feature of the low-elevation margins of the southern hemisphere lands, i.e., the former Gondwanaland heartlands.

Marginal to those old "heartlands" are youthful volcanic belts such as in the tectonically active zones of the East Indies, New Guinea and the Southwest Pacific, as well as in the Caribbean and West Indies. Pioneering work on the soils was done particularly by Dutch workers, with the Agricultural Research Center in Wageningen playing an important role. Attention was paid particularly to the soil salinity question in the newly exposed polders of the drained marine embayments, and secondarily to the former colonial lands of the East Indies. Historically, the latter were the principal source of wealth for the Netherlands, but this has changed during the last half century. The East Indies provided a unique opportunity to study the youthful soils of the volcanic cones of the Sunda Islands.

International soil map

After WWII there was a fairly widespread demand for an international soils map. Many hurdles had to be overcome. There had to be an agreed scale, an agreed legend, agreed colors, and an agreed publisher. In view of the "cold war" raging at the time, diplomacy was required. Victor Kovda of the USSR Academy of Science was an obvious leader, coming from the "old school" of academicians, chosen on the basis of long experience and appropriate qualities. UNESCO with its headquarters in Paris was well-placed. However, its ranks were heavily weighted by appointees from left-leaning governments, many of whom were classically incompetent. The United Sates finally decided to boycott the entire operation. Nevertheless, the Kremlin had its own agenda, notably its "Atlas Mira", a worldwide cartographic program that obviously carried a strong political message. Its soils maps were largely marked "SECRET" which was a hurdle partially circumvented by the simple procedure of giving them false coordinates, a "problem" easily overcome by even the most simple-minded adversary. At the same time the aviation authorities in Washington were embarked on a campaign for making aeronautical charts of the World on a 1:1 million scale. This provided an agreed scale where the lack of detail kept military matters conveniently out of sight.

The legend for the international soils map required much consultation and compromise, but with patience and diplomacy was eventually achieved by bringing in the less politicized FAO, the U.N. Food and Agriculture Organization, with its headquarters in Rome (FAO-UNESCO, 1974). The entire system is summarized by F. O. Nachtergaele (in Hillel et al., 2005, vol. l, pp. 216–222). This contains a detailed reference list for the eventual plan, which has emerged as the WRB, or "World Reference Base for Soil Resources", and created with the cooperation of the ISSS (International Society of Soil Science) and IUSS (International Union of Soil Sciences). This modified WRB developed a two-tier system: *(a)* a foundation of 30 soil reference groups that aimed at an objective to permit field recognition rather than lab analysis; and *(b)* a second tier of 121 qualifiers (FAO, 2001). The most recent update introduces two new reference groups (Stagnosols and Technosols), a revised qualifier system, many new qualifiers, and improved definitions. It, and the history of soil science, continues to evolve.

Rhodes W. Fairbridge

Bibliography

Ambrose, J.W., 1964. Exhumed paleoplains of the Precambrian shield of North America. *Am. J. Sci.*, **262**: 817–857.

Bennett, H.H., 1939. *Soil Conservation.* New York: McGraw-Hill, 993 pp.

Birkeland, P., 1974. *Pedology, Weathering and Geomorphological Research.* New York: Oxford University Press, 285 pp.

Boulaine, J., 1989. *Histoire des Pédologues et de la Science des sols.* Paris: Masson, 286 pp.

Buchanan, F., 1807. *A Journey from Madras Through The Countries of Mysore, Kanara and Malahar.* London: East India Co., Vol. 2, 436–461; vol. 3, 66, 89, 251, 258, 378.

Büdel, J., 1982. *Climate Geomorphology.* (translated from the German of 1977). Princeton, NJ: Princeton University Press, 443 pp.

Erhart, H., 1956. *La Genèse des Sols.* Paris: Masson. 90 pp.

Erhart, H., 1973a. Itinéraires géochimiques et cycle géologique de l'aluminium; genèse des minerais d'alumine, latéritisation, bauxitisation, aluminification. Paris: Doin, 253 pp.

Erhart, H., 1973b. *Itinéraires géochimiques et cycle géologique du silicium: katamorphisme des silicates primaires, genèse et évolution de la silice de néoformation.* Paris: Doin, 217 pp.

Fairbridge, R.W., 1982. The fracturing of Gondwanaland. In Scrutten, R.A., and Talwani, M., eds., *The Ocean Floor.* New York: Wiley, pp. 229–235.

Fairbridge, R.W., and Finkl, C.W., Jr., eds., 1979. *The Encyclopedia of Soil Science, Part 1.* Stroudsburg, PA: Dowden, Hutchinson & Ross, 646 pp.

Fairbridge, R.W., and Finkl, C.W., Jr., 1980. Cratonic erosional unconformities and peneplains. *J. Geol.*, **88**: 69–86.

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FAO, 2006. World Reference Base for Soil Resources. World Soil Resources Report 103. Rome: Food and Agriculture Organization of the United Nations, 132 pp.

FAO-UNESCO, 1971. *Soil Map of the World*, Vol. I, Legend. Paris, France: UNESCO, 59 pp.

Finkl, C.W., 2005. Coastal soils. In Schwartz, M.L., ed., *Encyclopedia of Coastal Science.* Dordrecht: Springer-Verlag, pp. 278–302.

Finkl, C.W., and Fairbridge, R.W., 1979. Paleogeographic evolution of a rifted cratonic margin: S.W. Australia. *Palaeogeogr., Palaeoclim., Palaeoecol.*, **26**: 221–252 (with discussion by van de Graaff, 1981, ibid., **34**: 163–172).

Glinka, K.D., 1914. *Die Typen der Bodenbildun*, ihre Klassifikation und Geographische Verbreitung. ihre Classificatiob. Berlin: Borntraeger. 365 pp.

Good, G.A., ed., 1998. *Sciences of the Earth* (2 vols.). New York: Garland, 901 pp.

Haug, E., 1907. *Traite de Geologie.* Paris: A. Colin, 1538 pp.

Hillel, D., 1991. *Out of the Earth: Civilization and the Life of the Soil.* New York/Toronto, Canada: Free Press/Collier Macmillan, 321 pp.

Hillel, D., (ed. in chief), 2005. *Encyclopedia of Soils in the Environment*, 4 Vols. Amsterdam: Elsevier.

Isbell, R.F., 1996. *The Australian Soil Classification.* Collingwood, Victoria: CSIRO, 143 pp.

Jennings, J.N., and Mabbutt, J.A., eds., 1967. *Landform Studies from Australia and New Guinea.* Cambridge, MA: Cambridge University Press, 434 pp.

Jenny, H., 1941. *Factors of Soil Formation.* New York: McGraw-Hill, 281 pp.

Jenny, H., 1961. *E. W Hilgard and the Birth of Modern Soil Science.* Pisa: Agrochimica, 145 pp.

King, L.C., 1967. *The Morphology of the Earth: A Study and Synthesis of World Scenery*, 2nd edn. Edinburgh: Oliver & Boyd, 699 pp.

Krupenikov, I.A., 1981. *History of Soil Science* (In Russian). Nauka: Moscow, 327 pp.

Kukla, G.J., An, Z.S., Melice, J.L., Gavin, J., and Xiao, J.L., 1990. Magnetic susceptibility record of Chinese loess. *Trans. R. Soc. Edinburgh, Earth Sci.*, **81**: 263–288.

McDonald, P., ed., 1994. *The Literature of Soil Science.* Ithaca, NY: Cornell University Press, 448 pp.

Mulcahy, M.J., 1960. Laterites and lateritic soils in southwestern Australia. *J. Soil Sci.*, **11**: 206–226.

Oliver, J.E., ed., 2005. *Encyclopedia of World Climatology.* Dordrecht, The Netherlands: Springer-Verlag, 854 pp.

Powell, J.M., 1988. *An Historical Geography of Modern Australia: the Restive Fringe.* Cambridge, MA: Cambridge University Press, 400 pp.

Rossiter, M.W., 1975. *The Emergence of Agricultural Science: Justus Liebig and the Americans, 1840–1880.* New Haven: Yale University Press, 275 pp.

Ruhe, R.V., 1965. Quaternary paleopedology. In Wright, H.E., and Frey, D.G., eds., *The Quaternary of the United States.* Princeton, NJ: Princeton University Press, pp. 755–764.

Simonson, R.W., 1968. Concept of soil. *Adv. Agron.*, **21**: 1–47.

Simonson, R.W., 1989. *Historical Highlights of Soil Surveys and Soil Classification with Emphasis on the United States (1899–1970).* Wageningen, The Netherlands: International Soil Reference and Information Centre, 83 pp.

Soil Survey Staff, 1960. *Soil Classification: A comprehensive system (7th Approximation).* Washington, DC: U.S. Dept. of Agriculture, Natural Resources Conservation Service, 265 pp.

Soil Survey Staff, 1996. *Keys to Soil Taxonomy*, 7th edn. Washington, DC: U.S. Dept. of Agriculture, Natural Resources Conservation Service, 644 pp.

Struever, S., ed., 1971. *Prehistoric Agriculture.* New York: Natural History Press, 733 pp.

Tardy, Y., 1992. Diversity and terminology of lateritic profiles. In Martini, I.P., and Chesworth, W., eds., *Weathering, Soils and Paleosols.* New York: Elsevier, pp. 379-405.

Tardy, Y., and Roquin, C., 1998. *Derive des Continents: Paleoclimats er Alterations Tropicales.* Paris: Editions BRGM, 473 pp.

Thomas, M.F., 1994. *Geomorphology in the Tropics.* Chichester: Wiley, 460 pp.

Vita-Finzi, C., 1969. *The Mediterranean Valleys: Geological Changes in Historical Times.* London: Cambridge University Press, 140 pp.

Warkentin, B., 2006. *Footprints in the Soil: People and Ideas in Soil History.* Amsterdam: Elsevier, 572 pp.

Yaalon, D.H., ed., 1971. *Paleopedology: Origin, Nature, and Dating of Paleosols; papers.* Jerusalem: International Society of Soil Science, 350 pp.

Yaalon, D.H., and Berkowitz, eds., 1997. *History of Soil Science: International Perspectives.* Reiskirchen, Germany: Catena Verlag, 438 pp.

Cross-references

Biogeochemical Cycles
Conservation
Health Problems in Soil
Neolithic Revolution

HISTOSOLS

Synopsis

Etymology. Peat and muck soils; from Gr. *histos*, tissue.

Parent material. Incompletely decomposed plant remains, with or without admixtures of sand, silt or clay.

Environment. Histosols occur extensively in boreal, arctic and subarctic regions. Elsewhere, they are confined to poorly drained basins, depressions, swamps and marshlands with shallow groundwater, and highland areas with a high precipitation/evapotranspiraction ratio (WRB, 1998).

Profile development. Transformation of plant remains through biochemical disintegration and formation of humic substances creates a surface layer of mold. Translocated organic material may accumulate in deeper tiers but is more often leached from the soil (WRB, 1998).

Use. Sustainable use of peatlands is limited to extensive forms of forestry or grazing. If carefully managed, Histosols can be very productive under capital-intensive forms of arable cropping/horticulture, at the cost of sharply increased mineralization losses. Deep peat formations and peat in northern regions are best left untouched. In places, peat bogs are mined, e.g., for production of growth substrate for horticulture, or to fuel power stations.

Details

The term Histosol was first used in 1960 in the U.S. System of Soil Classification to refer to peaty soils. More recently the World Reference Base for Soils (WRB, 1998; FAO, 2001) considers Histosols as soils having a histic or folic superficial horizon (see also Zech and Hintermaier-Erhard, 2007). The thickness of these horizons has to be greater than 10 cm if the soil overlies a lithic or paralithic contact, and it has to be greater than 40 cm if covering a mineral soil. Histosols cannot have an andic or vitric horizon in the upper 30 cm.

In the recently published update of the WRB (2006) the definition of Histosols is not based on the diagnostic horizons (histic, folic) but on the presence of organic material. The later is defined as a material containing large amounts of organic debris that accumulate at the surface of the soil and in which the mineral component does not significantly influence soil properties. The diagnostic criteria are:

1. contains a 20% or more organic carbon in the fine earth (by mass); or
2. if saturated with water for 30 consecutive days or more in most years (unless drained), one or both of the following
   a. (12 + [clay percentage in the mineral fraction x 0.1]) percent or more organic carbon in the fine earth (by mass), or
   b. 18% or more organic carbon in the fine earth (by mass).

Histic and folic horizons are now defined as a surface, or subsurface horizon occurring at shallow depth, consisting in poorly-aerated (i.e saturated with water for 30 consecutive days or more in most years) or well-aerated (i.e not saturated with water for more than 30 consecutive days) organic material, respectively.

Those countries with a significant cover of peaty soils have developed their own classifications and different criteria for the histic and folic horizons. In the United Kingdom, Ireland, Norway and Germany the thickness of the organic material has to be greater than 30 cm to be considered a histosol; while in Holland it must be greater than 40 cm. The Soil Survey Staff (1990) and FAO (1988) established a minimum thickness of 40 cm (60 cm if the soil volume is dominated by *Sphagnum* fibers).

The different horizons composing the Histosols have specific typical or secondary properties resulting from the interaction of factors of formation. These properties allows the establishment of lower level units of classification. For instance, typically associated porperties as the type of peat material are used to indentify folic, limnic and lignic types (those having a folic or limnic horizon, or having intact wood fragments representing more than a quarter of the volume of the horizon); the degree of peat decomposition defines fibric, hemic and sapric types (having more than 2/3 of the volume of recognizable plant tissues, between 2/3 and 1/6, or less than 1/6 respectively); the water regime defines the ombric (fed by rainwater), rheic (saturrated with ground water or superficial waters), floatic (floating on water, as quaking bogs) and subaquatic (permantly submerged under water at a depth less than 200 cm) types; the presence of ice defines the cryic (having a cryic horizon) and glacic (with a layer of ice more than 30 cm thick in the upper meter of the soil) types; the kind of inorganic material defines the vitric (vitric properties in at least 30 cm of the upper meter), andic (at least 30 cm cumualtive of one or more layers with andic properties), salic (having a salic horizon in the upper meter) and calcic (having a calci horizon or secondary carbonates in the upper meter) types; and the presence of continuous hard rock at shallow depth (within the upper meter) or more having artefacts that represent more than 10% of the volume enable the definition of leptic and technic Histosols.

The diversity of other secondary biogeochemical and physical aspects lead to a further description of the units. The thionic Histosols have a thionic horizon or sulfidic material; the ornithic have ornithogenic material; the calcaric have calcaric material; the alcalic have a high pH; the toxic contain organic or inorganic substance in toxic concentrations; the dystric and eutric differ on the degree of base saturation. Low soil temperatures and cryoturbation features are present in gelic and turbic Histosols, respectively. An oximorphic pattern and an iron pan define the petrogleyic and placic Histosols. While features related to human perturbations as artificial drainage, moved material or a layer of recent sediments (5 to 50 cm thick) indentify the drainic, transportic and novic Histosols.

The units described above correspond to those defined in the World Reference Base (WRB, 2006) under the Histosol group. However, there are other classification systems where organic rich soils are treated differently. Within Soil Taxonomy histosols are classified at the order level and as suborders they include folist, fibrists, saprists and hemists. In the Canadian System of Soil Classification organic-rich soils are included in the Organic order, which has four great groups: fibrisol, mesisol, humisol and folisol.

The main properties of the Histosols are related to the organic component, since the inorganic component is mainly accessory. Some of the most important properties of the organic components are the cation exchange capacity and the pH. Histosols exhibit a wide range of pH values from 7.8 (alkaline peat) to values lower than 2 (frequent in drained peats containing metal sulfides). Other important properties are the low bulk and particle densities and the high porosity, which influence the rate of compaction and subsidence of the soil surface.

It has been estimated that Histosols cover some 275 million ha (Table H2, Figures H1 and H2). Half is found in the boreal and subarctic zones of the Northern Hemisphere, and is particularly abundant in Central and Northern Canada, Alaska, Northern

Table H2 Areal distribution of Histosols (in 1000s of hectares)

	Africa	Australasia	Europe	North America	North and C. Asia	South and C. America	South and SE Asia	Total
Histosols	12270	1167	32824	93462	99451	9245	24829	273248

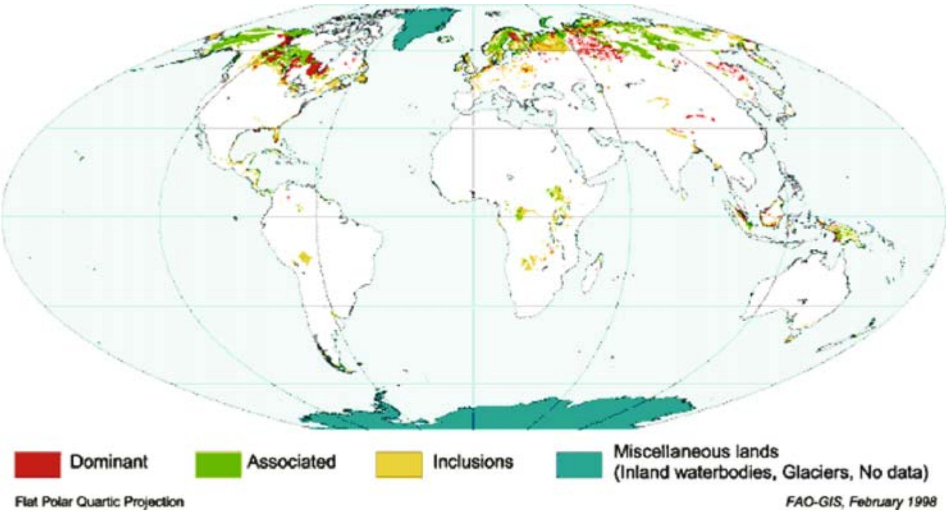


Figure H1 Global distribution of Histosols.

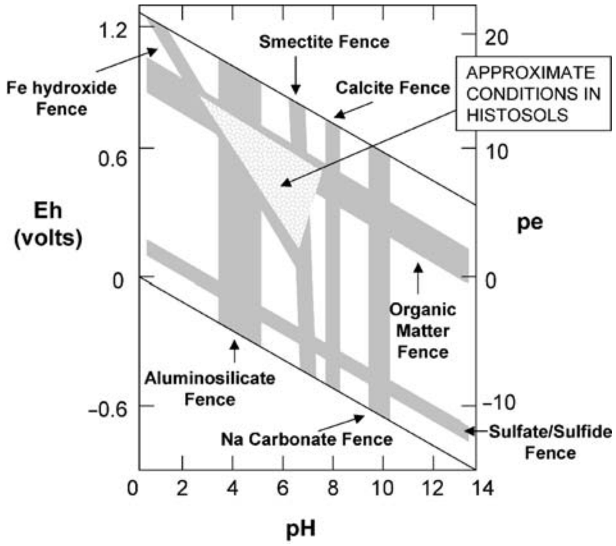


Figure H2 Redox–pH conditions in Histosols are approximately represented by the triangular area, and are principally determined by reactions along the organic matter fence of the pedogenic grid. The lowest pH occurs in the presence of oxidizing sulfides and the highest where calcite is present. The most reduced conditions (lowest pe) are found when the Histosols are water-saturated.

Finland and Siberia. A third of the total area is distributed in the middle latitudes, and is mainly associated with mild, rainy oceanic climates, though there are also inland occurrences especially in mountainous regions. In the former case they can be found from the sea level up to an altitude of a few hundred meters (Ireland, United Kingdom, Western Europe, New Zealand). In mountainous regions inland, they appear at elevations between 1 000 and 4 000 m a.s.l. Finally a small proportion – close to a sixth of the total surface area – is located in the tropics, principally associated with mangroves (particularly in Southeast Asia) on the one hand, and on the other, in mountainous areas of Africa and South America.

In the diverse environments in which they occur, Histosols are associated with a variety of other soils. In sub-Arctic areas they are found with poorly drained soils, having gleic or stagnic properties, Gleysols in particular. In boreal areas, under less cold conditions, they may appear with Podzols. In temperate regions they occur with Fluvisols, Gleysols and Vertisols, and in coastal areas they are associated with mangroves. They may also occur with Solonchaks, and less frequently with Andosols, Cambisols and Regosols.

Histosols are thus present in a wide range of environments and include a great variety of soils. This diversity ranges from mineral soils very rich in organic matter (muck) to soils composed almost exclusively by peat formed of mosses (boreal areas); heathers, sedges and grasses (temperate areas); and from the typical vegetation of mangroves and swamps (tropical areas).

J. C. Nóvoa Muñoz, X. Pontevedra Pombal,
and A. Martínez Cortizas

Bibliography

FAO, 1988. Soil Map of the World – Revised legend. World Soil Resources Report 60, Rome, Italy, 119 pp.

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

IUSS, ISRIC, FAO, 2006. Word reference base for soil resources and communication. World Soil Resources Reports 103, International Union of Soil Sciences, ISRIC World Soil Information, FAO, Rome, 128 pp.

Soil Survey Staff, 1998. *Keys to Soil Taxonomy*, 4th edn. SMSS Technical Monograph No. 6. Blacksbury, VA, 422 pp.

World Reference Base for Soil Resources (WRB), 1998. FAO World Soil Resources Report 84, Rome, Italy, 90 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag. 130 pp.

Cross-references

Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils
Hydric Soils
Mire
Peat
Redox Reactions and Diagrams in Soil

HOODOO

A pinnacle or slender column of easily eroded, poorly or unconsolidated sediment, characteristic of semi-arid badlands, and often with a cap of less easily eroded material at the top.

HORIZON

A layer in soil that is roughly parallel to the ground surface and which is distinguished from layers above or below it on the basis of physical, chemical or biological differences e.g., texture, mineralogy, or humus-content. The simplest complete soil body would have an A Horizon at the surface A simple soil profile would have an **A horizon**, typically the horizon of eluviation, at the surface; a **B horizon**, typically the horizon of illuviation, immediately below the A; and a **C horizon**, also referred to as the soil parent material, under the B. Each horizon may itself be divided into constituent horizons, the details of which will be found in the Articles Classification of Soils. In the two principal soil classifications the WRB and Soil Taxonomy, certain horizons are designated diagnostic horizons, and are used directly to classify the soil in which they occur, e.g., vertic horizon.

Cross-references

Anthropogenic
Classification of Soils: Soil Taxonomy
Horizon Designations in the WRB
Profile

HORIZON DESIGNATIONS IN THE WRB

See *Soil Horizon Designations in the WRB Soil Classification System*.

HUMIC SUBSTANCES

Apart from the basic interest of quantifying the accumulation of stabilized organic matter in the different soil types, the biogeochemical modeling of the carbon cycle requires realistic data on the nature, formation mechanisms and resilience of the sequestered forms of carbon. This involves molecular characterization of the soil organic matter to assess its quality, which is connected to its environmental properties.

Humus chemistry

Soil organic matter constituents: biomacromolecules and humic substances

A proportion of soil organic matter shows a definite chemical composition with structural features that are shared with the macromolecular constituents of the biomass e.g., celluloses, hemicelluloses, lignins, cutins, suberins, and proteins, etc., from plant and microbial origins. These biological constituents more or less readily break down in soils, mostly into CO_2 and H_2O (mineralization process). Nevertheless, even in biologically active environments, a significant amount of soil organic matter may behave in a recalcitrant fashion for a long time (centennial timescale) as a result of chemical modifications and interactions with other soil constituents. In addition, soils also contain heterogeneous, physicochemically active, biodegradation-resistant macromolecular materials generically referred to as **humic substances**. This material represents the largest pool of organic carbon on the Earth's surface and is characteristically composed of a polydisperse mixture of macromolecules with chaotic structure, in which it is not possible to establish stoichiometric structural models.

Humic substances can be operationally classified into three separate fractions defined in terms of their solubility properties (Duchaufour and Jacquin, 1975). These are:

1. *Humic acids*, which are extracted from soils with alkaline solutions, and turning into insoluble precipitate after acidification. Humic acid is commonly referred to with the conventional acronym HA.
2. *Fulvic acids*, which are yellowish in color and soluble both in acid and alkaline solutions.
3. *Humins*, which are insoluble in acid and alkaline solutions. They are largely heterogeneous, strongly associated with the mineral fraction, or composed of particulate, transformed remains or stable microaggregates (Almendros and González-Vila, 1987).

Laboratory attempts to divide the above fractions into subfractions with defined, repeating structures (for instance based on molecular weight, polarity etc.), have been largely unsuccessful, since humic substances conform to a continuum where it is admitted that there are no two macromolecules exactly alike. In consequence, most experimental approaches for their structural characterization are based on studying them as a whole.

Traditionally, there is a dual interest in the study of humic substances: they are a source of environmental information but they also behave as active soil constituents with regard to soil physico-chemical activity. Progress in these research lines requires further development of analytical techniques for molecular characterization of macromolecular systems (Kögel-Knabner, 2000).

Limitations of the molecular characterization of humic substances

Both fulvic acids and humins are difficult to isolate or purify in the laboratory. In consequence, most of the studies on soil organic matter have traditionally focused on the HA fraction.

Humic acids have extremely complex origins and macromolecular structures (Figure H3) that depend on starting materials and environmental conditions (Hayes et al., 1989; Schnitzer and Khan, 1972; Stevenson, 1982). In brief, they include aromatic and aliphatic (*O*-alkyl and alkyl) domains and oxygen-containing functional groups in surfaces with different reactivities (Wershaw et al., 1977).

Due to their lack of defined chemical structure, their compositional differences between soils are based on broad-sense analytical descriptors, for instance *(i)* the extent of the different structural domains, *(ii)* the presence of discrete structural regions with selectively preserved macromolecular entities having certain resemblance with microbial or plant biomacromolecules, or *(iii)* the occurrence of diagnostic biomarker compounds with a chemotaxonomic value. Owing to our current limitations in the structural analysis of HAs, most successful methodologies take advantage of two complementary approaches. The first one consists of chemical or thermal degradation followed by identification of the fragments by techniques such as gas chromatography/mass spectrometry. Examples of typical fragments released from HAs by these techniques are alkanes, fatty acids, α,ω-alkanoic diacids, OH-fatty acids, phenolic acids, benzenecarboxylic acids, furan compounds and some N-and S-containing molecules. Nevertheless, these techniques often lead to selective loss of specific, labile "building blocks" as well as to non-stoichiometric yields of the different constituents. On the other hand, mild degradative techniques leave large amount of non-degraded residue

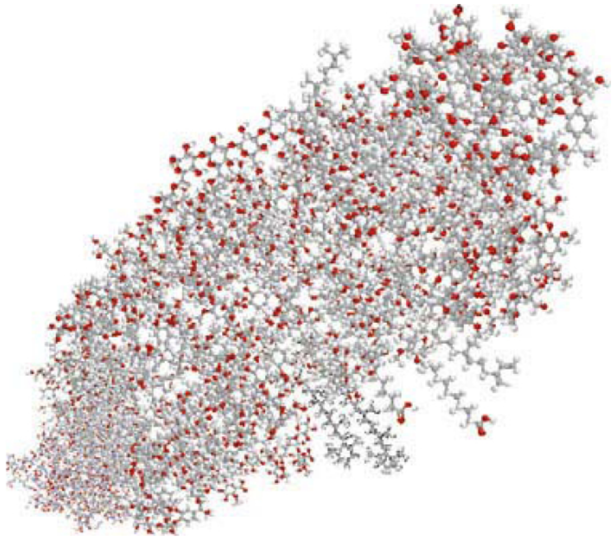


Figure H3 Hypothetical structure of a portion of a humic acid macromolecule. The structure was build up with a molecular modeling software and partial minimum-energy three-dimensional arrangement for discrete sub-structures, which include lignin-like backbone (mainly central part of the model), some polysaccharide-like components, protein residues and alkyl molecules visible in peripheral location.

but are often suitable for picking up signature compounds providing valid clues on the HA precursors or their degree of alteration (Almendros and González-Vila, 1987; Schnitzer and Khan, 1972).

The second approach is based on non-destructive methods mainly spectroscopy in the visible, infrared and nuclear magnetic resonance ranges (Figures H4 and H5). These techniques provide information about the relative amounts of the major structural units (alkyl, *O*-alkyl, aromatic and so on) in some cases enabling a rough quantitation of some functional groups (González-Vila et al., 1983; Preston, 1996; Wilson, 1981).

There is no current consensus on the three-dimensional structure of the HAs. It is assumed that consists of a flexible network formed by a hierarchical aggregation of micelles in some cases including fairly defined domains resembling known macromolecules in living organisms. In terms of the hydration state, soil HAs can display microporous structure enabling diffusion of low molecular weight compounds. Humic acids are amphyphilic, with hydrophobic and hydrophilic, internal and external, reactive surfaces. Classical wet chemical methods based on titration of functional groups only qualitatively agrees with the results of spectroscopic techniques indicating the dominance of carboxyl, phenolic hydroxyl, alcoholic and quinoid groups (Schnitzer and Gupta, 1965; Schnitzer and Khan, 1972).

In general, it could be assumed that the total amount and spatial arrangement of the functional groups has a direct and indirect bearing on the environmental properties of the HAs. Whereas the external exposure of reactive surfaces with a portion of their functional groups confer to the HA its colloidal properties, other groups would contribute to the secondary and tertiary structure

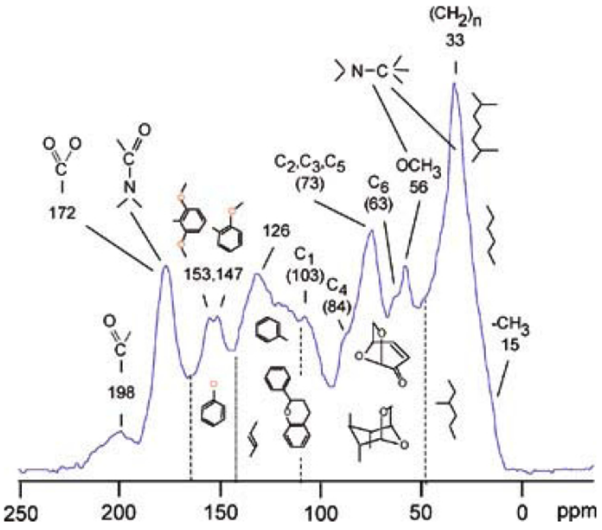


Figure H4 Solid-state nuclear magnetic resonance spectrum of a humic acid from soil (Orthieutric Cambisol) developed on Mediterranean pine forest. Spectral ranges and main peaks: 0–46 ppm = alkyl + α-amino (13 = methyl, 21 = acetate, 33 = polymethylene); 46–110 ppm = *O*-alkyl (56 = methoxyl, α-amino; numbers in brackets refer to C-types in glucopyranosyde-derived structures; 103–105 = anomeric C in carbohydrate, quaternary aromatic carbons in tannins); 110–160 ppm = aromatic/unsaturated (126 = unsubstituted, 147–153 = heterosubstituted, vanillyl + syringil lignin units); 160–200 ppm = carbonyl (172 = carboxyl + amide, 198 = ketone/aldehyde).

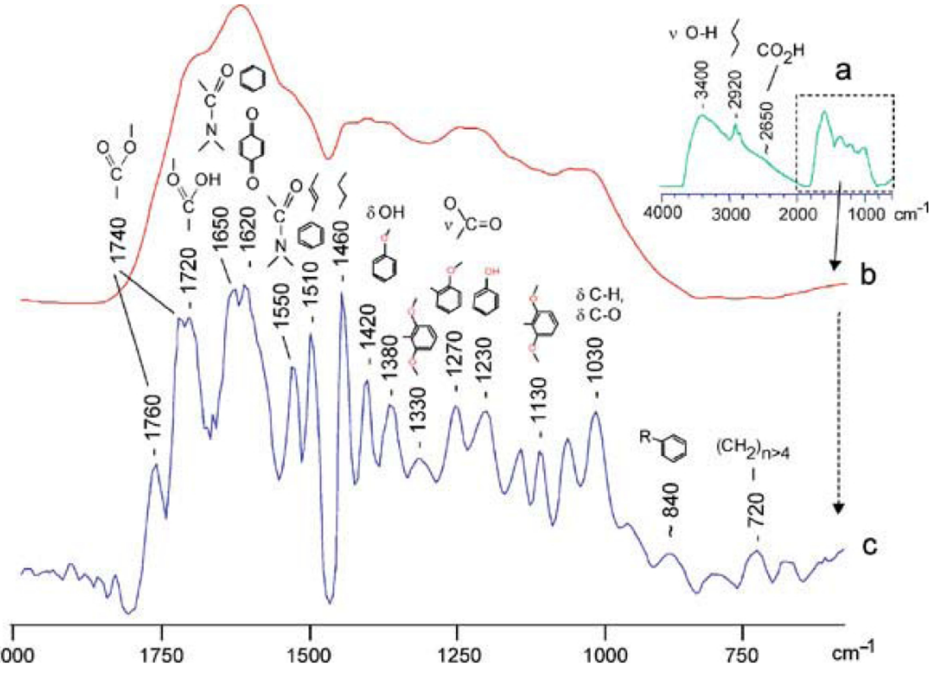


Figure H5 Infrared spectrum of a humic acid from soil (Orthieutric Cambisol) developed on Mediterranean secondary bush, (a) whole spectrum showing bands for O–H and alkyl C–H stretching, (b) detail of the diagnostic region of the spectrum and (c) resolution-enhanced spectrum obtained by derivative algorithms (Almendros and Sanz, 1992) showing details on structural subunits and probable functional groups indicated on the peaks.

through H-bonding, hydrophobic, charge-transfer, free-radical interactions, and other processes (Almendros et al., 1998). Unfortunately, the inconspicuous results of the analyses of functional groups when quantified through wet chemical methods (which are probably not representative of the real activity displayed by the HAs in natural conditions) is one out of a series of problems derived from the chaotic structure of the HAs.

The very dark color of HAs suggests, in addition to large variety of chromophor and auxochrome groups, a high concentration of stable free radicals. The latter have been postulated to consist of semiquinone groups, the occurrence of which being supported by electron spin resonance (Lisanti et al., 1974).

As expected, the quantitation of any defined constituent or structural moiety in a continuum of units with a series of shared features is a complicated task and has caused a series of historical controversies. For instance, the relatively recent introduction of the ^{13}C nuclear magnetic resonance has led to a reappraisal of aromaticity in HAs and to a critical review of the results from drastic oxidative degradation methods (Almendros and Sanz, 1992; Hatcher et al., 1981). In fact, it is currently admitted that aliphatic structures in HAs are much more abundant than previously believed (classical structural models to a large extent based on the chemistry of lignin and coal). In any case, it is clear that no individual experimental technique gives a clear picture of the structure of the HAs, the use of several complementary methods being more reliable.

To some extent, the limitations of powerful analytical and instrumental techniques which are in fact successful for the molecular characterisation of complex biomacromolecules could be due to the fact that most of the HA structure consists of a "megamolecule", formed by a network of C–C and C–O links, with no discrete structural units but a similar stability to chemical and biological degradation of all bonds involved in the whole structure. In fact, distinguishing between the chemical variability of the HAs resulting from the monomer composition within individual macromolecules, or from the presence of different types of micelles in the polydisperse HA system, has no special meaning in the state of the art in humus chemistry.

Such a situation could be the result of progressive free-radical condensation of low MW products in soils, but it could also be postulated that solid-state abiotic reactions for instance thermal or acid-catalyzed dehydrations could exert a substantial role mainly at the advanced transformation stages – maturation – of the humic substances.

The practical value of basic and applied research on structural and functional features of the humic substances

Soil humus is traditionally described as a continuous source of slow-release nutrients and an active pool of organic colloids with a major role in regulating processes of plant nutrition, toxic ion mobility and the aggregation, structure and water holding capacity of the soil (Hargitai, 1989; Khan and Schnitzer, 1972). As a consequence of the progressive depletion in soil organic matter, most efforts are currently directed to the sustainable management of the soil humus levels through a rational disposal of external organic matter sources such as agro industrial wastes, composted urban refuse and sedimentary humic resources such as peat, lignites and their transformation products (Almendros et al., 1990b; González-Vila et al., 1999).

Humic substances are also studied to obtain environmental information. It was previously indicated that HAs have a heterogeneous structure in part derived from the microbial reworking of plant biomacromolecules, to large extent lignin. Owing to the variable composition of the HAs, and their average residence time from hundreds to thousands of years, modern biogeochemical research tends to consider the chemical structure of humic substances as a long-term biogeochemical record of the current and past environmental processes that are to some extent responsible for the structure and activity of the trophic system.

In fact, soil organic matter represents a source of analytical descriptors for the early diagnosis of soil degradation in studies focused to assess either soil resilience or the impact of external perturbation such as reforestation, cultivation, bush encroachment, or wildfires (Almendros et al., 1990a; Duchaufour and Jacquin, 1975; Oyonarte et al., 1994; Schnitzer and Khan, 1972).

Soil Dependant Factors in Organic Matter Stabilization

Both the *chemical composition* and the *interactions of organic matter* (humic and non-humic) with other organic and inorganic soil constituents (Greenland, 1971) are involved in the accumulation of stable C forms in soil (Figure H6). Among these (climate-independent) factors that bear on the retention of C forms in soils the following are emphasized.

Intrinsic factors

This group would include those factors related to the occurrence of specific components in soil organic matter and the different organizational levels of the macromolecules. No unique major limiting factor is responsible for the high resistance to biodegradation of the HAs. Classical structural descriptors such as aromaticity, polydispersity or the content of oxygen-containing functional groups contribute only to a partial extent. The resistance to biodegradation seems to depend on complex interactions between structural factors so that the disordered cross-linked HA macromolecular structure probably has a major influence in restricting the performance of soil enzymes.

The resistance of individual structural units

To some extent it could be considered that the stability of the organic matter against degradation (thermal, chemical, biological) is connected to the relative amounts of its different structural units (aromatic, alkyl, N- and O-containing). Aromatic units have traditionally been considered recalcitrant to degradation when compared to aliphatic (*O*-alkyl and alkyl) structures. Of the latter, *O*-alkyl (mainly carbohydrate-derived) is also known to be the moiety preferentially used by soil microorganisms. Apart from semiquantitative spectroscopic techniques, the most successful approaches to recognize compositional differences between soil organic matter fractions have been based on mild degradation techniques (yielding a variable amount of non-degraded residue), or multi-stage degradations causing progressive removal of different macromolecular constituents (Almendros and González-Vila, 1987).

Intramolecular bridging factors

The chemical stability of the soil organic matter against degradation is closely related to its degree of structural condensation (for instance, on the number and strength of intramacromolecular

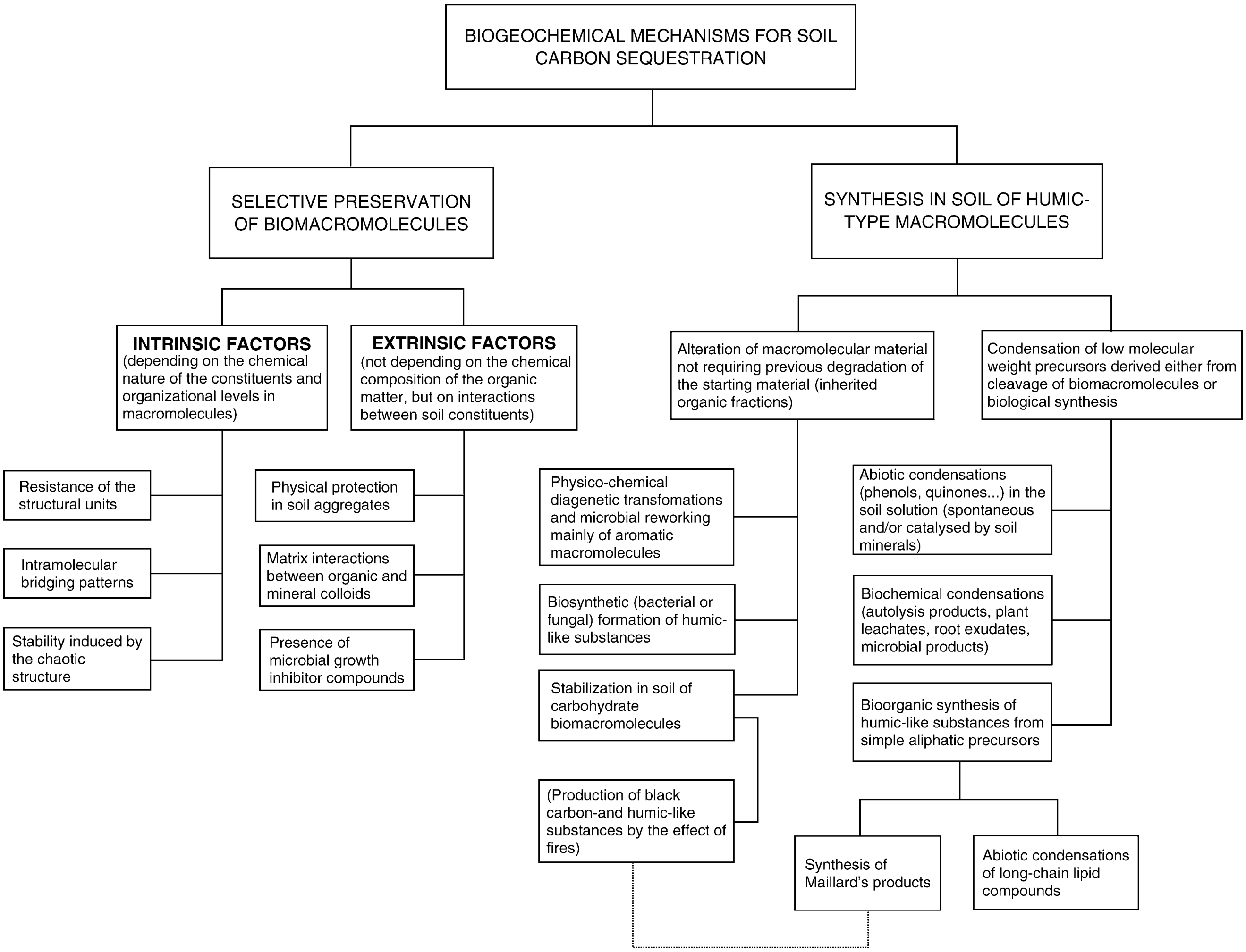


Figure H6 Hypothetical soil-dependent processes responsible for the formation of humic substances and soil C sequestration.

bridges, which also depend on the proportions of polyfunctional "building blocks"). This could be illustrated by the different resistance to enzymatic attack shown by the syringyl- and guaiacyl-type plant lignins, the former with a higher number of methoxyl groups on their phenolic units, which confer to the whole structure lower connectivity possibilities between its structural units (Martínez et al., 1990).

Stability induced by the chaotic structure

The high heterogeneity of the HA structure probably plays a major role in resistance to biodegradation. In fact, during humification, there is a noticeable increase in the complexity of soil macromolecules (fractal chaotic structure of humic colloids), progressively becoming scarcely recognizable by microbial enzymes (Almendros and Dorado, 1999). This complexity may increase with successive environmental perturbations, while at the same time, incorporating additional information on the "long term record" in the humic structure. In any case, this leads to materials that are not advantageous sources of carbon or energy for the microbial species.

Extrinsic factors

This review is centered on soil-dependent processes so that the well-known effects of climatic and local factors (temperature, waterlogging, topography, and so on) are addressed elsewhere in this volume. However, there is a series of factors controlling C-sequestration in which the chemical composition of the sequestered matter is not involved.

Physical protection

Mainly in the case of organic matter recently incorporated in soil, there are a number of stabilization factors depending on soil microcompartmentalization patterns. Soil horizons are composed of aggregates of different sizes, which provide a large number of microenvironments where chemical and biological reactions occur at different rates depending on water availability, diffusion processes and the accessibility of microbial enzymes, among other factors. In general, physical protection of otherwise biodegradable organic matter takes the form of the so-called *selective preservation processes* (Eglinton and Logan, 1991). This preservation can be associated with encapsulation of organic matter by colloidal minerals representing an efficient barrier to enzyme diffusion in microaggregates (Skjemstadt et al., 1996). In most cases the organic matter protected by fine clay consists of recalcitrant alkyl C forms, which tend to accumulate preferentially with decreasing soil particle size (Schulten and Schnitzer, 1990). Other factors such as the *influence of carbonates* in stabilizing both particulate and soluble organic matter forms are also important in calcic soils (Oyonarte et al., 1994). Also the indirect *contribution of soil lipids* should not be ruled out in the stabilization of waterproof soil aggregates (Oades et al., 1987; Spaccini et al., 2000), in providing the efficient encapsulation of organic matter.

Matrix interactions between organic and mineral surfaces

Effective physico-chemical interactions between reactive surfaces of organic and mineral colloids may increase overall resistance of the organic matter to chemical and biological degradation. One of such processes is the well-known effect of allophanic materials on organic matter stabilization in soils developed on specific volcanic ashes (Calvo de Anta and Díaz-Fierros, 1982). Nevertheless, practically all soils contain substantial amount of humic substances tightly bonded – insolubilized – in the mineral matrix (mainly associated to clays and sesquioxides). This fraction is commonly referred to as *extractable humin* (Merlet, 1971).

Microbial growth inhibitor compounds

The antimicrobial compounds and enzyme inhibitors (terpenes, phenols, fungal antibiotics for example) released to soil by plants or microorganisms may effectively decrease C recycling rates (Lynch, 1976). For instance, the accumulation of thick humiferous horizons in most pine forests or ericaceous brushwood under temperate climates is often attributed to the role of specific phenolic and diterpene compounds released by vegetation. Not only gymnosperms but also several Mediterranean sclerophyl bush species contain essential oils with an originally allelophatic function in the living plant, which continue to be active in the soil. This enhances the nonselective preservation of plant macromolecular constituents (Davies, 1971).

Formation of humic substances

Assuming that humic substances are the most resistant organic fractions of the soil, the humification process should be considered to be of capital importance with regard to the understanding of soil quality and the mechanisms of C sequestration.

Owing to the fact that the overall formation of humic substances requires hundreds of years and the contribution of a large variety of agents and starting materials, it is to be expected, perhaps, that information on the subject is only of a general nature, with several controversial points still requiring clarification. While classical concepts have postulated lignin and aromatic microbial metabolites as major starting materials, recent evidence indicates the importance of alternative humification mechanisms that are exclusively based on aliphatic precursors such as **carbohydrates** (either by catalytic dehydration reactions in soil reducing microcompartments or by the effect of fires, for example) and **lipids** (alteration of aliphatic biomacromolecules that include non-hydrolyzable esters or condensation of unsaturated fatty acids).

Consequently, among the processes contributing to the retention of organic matter in soil, special emphasis will now be paid to the mechanisms of humification *sensu stricto*, i.e., a series of not-exclusive, convergent, inter-related processes.

Stabilization mechanisms through alteration of preexisting macromolecular material not requiring complete previous degradation of the starting organic matter

Progressive structural alteration of biomacromolecules and formation of inherited organic fractions

The accumulation in soil of altered particulate fractions such as *inherited humins* is considered an effect of diagenetic transformation of resistant plant constituents. These alterations prevail on humus types with low and medium biological activity, and occur mainly from the original presence of recalcitrant plant and microbial biomacromolecules (Almendros et al., 1996; Duchaufour and Jacquin, 1975).

The structural reorganization of macromolecules that is induced by microorganisms (*microbial reworking*) is an important source of organic matter with a higher stability that precursor materials to biodegradation (Tegelaar et al., 1989). In the case of lignins, this process causes an increase in molecular complexity, which is accompanied by the incorporation of N-containing products and alkyl structures mostly derived from the microbial biomass (Goulden and Jenkinson, 1959). Similar processes occur during the microbial alteration of a series of imperfectly known aliphatic biomacromolecules (Goñi and Hedges, 1990). These include different types of biopolyesters i.e., – cutins and suberins (Holloway, 1972; Kolattukudy, 1977) and the so-called cutans, suberans, botryococcanes, and recalcitrant biomacromolecules from vascular plants or microorganisms with structures yet to be determined (Nip et al., 1986) – probably “hybrid” substances with lipid and carbohydrate domains. The occurrence of *non-hydrolyzable amides and esters* is a characteristic feature of these substances (Derenne et al., 1991; Largeau et al., 1985) possibly due to the occurrence of steric impediments in organic matrices, molecular encapsulation, solid solution mechanisms, among others.

The importance of these aliphatic precursors of humic substances is currently considered to be highly significant even in the case of terrestrial soils (Almendros and Sanz, 1992; Hatcher et al., 1981). This contrasts with classical studies, which emphasized the importance of aliphatic compounds only in hydromorphic soils and aquatic humus, environments more favorable for their selective preservation (Huc et al., 1974). In this context, the literature commonly alludes to the fact that the resistance of lignin to microbial attack has been overemphasized in classical studies (mainly based in the pioneer studies by Waksman (1936) on peat soils), whereas further research provides evidence that enzymatic degradation of lignin may occur at a similar rate than that of other plant constituents (Stevenson, 1982). Moreover, recent studies (Almendros et al., 2000) point out that humification should not be necessarily regarded as a preferential concentration of any specific constituent of plant biomass.

Accumulation and alteration of biosynthetically-formed compounds analogous to humic substances

Microbial synthesis is known to be highly effective in the accumulation of biodegradation-resistant, black-colored substances in soil (Martin and Haider, 1971). The quantitative importance of the so-called *fungal melanins* (Bell and Wheeler, 1986) has been shown in most soil types (Almendros and Dorado, 1985; Haider and Martin, 1967). In living fungi, melanins confer some adaptive advantages e.g., protection against solar irradiation, desiccation, and enzymatic attack. When fungi die, their melanins accumulate in soil. In some cases, fungal melanins are products of well-defined biosynthetic paths such as those based on the condensation of binaphthyl compounds. In these pigmented fungi (e.g., *Cenococcum*, *Alternaria*, *Aureobasidion*, *Ulocladium*) a typical pigment (green-colored in alkaline solution) is also produced (Almendros et al., 1985; Kumada and Hurst, 1967). The corresponding melanins can be readily recognized by chromatographic separation or by derivative spectroscopy since the presence of 4,9-dihydroxyperylene-3,10-quinone units is indicated by well-defined peaks (455, 530, 570, 620 nm) (Kumada and Sato, 1967). Anthraquinones (red to orange) are other fungal pigments that can be identified after wet chemical isolations.

It is not only fungal-derived fractions that behave as surrogate indicators of the extent to which some fungal species contribute to the accumulation of soil humic substances, but these quinoid melanins also exert some active role on soil properties. The tendency to form extremely stable organo-mineral complexes, and the resistance to biodegradation, are much more marked in these fungal-derived metabolites than in humic substances formed by alternative processes (Almendros and Dorado, 1985).

Humus neoformation through condensation of low molecular weight precursors derived either from cleavage of biomacromolecules or biological synthesis

Intra- or extracellular biochemical processes not related to primary metabolism

A large variety of reactive compounds from plants and microorganisms is released to the soil solution. There they coexist for a short time, until they are removed through biodegradation or condensation into macromolecular structures (Carballas et al., 1971). These reactions may occur, for example, by enzymatic condensation of compounds generated during the biodegradation of lignin and other biomacromolecules (Suflita and Bollag, 1981). The e*nzymatic browning processes* have been studied mainly in food chemistry and are probably similar to the reactions occurring in soil, where the additional presence of clays and colloidal oxides could stabilize these condensation products. *Cell autolysis* (i.e., the combination of the content of lysosomes and vacuoles in stages previous to cell death) is also a source of uncontrolled reactions leading to free-radical containing macromolecules (Andreux, 1969). This heterogeneous group of bioorganic reactions also include the condensation of precursor compounds continuously released to soil as *leaf leachates* (of which there is a high yield in some tropical soils), or *root exudates* (with a large quantitative influence in grassland ecosystems) whose condensation is favored by the soil matrix and soil enzymes.

Abiotic synthesis from aromatic or aliphatic simple precursors

The possibility of high-perfomance humification processes in microorganism-lacking media has been mainly demonstrated in model systems. A large series of simple laboratory experiments have evidenced spontaneous condensations in concentrated mixtures of reactive compounds such as phenols or aminoacids turning into brown-colored, high molecular weight condensation products (Preston and Rauthan, 1982). Among these analogs to HAs are the *catechol-glycine type* substances, which occur in the dark for a few days and at room temperature (Andreux et al., 1977). On the other hand, short-chain *aliphatic compounds* (mainly when they have unsaturated bonds) may also condense into resins, or into substances with certain resemblance to fulvic acids. This has been described e.g., in model products of the polymaleic acid type (Martin et al., 1984). When the molecular complexity and the hydrophobicity of such aliphatic condensation humic-like products increases, long-chain compounds in soil such as fatty acids and alkanes can be entrapped into the resulting continuously-growing microporous macromolecular networks. This could represent another formation pathway for the alkyl domain in humic matter.

Synthesis of analogous to Maillard's products

The condensation of aminoacids and carbohydrates (Maillard, 1916) is a classical process occurring during the cooking of food. These products are formed by successive reactions at relatively high temperatures (>100 °C) leading to macromolecules derived from mono- or bimolecular reactive products (Ellis, 1959). It has been indicated that similar slow reactions might occur, over the course of years, in soils and sediments (Ikan, et al., 1986) where organic matter is preserved from rapid biodegradation by low temperatures, waterlogging, oligotrophy or presence of antiseptic products. In general, Maillard's reactions have been invoked to explain the formation of marine HAs or dissolved organic matter (Benzing-Purdie and Ripmeester, 1983).

Maillard's browning products have several features in common with substances abiotically formed during dehydration of carbohydrates in nitrogen-lacking media (*pseudomelanoidins*). The N-compounds to a large extent increase the reaction rates, and the condensation occurs at comparatively lower temperature (Benzing-Purdie et al., 1983). Upon acid-catalyzed dehydration, sugars may lead to a variety of reactive anhydrosugar compounds ranging from levoglucosenone to furans. In fact, at an advanced stage benzenic compounds can be formed (Almendros et al., 1989; Popoff and Theander, 1976). Such reactions can occur in both solution and the solid state and are comparable to typical caramelization or charring of carbohydrates and other high oxygen-content molecules (Almendros et al., 1997; Feather and Harris, 1973; Hodge, 1953). Studies indicate that peatlands (where conditions are prone to favor acid-catalyzed carbohydrate dehydration) or soils affected by the high temperatures that occur during wildfires or controlled burnings, are the most probable environments for these humification paths (exclusively based on carbohydrates, but favored by mineral catalysts and by additional reactive compounds in soil) (Kumada, 1983; Shindo, 1986). In extreme situations, such as soils affected by fire, and depending on the intensity of the heating, the processes lead to a series of progressively charred organic particles and finally to particulate C – the so-called "black carbon" (Haumaier and Zech, 1985).

Currently controversy attends the importance of black carbon to soil properties and C sequestration. It is highly recalcitrant to destruction and is often claimed to be ubiquitous in the environment. In consequence, the cumulative effects of fires in the past (e.g., in ecosystems with pyrophytic vegetation or in soils where crop wastes are periodically removed by controlled burnings) may lead to soils containing C forms with a larger residence time than humus substances formed through processes where fire is not involved. Nevertheless, in the case of tropical soils, the efficient biodegradation of black carbon has also been suggested (Poirier et al., 2002).

In general, a realistic assessment of the role of black carbon in the environment is hindered by the current lack of valid surrogate indicators even for the qualitative identification of charred materials in the soil. For instance, it has been suggested that the release of benzenecarboxylic acids after laboratory oxidative degradation of the HAs, is an indicator of the impact of fires (Glaser et al., 1998). Nevertheless, these acids are also formed by oxidative degradation of non-heated lignin preparations (for example), and their yields depend on the temperature at which the laboratory degradation is performed (Almendros et al., 1989). In any case, it is clear that fire increases the stability of the soil organic matter to further thermal, chemical and biological degradation. Laboratory incubation experiments systematically show decreased C mineralization rates (CO_2 released per unit of soil C) when soils are heated under controlled conditions.

There is no unique, if any, descriptor for the impact of fire on soil organic matter. From the viewpoint of the changes in molecular composition of humic materials, fire commonly involves decarboxylation, progressive decrease in colloidal properties, and increase in aromaticity. This latter important feature is caused by the selective degradation of aliphatic moieties in humic substances, but also by neoformation of cyclic and polycyclic units. An additional noteworthy feature in heated soils is the formation of substantial amounts of heterocyclic N-compounds that are practically lacking in most soils not affected by severe fires (Almendros et al., 2003). The overall effect of the above thermal transformations is reflected in the quantitative patterns of humic fractions (Almendros et al., 1990a): water-soluble fractions and fulvic acids being transformed into HA-like substances, further transformation of HAs into humin, and final conversion of the latter into black carbon. It has also been observed that medium-intensity fires induce water repellency in soils (De Bano et al., 1970; Savage et al., 1972), which may also have a substantial, indirect role on the efficiency of physical and microbiological processes in the soil system (Giovannini et al., 1983), favoring the accumulation of water-resistant aggregates.

Condensation of long-chain alkyl molecules

The reliability of the abiotic condensation of unsaturated lipids to form macromolecules not only in dissolved organic matter such as marine HAs, but mainly in terrestrial soils, has been postulated in the last few years. The classical idea that alkyl molecules were mostly “peripheral constituents” of the humic macromolecules – that would consequently have an “aromatic core” – was largely based on indirect evidence (for instance, the large yields of aliphatic compounds after mild laboratory degradation methods) (Haworth, 1971). Concerning the fate of alkyl molecules there is an alternative that follows from the general observation that free fatty acids and glycerides are rapidly removed from solvent-extractable forms during incubation experiments. At first sight this might lead to the suggestion that these compounds underwent rapid biodegradation. In fact, most alkyl material is oxidized by soil microorganisms, but unsaturated lipids in particular could rapidly condense into polyalkyl networks formed through mid-chain bridging. In advanced transformation stages, cyclohexane structures and even aromatic rings could be formed and the macromolecular stability would increase through further internal cross-linking. Such photo-oxidation reactions have been considered the only possible humification path for open-sea humic-like organic matter, since planktonic vegetation practically lacks lignin (Harvey and Boran, 1985). Concerning terrestrial soils, the presence of oxides, clays and other inorganic catalysts could increase the condensation rates of unsaturated fatty acids (mainly when acids are still joined together as triglycerides). Consequently, the rapid decrease in the amounts of solvent-extractable fatty acids from incubated soils can also be explained by condensation and fixation of these compounds into more stable C forms no longer extractable by solvents. In particular, the photochemical aging and resinification of lipids and their association with pre-existing humic substances could play an important role during the long summers characteristic of dry, hot Mediterranean ecosystems where biological activity is limited by the lack of water in the topsoil. Laboratory experiments show the formation of resins insoluble in organic solvents, from natural unsaturated fats such as linseed oil, mainly in the presence of traces of metallic oxides (Almendros et al., 1996).

Gonzalo Almendros

Bibliography

Almendros, G., and Dorado, E., 1985. Estudio de acidos húmicos de tipo P. Distribución de los pigmentos verdes en las diferentes fracciones húmicas del suelo. *An. Edafol. Agrobiol.*, **43**: 547–559.

Almendros, G., and Dorado, J., 1999. Molecular characteristics related to the biodegradability of humic acid preparations. *Eur. J. Soil Sci.*, **50**: 227–236.

Almendros, G., and González-Vila, F.J., 1987. Degradative studies on a soil humin fraction. Sequential degradation of inherited humin. *Soil Biol. Biochem.*, **19**: 513–520.

Almendros, G., and Sanz, J., 1989. Compounds released from humic acids upon BF_3-MeOH transesterification. *Sci. Total Environ.*, **81/82**: 51–60.

Almendros, G., and Sanz, J., 1992. A structural study of alkyl polymers in soil after perborate degradation of humin. *Geoderma*, **53**: 79–95.

Almendros, G., Martínez, A.T., and Dorado, E., 1985. Production of brown and green humic-like substances by *Ulocladium atrum*. *Soil Biol. Biochem.*, **17**: 257–259.

Almendros, G., González-Vila, F.J., and Martin, F., 1989a. Room temperature alkaline permanganate oxidation of representative humic acids. *Soil Biol. Biochem.*, **21**: 481–486.

Almendros, G., Sanz, J., and Sobrados, I., 1989b. Characterization of synthetic carbohydrate-derived humic-like polymers. *Sci. Total Environ.*, **81/82**: 91–98.

Almendros, G., González-Vila, F.J., and Martin, F., 1990a. Fire-induced transformation of soil organic matter from an oak forest: an experimental approach to the effects of fire on humic substances. *Soil Sci.*, **149**: 158–168.

Almendros, G., Leal, J.A., González-Vila, F.J., and Martin, F., 1990b. The effect of composting on the chemical composition of the organic colloidal fraction from domestic sewage sludge. *Lect. Notes Earth Sci.*, **33**: 205–216.

Almendros, G., Guadalix, M.E., González-Vila, F.J., and Martin, F., 1996. Preservation of aliphatic macromolecules in soil humins. *Org. Geochem.*, **24**: 651–659.

Almendros, G., Dorado, J., González-Vila, F.J., and Martin, F., 1997. Pyrolysis of carbohydrate-derived macromolecules: its potential in monitoring the carbohydrate signature of geopolymers. *J. Anal. Appl. Pyrolysis*, **40–41**: 599–610.

Almendros, G., Guadalix, M.E., González-Vila, F.J., and Martín, F., 1998. Distribution of structural units in humic substances as revealed by multi-step selective degradations and ^{13}C-NMR of successive residues. *Soil Biol. Biochem.*, **30**: 755–765.

Almendros, G., Dorado, J., González-Vila, F.J., Blanco, M.J., and Lankes, U., 2000. ^{13}C NMR assessment of decomposition patterns during composting of forest and shrub biomass. *Soil Biol. Biochem.*, **32**: 793–804.

Almendros, G., Knicker, H., and González-Vila, F.J., 2003. Rearrangement of carbon and nitrogen forms in peat after progressive thermal heating as determined by solid-state ^{13}C- and ^{15}N spectroscopies. *Org. Geochem.*, **34**: 1559–1568.

Andreux, F., 1969. Contribution à l'étude des processus de melanification des autolysats végétaux (*Juglans regia*). Thèse spécial, Nancy.

Andreux, F., Golebiowska, D., Chone, T., Jacquin, F., and Metche, M., 1977. Caractérisation et transformation en milieu mull d'un modèle humique issu de l'autoxidation du système catechol-glycine et marqué séléctivement au carbone-14. 5th Symposium IAEA "*Soil Organic Matter Studies*", Vol. II, 43, Vienna.

Bell, A.A., and Wheeler, M.H., 1986. Biosynthesis and functions of fungal melanins. *Ann. Rev. Phytopathol.*, **24**: 411–451.

Benzing-Purdie, L., and Ripmeester, J.A., 1983. Melanoidins and soil organic matter: evidence of strong similarities revealed by ^{13}CP-MAS NMR. *Soil Sci. Soc. Am. J.*, **47**: 56–61.

Benzing-Purdie, L., Ripmeester, J.A., and Preston, C.M., 1983. Elucidation of the nitrogen forms in melanoidins and humic acid by nitrogen-15 cross polarization – magic angle spinning nuclear magnetic resonance. *J. Agric. Food Chem.*, **31**: 913–915.

Calvo de Anta, R.M., and Díaz-Fierros, F., 1982. Mineralización del carbono y del nitrógeno en suelos forestales de Galicia. *An. Edafol. Agrobiol.*, **41**: 1–10.

Carballas, T., Andreux, F., Jacquin, F., 1971. Répartition des principaux constituants d'un végétal marqué au ^{14}C dans les composés humiques d'un sol à mull. *Bull. AFES*, **3**: 29–38.

Davies, R.I., 1971. Relation of polyphenols to decomposition of organic matter and to pedogenetic processes. *Soil Sci.*, **111**: 80–85.

DeBano, L.F., Mann, L.D., and Hamilton, D.A., 1970. Translocation of hydrophobic substances by burning organic litter. *Soil Sci. Soc. Am. Proc.*, **34**: 130–133.

Derenne, S., Largeau, C., and Casadevall, E., 1991. Occurrence of tightly bound isoprenoid acids in an algal, resistant biomacromolecule: possible geochemical implications. *Org. Geochem.*, **17**: 597–602.

Duchaufour, Ph., and Jacquin, F., 1975. Comparaison des procesus d'humification dans les principaux types d'humus forestiers. *Bull. A.F.E.S.*, **1**: 29–36.

Eglinton, G., and Logan, G.A., 1991. Molecular preservation. *Phil. Trans. R. Soc. Lond. B*, **333**: 315–328.

Ellis, G.P., 1959. The Maillard reaction. *Adv. Carbohydr. Chem.*, **14**: 63–134.

Feather, M.S., and Harris, J.F., 1973. Dehydration reactions of carbohydrates. *Adv. Carbohydr. Chem. Biochem.*, **28**: 161–224

Giovannini, G., Luchessi, S., and Cerevelli, S., 1983. Water-repellent substances and aggregate stability in hydrophobic soil. *Soil Sci.*, **135**: 110–113.

Glaser, B., Haumaier, L., Guggenberger, G., and Zech, W., 1998. Black carbon in soils: the use of benzenecarboxylic acids as specific markers. *Org. Geochem.*, **29**: 811–819.

Goñi, M.A., and Hedges, J.I., 1990. The diagenetic behaviour of cutin acids in buried conifer needles and sediments from a coastal marine environment. *Geochim. Cosmochim. Acta*, **54**: 3083–3093.

González-Vila, F.J., Lüdemann, H.-D., and Martín, F., 1983. ^{13}C-NMR structural features of soil humic acids and their methylated, hydrolyzed and extracted derivatives. *Geoderma*, **31**: 3–15.

González-Vila, F.J., Almendros, G., and Madrid, F., 1999. Molecular alterations of organic fractions from urban waste in the course of composting and their further transformation in amended soil. *Sci. Total Environ.*, **236**: 215–299.

Goulden, J.D.S., and Jenkinson, D.S., 1959. Studies on the organic material extracted from soil and compost. II. The infra-red spectra of ligno-proteins isolated from compost. *J. Soil Sci.*, **10**: 264–270.

Greenland, D.J., 1971. Interactions between humic and fulvic acids and clays. *Soil Sci.*, **111**: 34–41.

Haider, K., and Martin, J.P., 1967. Synthesis and transformation of phenolic compounds by *Epicoccum nigrum* in relation to humic acid formation. *Soil Sci. Soc. Am. Proc.*, **31**: 766–772.

Hargitai, L., 1989. The role of humus status of soils in binding toxic elements and compounds. *Sci. Total Environ.*, **81/82**: 643–651.

Harvey, G.R., and Boran, D.A., 1985. Geochemistry of humic substances in seawater, Chapter 9. In Aiken, R.G., McKnight, D.M., Wershaw, R.L., and MacCarthy, P., eds., *Humic Substances in Soil, Sediment and Water*, pp. 233–247.

Hatcher, P.G., Maciel, G.E., and Dennis, L.W., 1981. Aliphatic structures of humic acids, a clue to their origin. *Org. Geochem.*, **3**: 43–48.

Haumaier, L., and Zech, W., 1995. Black carbon – possible source of highly aromatic components of soil humic acids. *Org. Geochem.*, **23**: 191–196.

Haworth, R.D., 1971. The chemical nature of humic acid. *Soil Sci.*, **111**: 71–79.

Hayes, M.H.B., MacCarthy, P., Malcolm, R.L., and Swift, R.S., eds., 1989. *Humic Substances. II. In Search of Structure.* New York: Wiley.

Hodge, J.E., 1953. Chemistry of browning reactions in model systems. *J. Agric. Food Chem.*, **1**: 928–943.

Holloway, P.J., 1972. The composition of suberin from the corks of *Quercus suber* L. and *Betula pendula* Roth. *Chem. Phys. Lipids*, **9**: 158–170.

Huc, C., Durand, B., and Jacquin, F., 1974. Caractérisation des acides humiques de sédiments marins récents et comparaison avec leurs homologues terrestres. *Bull. ENSAIA*, **16**(1/2): 59–75.

Ikan, R., Ioselis, P., Rubinsztain, Y., Aizenshtat, Z., Pugmire, R., Anderson, L.L., and Ishiwatari, R., 1986. Carbohydrate origin of humic substances. *Naturwissenschaften*, **73**: 150–151.

Khan, S.U., and Schnitzer, M., 1972. The retention of hydrophobic organic compounds by humic acid. *Geochim. Cosmochim. Acta*, **36**: 745–754.

Kögel-Knabner, I., 2000. Analytical approaches for characterizing soil organic matter. *Org. Geochem.*, **31**: 609–625.

Kolattukudy, P.E., 1977. Biosynthesis and degradation of lipid polymers, Chapter 15. In Tevini, M., and Lichtenthaler, H.K., eds., *Lipids and Lipid Polymers in Higher Plants.* Berlin, Heidelberg, New York: Springer-Verlag, pp. 271–292.

Kumada, K., 1983. Carbonaceous materials as a possible source of soil humus. *Soil Sci. Plant Nutr.*, **29**: 383–386.

Kumada, K., and Hurst, H.M., 1967. Green humic acid and its possible origin as a fungal metabolite. *Nature*, **214**: 631–633.

Kumada, K., and Sato, O., 1967. Studies on the chemical properties of P type humic acid. *Trans. Int. Symp. Humus Planta*, **4**: 131–133.

Largeau, C., Derenne, S., Casadevall, E., Kadouri, A., and Sellier, N., 1985. Pyrolysis of immature Torbanite and of the resistant biopolymer (PRBA) isolated from extant alga *Botryococcus braunii*. Mechanism of formation and structure of Torbanite. *Adv. Org. Geochem.*, **10**: 1023–1032.

Lisanti, L.E., Testini, C., and Senesi, N., 1974. Richerche sulle proprietá paramagnetiche dei composti umici.V: Applicazione della spettrometria EPR per la determinazione delle concentrazioni radicaliche. *Agrochimica*, **18**: 134–141.

Lynch, J.M., 1976. Products of soil microorganisms in relation to plant growth. *Crit. Rev. Microbiol.*, 67–107.

Maillard, M.L.-C., 1916. Synthèse des matières humiques par action des acides aminés sur les sucres réducteurs. *Ann. Chim.*, **5**: 258–317.

Martin, J.P., and Haider, K., 1971. Microbial activity in relation to soil humus formation. *Soil Sci.*, **111**: 54–63.

Martin, F., González-Vila, F.J., and Lüdemann, H.-D., 1984. About the similarity between polymaleic acid and water soluble humic fractions. *Z. Naturforschung*, **369**: 244–248.

Martínez, A.T., Barrasa, J.M., Almendros, G., and González, A.E., 1990. Fungal transformation of lignocellulosics as revealed by chemical and ultrastructural analyses. In Coughlan, M.P., and Amaral Collaço, M.T., eds., *Advances on Biological Treatments of Ligno-cellulosic Materials.* Londres: Elsevier, pp. 129–147.

Merlet, D., 1971. Mise au point technique concernant l'extraction et la caractérisation des composés organiques dans les sols. Centre de Pédologie Biologique. Doc. No. 15, Nancy, France.

Nip, M., Tegelaar, E.W., de Leeuw, J.W., and Schenck, P.A., 1986. A new non-saponifiable highly aliphatic and resistant biopolymer in plant cuticles. *Naturwissenschaften*, **73**: 579–585.

Oades, J.M., Vassallo, A.M., Waters, A.G., and Wilson, A., 1987. Characterization of organic matter in particle size and density fractions from a Red-brown Earth by solid-state ^{13}C NMR. *Aust. J. Soil Res.*, **25**: 71–82.

Oyonarte, C., Pérez–Pujalte, A., Delgado, G., Delgado, R., and Almendros, G., 1994. Factors affecting soil organic matter turnover in Mediterranean ecosystems from Sierra de Gador (Spain): an analytical approach. *Commun. Soil Sci. Plant Anal.*, **25**: 1929–1945.

Poirier, N., Derenne, S., Balesdent, J., Rouzaud, J.-N., Mariotti, A., and Largeau, C., 2002. Abundance and composition of the refractory organic fraction of an ancient, tropical soil (Pointe Noire, Congo). *Org. Geochem.*, **38**: 383–391.

Popoff, T., and Theander, O., 1976. Formation of aromatic compounds from carbohydrates. Part III. Reaction of D-glucose and D-fructose in slightly acidic, aqueous solution. *Acta Chem. Scand.*, **30**: 397–402.

Preston, C.M., 1996. Applications of NMR to soil organic matter analysis: history and prospects. *Soil Sci.*, **161**: 144–166.

Preston, C.M., and Rauthan, B.S., 1982. A hydrogen-1, carbon-13, and nitrogen-15 nuclear magnetic resonance study of *p*-benzoquinone

polymers incorporating amino nitrogen compounds ("synthetic humic acids"). *Soil Sci.*, **134**: 227–293.
Savage, S.M., Osborn, J., Letey, J., and Heaton, C., 1972. Substances contributing to fire-induced water repellency in soil. *Soil Sci. Soc. Am. Proc.*, **36**: 674–678.
Schnitzer, M., and Gupta, U.C., 1965. Determination of acidity in soil organic matter. *Soil Sci. Soc. Proc.*, **1965**: 274–277.
Schnitzer, M., and Khan, S.U., 1972. *Humic Substances in the Environment.* New York: Marcel Dekker.
Schulten, H.-R., and Schnitzer, M., 1990. Aliphatics in soil organic matter in fine-clay fractions. *Soil Sci. Soc. Am. J.*, **54**: 98–105.
Shindo, H., Matsui, Y., and Higashi, T., 1986. Humus composition of charred plant residues. *Soil Sci. Plant Nutr.*, **32**: 475–478.
Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., and McClure, S.G., 1996. The chemistry and nature of protected carbon in soil. *Aust. J. Soil Res.*, **34**: 251–271.
Spaccini, R., Conte, P., Piccolo, A., Haberhauer, G., and Gerzabek, M.H., 2000. Increased soil organic carbon sequestration through hydrophobic protection by humic substances. *Proceedings of the 10th International Meeting of the International Humic Substances Society* (IHSS10), 24–28 July, Tolouse (France), p. 419.
Stevenson, F.J., 1982. Biochemistry of the formation of humic substances. In Stevenson, F.J., ed., *Humus Chemistry.* 195–220.
Suflita, J.M., and Bollag, J.M., 1981. Polymerization of phenolic compounds by a soil–enzyme complex. *Soil Sci. Soc. Am. J.*, **45**: 297–302.
Tegelaar, E.W., de Leeuw, J.W., Derenne, S., and Largeau, C., 1989. A reappraisal of kerogen formation. *Geochim. Cosmochim. Acta*, **53**: 3103–3106.
Waksman, S.A., 1936. *Humus, Origin, Chemical Composition and Importance in Nature.* Baltimore, MA: Williams and Wilkins.
Wershaw, R.L., Pinckney, D.J., and Booker, S.E., 1977. Chemical structure of humic acids – Part 1. A generalized structural model. *J. Research U.S. Geol. Surv.*, **5**: 565–569.
Wilson, M.A., 1981. Application of nuclear magnetic resonance spectroscopy to the study of the structure of soil organic matter. *J. Soil Sci.*, **32**: 167–186.

Cross-references

Carbon Cycling and Formation of Soil Organic Matter
Carbon Sequestration in Soil

HUMID

A word applied to climates in which annual precipitation is between 500 mm (in cool regions) and 1 500 mm (in hot regions). Applied to soils the term implies a year-round dampness without the macroscopic appearance of free water. A forest vegetation is characteristic of humid soils. See *Moisture regimes*.

HUMMOCK

A small hill or protuberance on a landscape. Hummocky landscapes are particularly common in regions affected by continental glaciations. They principally originate when materials on or within the ice, is deposited onto the landscape as a moraine.

HYDRIC SOILS

Hydric soils are reduced soils, approximately defined in terms of pe and pH as in Figure H7. The low redox state is a

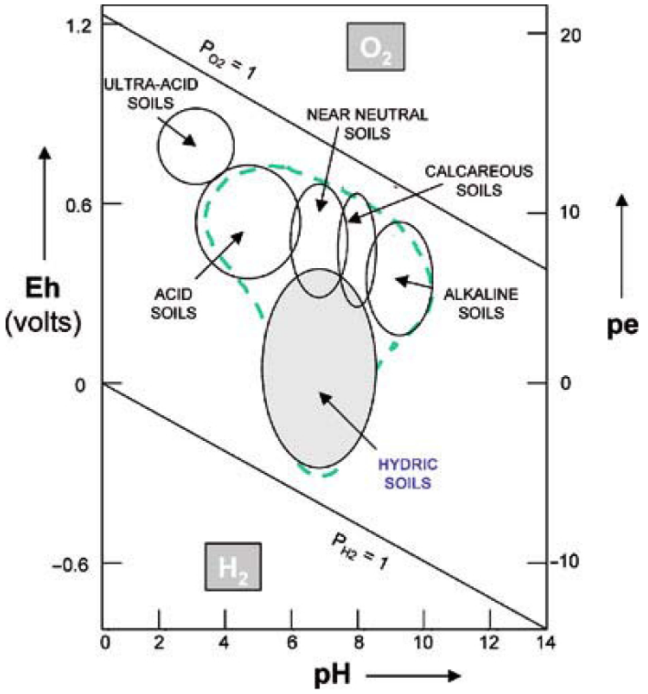


Figure H7 Hydric soils in relation to the other soil. The *dashed outline* is the field of pe–pH conditions of most mineral soils.

Table H3 The sequence of representative reduction reactions in neutral soils. The pe values in the second column are the ranges over which the reductions are initiated at pH 7. (from Sposito, 1989)

Reduction half reaction	Range of pe
$1/4O_2(g) + H^+(aq) + e^-(aq) = 1/2H_2O$	5.0–11.0
$1/2NO_2^-(aq) + H^+(aq) + e^-(aq) = 1/2NO_2^-(aq) + 1/2H_2O$	3.4–8.5
$1/2NO_3(aq) + 6/5H^+(aq) + e^-(aq) = -1/10N_2(g) + 3/5H_2O$	
$1/8NO_3(aq) + 5/4H^+(aq) + e^-(aq) = 1/8NH_4^+(aq) + 3/8H_2O$	
$1/2MnO_2(s) + 2H^+(aq) + e^-(aq) = 1/2Mn^{2+}(aq) + H_2O$	3.4–6.8
$Fe(OH)_3(s) + 2H^+(aq) + e^-(aq) = Fe^{2+}(aq) + 3H_2O$	1.7–5.0
$FeOOH(s) + 2H^+(aq) + e^-(aq) = Fe^{2+}(aq) + 2H_2O$	
$1/8SO_4^{2-}(aq) + 9/8H^+(aq) + e^-(aq) = 1/8HS^-(aq) + 1/2H_2O$	−2.5–0.0
$1/4SO_4^{2-}(aq) + 5/4H^+(aq) + e^-(aq) = 1/8S_2O_3(aq) + 5/8H_2O$	
$1/8SO_4^{2-}(aq) + 5/4H^+(aq) + e^-(aq) = 1/8H_2S(aq) + 1/2H_2O$	

consequence primarily of saturation of part or all of the solum with water.

This effectively excludes a new influx of oxygen once any initial oxygen in the soil has been consumed (for example during the bacterial decay of organic matter). To continue their metabolic processes, the bacterial populations must then utilize other electron acceptors than oxygen. At pH 7 the theoretical order would follow the sequence shown in Table H3. Figure H8 incorporates some of these reactions into the pe–pH framework, and indicates the overall direction of electron flow in the soil. Typical hydric soils in the WRB system are Gleysols, Histosols and water saturated varieties of other groups, particularly Fluvisols (FAO, 2001, 2006; Zech and Hintermaier, 2007).

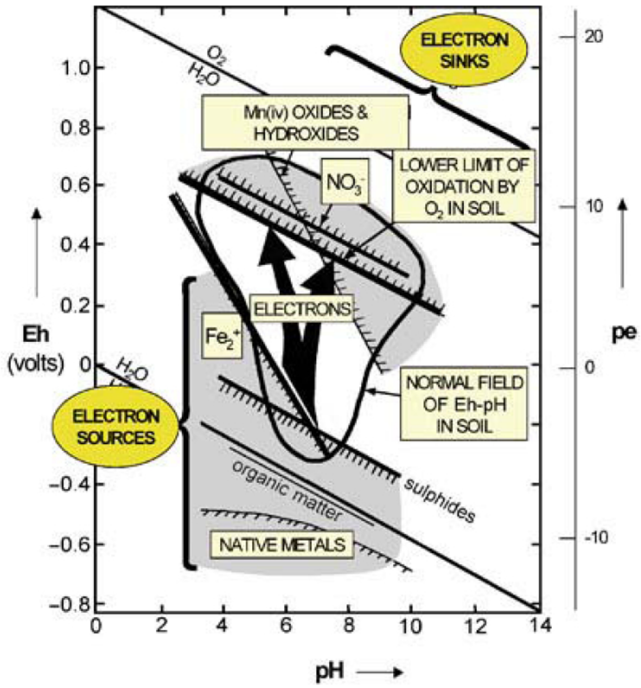


Figure H8 Generalized flow of electrons in soil between sources and sinks of electrons.

The characteristic environment of hydric soils is a topographic low on a landscape, with a high water table. Prime candidates are coastal (marine or lacustrine) and riparian lowlands, especially where the parent materials are clay-rich and poorly drained. The typical pedogenic processes are:

1. Gley formation. (Schlichting and Schwertmann, 1973).

   The redox–pH conditions in hydric soils (Figure H7) lead to the reduction of iron and manganese and the production of soluble and therefore easily mobilized species (Fe^{II} and Mn^{II}) from the solid, oxidized forms that are not readily mobilized (Figure H9). The result is a loss of darker colors in the solum and a predominance of shades of gray. This is called gley formation (gleyzation or gleyification). Gley formation may affect any soil, especially in lower horizons. Thus in the environments already mentioned, gleyic varieties of Fluvisol are common. When gley formation reaches to within 50 cm of the surface, Gleysols are the characteristic soil type to form.
2. Sulfate reduction. (Alpers, Jambor, and Nordstrom, 2000).

   In the most reduced zone of soil formation, sulfate reducing bacteria use the sulfate ion as the terminal electron acceptor, and sulfate is reduced to sulfide. Since ferrous iron will generally be present in solution under these conditions, pyrite may form, commonly via a short range order, metastable, precursor phase. Near shore environments, where SO_4^{2-} ions of marine origin may be expected, are likely localities for soils affected by this process, and the typical

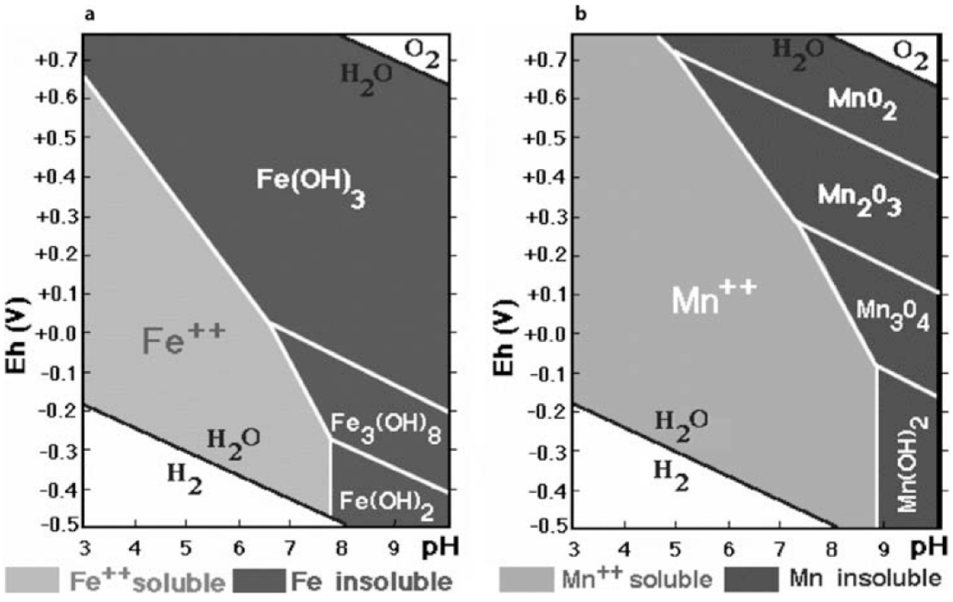


Figure H9 Predominance field of (**a**) Fe^{2+} and (**b**) Mn^{2+} in aqueous systems. (Dorronsoro, B. et al., 2007).

soil type is a Tidalic Fluvisol (Thionic). Within the field of hydric soils, the sulfate-sulfide geochemical fence divides the conditions of Gleysol formation from those of thionic or sulfidic soils (Figure H10).

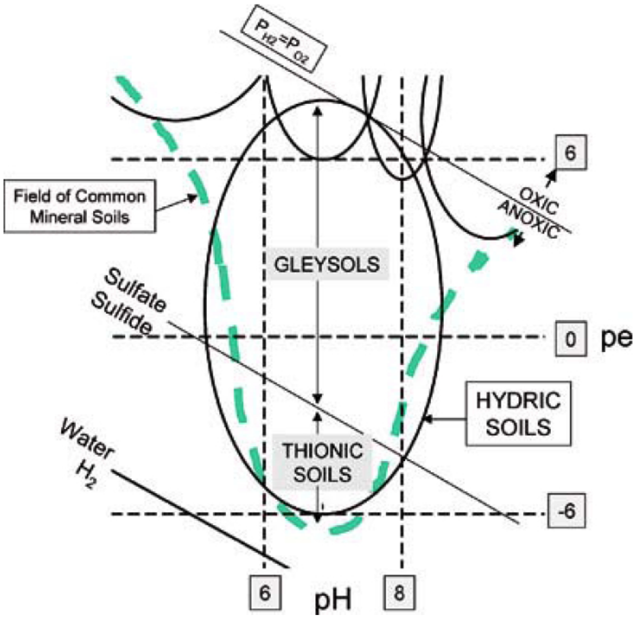


Figure H10 Detail of Figure H7 showing an elaboration of the field of hydric Soils between Gleysols (pe values above the sulfate–sulfide fence) and thionic soils (pe values below the sulfate–sulfide fence). The term Thionic Soils in the figure is according to FAO (2001). It is equivalent to Sulfidic Soils in the usage of FAO (2006).

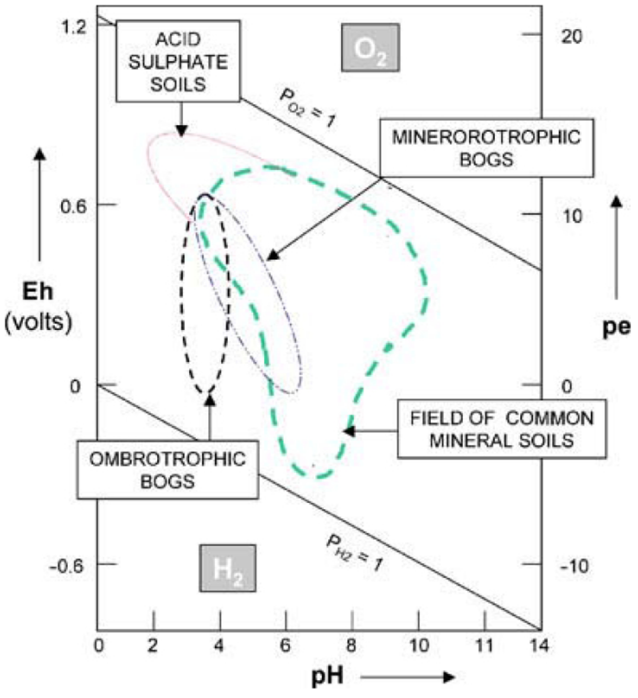


Figure H11 Redox–pH conditions in ombrotrophic and minerotrophic bogs.

3. Peat formation. (Martini and Chesworth, 2006).

Under humid climates and on water saturated surficial deposits, peat may form and accumulate (by paludification or terrestrialization). Within pe–pH space, the conditions found in peatlands differ from hydric soils in general (Figure H11). Ombrotrophic mires being fed solely from atmospheric sources, are not influenced by local groundwaters so tend not to be buffered by mineralogical reactions. Minerotrophic mires receive solutes from the area surrounding the mire, and in general follow the ferrous-ferric geochemical fence down to redox conditions within the field of the hydric soils. The characteristic soil type in this environment is the Histosol.

W. Chesworth, M. Camps Arbestain, F. Macías,
and A. Martínez Cortizas

Bibliography

Alpers, C.N., Jambor, J.L., and Nordstrom, D.K., eds., 2000. *Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance.* Washington, DC: Mineralogical Society of America, 608 pp.

Dorronsoro, B., Aguilar, J., Dorronsoro-Díaz, C., Stoops, G., Sierra, M., Fernández, J., and Dorronsoro-Fernández, C. 2007. Accessed at http://edafologia.ugr.es/hidro/conceptw.htm.

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FAO, 2006. World Reference base for soil resources. World Soil Resources Report 103. Rome: Food and Agriculture Organization of the United Nations. 132 pp.

Martini, I.P., Martínez Cortizas, A., and Chesworth, W., eds., 2006. *Peatlands.* New York: Elsevier, 587 pp.

Schlichting, E., and Schwertmann, U., eds., 1973. *Pseudogley and Gley: Genesis and Use of Hydromorphic Soils; Transactions of Commissions V and VI of the International Society of the Soil Science.* Weinheim: Verlag Chemie, 771 pp.

Sposito, G., 1989. *The Chemistry of Soils.* New York: Oxford University Press, 277 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag. 130 pp.

Cross-references

Gleysols
Histosols
Mire
Peat
Redox Reactions and Diagrams in Soil
Thionic or Sulfidic Soils

HYDROLOGICAL CYCLE

About 1.4 × 10^9 km^3 of water participates in the surface and near surface hydrological cycle of the Earth. The water is cycled between land, sea and air through a number of reservoirs, shown in simplified form in Figure H12. Clearly the major reservoir is the sea, with glacier (including polar) ice a distant second. All other near surface reservoirs constitute approximately 0.3% of the total, most of that being groundwater. Soil water, at 0.005%, would appear to be an almost negligible fraction, though in terms of ecological services its importance is immense. The role of water in soil is summarized in Table H4, and is treated specifically in the entry *Field water cycle*.

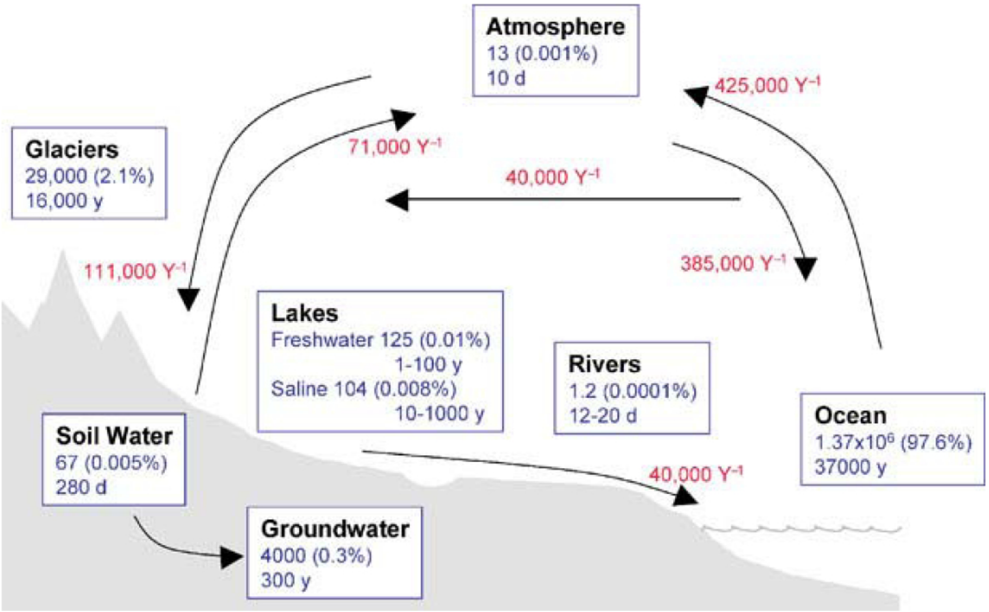


Figure H12 The hydrological cycle (after Reeburgh, 1997). Each box represents a reservoir, the size of which is given in 10^3 km^3 followed by the percentage that this represents of the whole freshwater resource, in parentheses. The bottom line in each box is an estimate of turnover (or residence) time. Transfer rates between reservoirs are given in km^3 yr^{-1}. The turnover time for soil is highly variable depending on soil type, texture and other factors including how the water is apportioned in the soil between large pores and channels through to capillaries and surface films. In an Arenosol, most water will drain in minutes to hours, in a Vertisol; the residence time could be tens of years.

Table H4 Functions of water in soil

1. Physical functions
   a. Agent of physical transport
      Macroscale factors: gravitational and evapo-transpirational potentials
      Microscale factors: capillary forces
   b. Medium that reactants diffuse through at reaction-sites
      At solid-liquid interface at soil pores for example
   c. Exerts partial pressure
      Proportional to chemical potential
   d. Helps physical breakdown of solids
      By freeze/thaw or thermal expansion/contraction at intergranular boundaries
2. Chemical functions
   a. Acts as a solvent
      Anomalously high dielectric constant accounts for its great range in this regard
   b. Chemical component of all typical weathering reactions in soil
      Hydration/dehydration, acid/base, solution/precipitation, ion-exchange
   c. Structural constituent of all common neoformations in soil
      Hydroxides, clay minerals, amorphous phases
   d. Acts as chemical buffer
      With thermodynamic activity close to 1 in all but saline soils
   e. Helps the break-up of mineral aggregates
      By chemical reaction in intergranular space particularly in parent material
3. Biological functions
   a. Stability field of water defines the limits of the life zone
      Limited by breakdown of water by oxidation or reduction under earth surface conditions[1]
   b. Promotes growth and development
      As a necessary nutrient
   c. Regulates internal functions in an organism
      Temperature regulation for example

[1] See Figure R1 in article Redox Reactions and Diagrams in Soil.

The importance of soil water stems from the position that soil holds in the biosphere. As an almost ubiquitous cover to the land surface, soil is a choke point through which energy and materials are cycled and distributed to other compartments of the biosphere. It serves as a flow-through reaction vessel where water acts as the principal agent of transport, and acquires much of its chemical composition as it reacts with minerals and organic matter. Figure H13 gives a general view of soil water composition in relation to the major mineral-forming regimes in soils according to the classification of Pedro (1979).

The human race exerts a considerable influence on the hydrological cycle. UNESCO (2006) estimates that currently we appropriate 8% of the world's annual renewable freshwater, and intercept 26% of annual evapotranspiration, and 54% of accessible runoff. Worldwide, agriculture is the dominant user (70%), followed by industry (20%) and domestic usage (10%). The contrast between the different apportioning of water between these three users in developed (46% : 40% : 14%) versus developing (81% : 11% : 8%) nations is marked, and is seemingly a reflection of greater versus lesser affluence.

With population increasing, and standards of living rising, water scarcities are becoming acute globally. Pollution of the freshwater resource is also of increasing concern in this regard. According to the World Resources Institute (2005), the worst examples come from China, where 7 060 million t d^{-1} of organically polluted water is discharged from industry, followed by the USA (2 433 million t d^{-1}), Russia (1 516 million t d^{-1}) and India (1 605 million t d^{-1}). In effect, the ability of the soil system to regenerate water of potable quality, one of the most important ecological services that the soil provides, is substantially at risk from human activities.

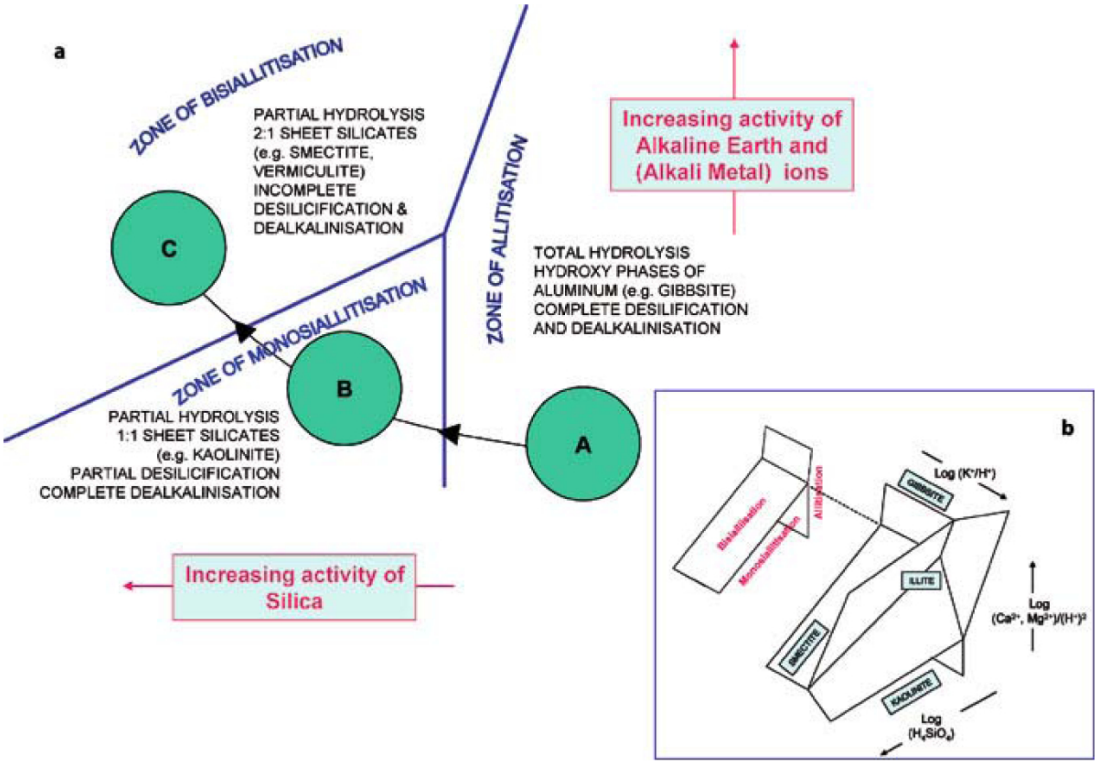


Figure H13 Schematic representation of three zones of mineral formation in soils. *2a:* Soil water *A* is the most acid and most dilute; low in alkali and alkaline earth ions; aluminosilicate clay minerals unstable; gibbsite stable; especially characteristic of excessively well drained soils and/or soils that have undergone weathering and leaching for periods of the order of millions of years (e.g., Alisols, and also bauxites and laterites). Soil water *B* may be as acid as *A*, but H_4SiO_4 activity is higher so that 1:1 clays are common (usually kaolinite); similar environments to *A*, but well, rather than excessively, drained (e.g., Ferralsols). Soil water *C* has a higher pH than *A* and *B*, and a higher concentration of alkaline earth and alkali metal ions; 2:1 sheet silicates stabilized, smectites common with Ca^{2+} and Mg^{2+} dominating the exchange sites at pH values between about 6 to 8, with Na^{+} more important at pH 8.5 and above; sequence of increasing pH particularly associated with the change from humid to more arid climates – a possible soil sequence being Cambisol–Chernozem–Kastanozem–Calcisol–Gypsisol–Solonchak. *2b* is the model soil system on which *2a* is based (Chesworth, 1980).

A further concern arises from the practice of irrigation. Food production for the current 7 billion human beings is heavily dependent on irrigation (Gleik, 1993, 1996). Some 16% of the approximately 1 500 million ha currently under arable agriculture, is irrigated. Virtually all (though surprisingly, not all) of the irrigated land is in semiarid to arid regions of the globe, or in regions of Mediterranean-type climates with contrasted wet and dry seasons. In all cases of large-scale irrigated agriculture in such localities, salinization is an increasing problem, just as it was in the first home of irrigation in Mesopotamia. This is true of California and the former USSR (Figure H14), among many examples, while in Australia; the problem has reached almost epidemic proportions. The Nile Delta provides a particularly poignant example (Figure H15).

There is now a growing debate on the effect that global warming is likely to have on the water cycle. A consensus is building that higher global temperatures will lead to a speeding up of the cycle, since warmer conditions can be expected to lead to greater evaporation. This will put more water vapor, already the most plentiful greenhouse gas on the planet, into the atmosphere, and can therefore be expected to add to global warming (Evans, 1996). Gleick (1993) believes that the impact of global warming on irrigated agriculture will be felt more keenly than the direct effect of higher temperatures.

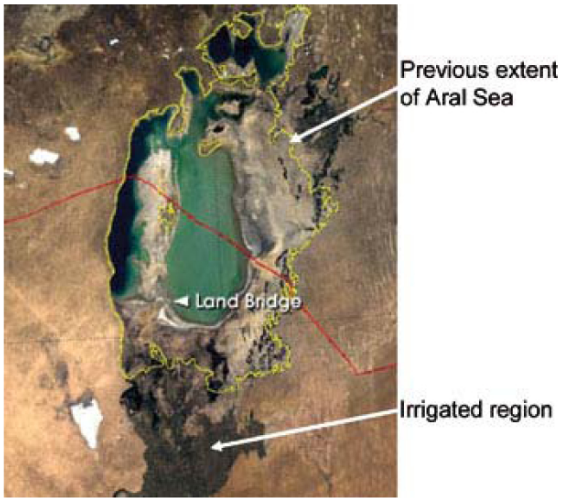


Figure H14 Over-exploitation of the water resource for cotton production, by Soviet Russian authorities led to salt deposition within irrigated soils south of the Aral Sea, as well as within the shrinking basin of the sea itself. Photo courtesy of NASA. The image was acquired 3 June 2001, and was the first to show that Vozrozhdeniye Island is now connected to the mainland.

Figure H15 Salt deposition at the surface of irrigated soils in the Nile Delta, Egypt. Until the Aswan High Dam was constructed, the Nile reliably delivered enough water to flush from the solum, any salt precipitates produced by evaporation, thereby sustaining agricultural productivity for at least 7000 years. Photo John Fitzsimons.

The data on the Earth's hydrologic cycle now being collected by the Aqua spacecraft of NASA's Earth Observing System (EOS), will be critical in determining whether the cycle is accelerating or not.

Ward Chesworth

Bibliography

Chesworth, W., 1980. The haplosoil system. *Am. J. Sci.*, **280**: 969–985.

Evans, T.E., 1996. The effects of changes in the world hydrological cycle on availability of water resources. In Bazzaz, F., and Sombroek, W., eds., *Global Climate Change and Agricultural Production.* Chichester: Wiley, p. 248.

Gleick, P.H., 1993. *Water in Crisis: A Guide to the World's Fresh Water Resources.* New York: Oxford University Press, 473 pp.

Gleick, P.H., 1996. Water resources. In Schneider, S.H., ed., *Encyclopedia of Climate and Weather,* Vol. 2. New York: Oxford University Press, pp. 817–823.

Pedro, G., 1979. Caracterisation generale des processus de l'alteration hydrolytique. Base des methods geochimique et thermodynamique. *Sciences du Sol, numero special: 'Alteration des Roches Cristallines en Milieu Superficiel'*, pp. 93–105.

Reeburgh, W.S., 1997. Figures Summarizing the Global cycles of biogeochemically important elements. *Bull. Ecol. Soc. Am.*, **78**(4): 260–267.

UNESCO, 2006. A *Shared Responsibility The United Nations World Water Development Report 2*. Paris: United Nations Educational, Scientific and Cultural Organization, 48 pp.

World Resources Institute, 2005. World Freshwater Resources. Accessed at http://earthtrends.wri.org/pdf_library/data_tables/wat2_2005.pdf.

Cross-references

Biogeochemical Cycles
Phase Rule and Phase Diagrams
Water Movement in Soil
Water Budget

HYDROMORPHIC

Applied to soils with textural features caused by an excess of water occasioned by poor drainage e.g., reduction of Fe and Mn, gleying, mottling, and ferrolysis. A website on hydromorphism in soils is maintained at http://edafologia.ugr.es/hidro/indexw.htm (last accessed June 2007). The fundamental redox-pH chemistry is dealt with in Martini et al., 2006, chapter 8).

Bibliography

Martini, I.P., Martínez Cortizas, A., and Chesworth, W., eds., 2006. *Peatlands*. New York: Elsevier, 587 pp.

Cross-references

Ferrolysis
Gleysols
Histosols
Hydric Soils
Mire
Peat
Redox Reactions and Diagrams in Soil
Salt Leaching
Thionic or Sulfidic Soils

HYDROPHILICITY, HYDROPHOBICITY

Concept and definitions

Surfaces that attract water are termed hydrophilic, whereas surfaces that repel water are termed hydrophobic. The degree to which a surface either attracts or repels water can be termed, respectively, the hydrophilicity or the hydrophobicity of that surface. Polar liquids like water and alcohols interact more strongly with hydrophilic surfaces. Similarly, nonpolar liquids such as petroleum-based solvents interact more strongly with hydrophobic surfaces.

Aggregation, water sorption, permeability, organic compound sorption, and other phenomena in soils are controlled by the nature of the surface interactions at solid /liquid/gas interfaces. In general, the surfaces of the inorganic components of soils are hydrophilic. The inorganic material in soils usually consists of oxides and silicates such as quartz, feldspars, and silicate clays. In contrast, soil organic matter is relatively hydrophobic and consists of plant residues in various stages of decomposition. The hydrophobic character imparted by organic matter improves aggregation in mineral soils. In this regard, Malik et al. (1991) found that addition of the polymer polyacrylamide improved water flow through a clayey soil. The greater porosity that results from good aggregation fosters greater permeability. The hydrophobic character of soil organic matter also retards the movement of pesticides (Chiou, et al., 1979). However, some inorganic materials are hydrophobic and some organic materials are relatively hydrophilic. Also, the hydrophobicity/hydrophilicity of solid surfaces and the surface tension at fluid interfaces can be altered by the addition of surfactant molecules.

Measurement of hydrophobicity/hydrophilicity

The degree to which a solid surface is either hydrophobic or hydrophilic can be determined by measurements of the contact angle formed between water, air, and that surface. On hydrophobic surfaces, water droplets form compact globs with relatively large contact angles. In contrast, water droplets spread to form flattened globs with smaller contact angles on hydrophilic surfaces (Figure H16).

The surface tension of liquid surfaces and the wettability of solid surfaces are properties that are closely related to the contact angle. In a clean glass cylinder, water wets the surface

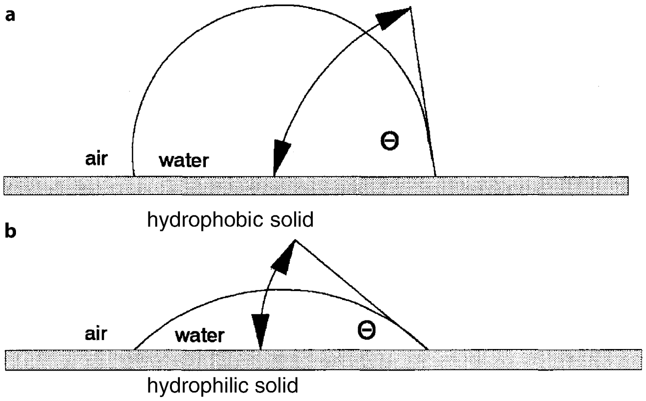


Figure H16 Contact angles formed between water droplets and (**a**) a hydrophobic surface and (**b**) a hydrophilic surface.

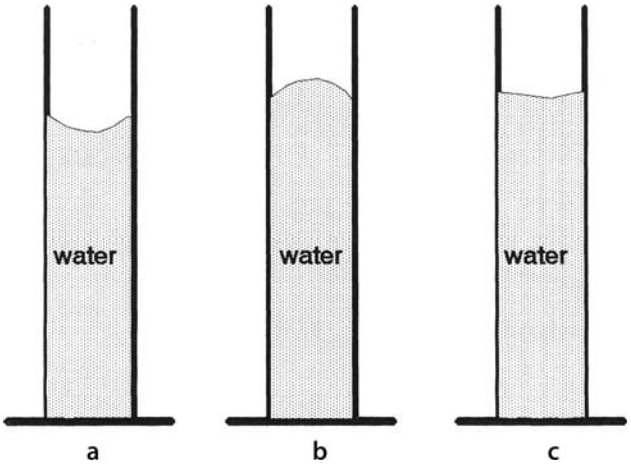


Figure H17 Meniscus formed between water and the walls of a glass cylinder; (**a**) clean glass, (**b**) oil-coated glass, (**c**) oil-coated glass with surfactant added.

and forms a small contact angle with the glass; this results in a concave meniscus. If the glass surface is coated with oil, water does not readily wet the surface and it forms a larger contact angle with the glass; this results in a convex meniscus. The surface tension of the water surface in a clean glass is small, whereas it is larger in an oil-coated glass. If a surfactant such as soap were added to the oil-coated glass, the water would more effectively wet the glass surface and the surface tension and contact angle would be reduced (Figure H17).

The contact angle of macroscopic solids with liquids such as water can be directly measured. However, the contact angle between liquids and finely powdered materials such as soils must be measured indirectly. Giese et al., (1991) measured the wicking rate of water and other liquids through powdered samples of the silicate clay minerals, talc and pyrophyllite. Using the Washburn Equation (Washburn, 1921) to calculate contact angles from the wicking rate, they determined that the contact angles with water for talc, pyrophyllite, and hectorite were 80.4, 79.2, and 63 degrees, respectively. The much lower contact angle measured for the charged clay mineral, hectorite, indicates that it has significantly less hydrophobic character than the uncharged minerals talc and pyrophyllite.

Nature of hydrophilic interactions

Lewis (1923) proposed a definition of acid-base behavior in terms of electron-pair donation and acceptance. Hydrogen bonding accounts for 70% of the cohesive energy of water (van Oss et al., 1987) and is a consequence of Lewis acid/base pairs; hydrogen from one molecule acts as an electron acceptor (Lewis acid) and forms a bond with the oxygen of an adjacent molecule which acts as an electron donor (Lewis base). The Lewis acid/base (i.e., electron acceptor/donor) character of materials is largely responsible for hydrophilic interactions in soils. The exchangeable cations in soils have a hydration shell of water strongly linked via ion-dipole bonds and this hydration shell strongly interacts via hydrogen bonding with adjacent water molecules.

Nature of hydrophobic interactions

Hydrophobic interactions are not directly caused by bonding i.e., no "hydrophobic bond" is formed. Hydrophobic interactions are interfacial phenomena caused by the net effects of attractive and repulsive forces that occur between solid surfaces, dissolved hydrocarbons, and highly polar solvents. Van Oss et al. (1987) argued that hydrophobic sorption of hydrocarbons from water is caused by a combination of long range and short-range forces. They suggested that the long-range forces consist primarily of van der Waals bonding, whereas the short-range forces are dominated by hydrogen bonding. They also suggested that an entropy effect may contribute to sorption; that is, a hydrocarbon molecule dissolved in water reduces the number of hydrogen bonds that can form between water molecules that are adjacent to the hydrocarbon molecule. Sorption of this hydrocarbon molecule to a solid surface would disrupt the ordered arrangement of water molecules enclosing the hydrocarbon molecule and allow complete hydrogen bonding between the water molecules. Sorption would be thermodynamically favored because it would increase the entropy of the system. Similarly, Hiemenz (1997) and Hassett and Banwart (1989) suggested that entropy effects may contribute to the sorption of hydrocarbons from water.

Hydrophobicity/hydrophilicity of clay minerals

Neutral-layer silicate clays (e.g., talc, pyrophyllite) are hydrophobic whereas, clays with an octahedral (e.g., montmorillonite, hectorite) and/or tetrahedral (e.g., vermiculite) charge deficit are hydrophilic. Schrader and Yariv (1990) found that the clay minerals, talc and pyrophyllite, are hydrophobic and are not as readily wetted by water as the hydrophilic clay mineral vermiculite. They explained the hydrophobic and hydrophilic properties of these minerals based on the electronic properties of the cleavage planes. They argued that talc and pyrophyllite are hydrophobic because the oxygens on the cleavage surfaces (siloxane surface) are not good electron donors (Lewis bases) and consequently do not form effective hydrogen bonds to water. In contrast, vermiculite is hydrophilic and they attributed this hydrophilicity to two factors: (1) hydration of exchangeable ions on the cleavage faces, and (2) the substitution of Al for Si in the cleavage faces of vermiculite making the oxygens good electron donors (effective Lewis bases) which hydrogen-bond to water (see also Sposito, 1984).

Organic cations are not as hydrophilic as inorganic cations. The hydration shell of organic cations is not as strongly bonded as that of inorganic cations. Boyd, et al., (1988b) found that replacing the inorganic exchange cations in montmorillonite with organic cations greatly increased the hydrophobic character. Jaynes and Boyd (1991) prepared a series of montmorillonites with reduced-charge and hence, reduced exchangeable cation content. These reduced-charge clays were then exchanged with small organic cations. The adsorption of aromatic hydrocarbon molecules from water to samples of these reduced-charge organo-clays substantially increased with greater charge reduction and hence, lower organic cation content. Hydrocarbon sorption was found to be proportional to surface area. This suggests that the hydrocarbons were adsorbed onto the siloxane surface and that this surface is hydrophobic. The hydrophilic character of octahedrally-substituted clays may be due entirely to hydration of the exchangeable cations.

Making hydrophilic clays hydrophobic

The clay fraction (<2 nm) of soils has a high surface area and it exerts a dominant control on the properties of soils. The clay fractions of soils are commonly composed of hydrophilic clay minerals such as montmorillonite, vermiculite, and kaolinite. As discussed previously, surfactants can be used to alter interactions at the interfaces between water, air, and solid surfaces. Similarly, the adsorption of natural humic substances can make the hydrophilic surface of soil clays hydrophobic. Boyd et al. (1988a) showed that soils could be made hydrophobic by treatment with quaternary ammonium salts. Jaynes and Boyd (1990) examined the sorptive character of hexadecyltrimethylammonium organo-clays prepared from pure samples of various clay minerals that naturally occur in soils. Jaynes and Boyd (1990) found that hydrocarbon sorption from water increased as the layer charge and organic cation content of the organo-clay increased. The amount of hydrocarbon sorbed was proportional to the carbon content and interlayer spacing of the organo-clay.

Summary

Hydrophobic substances weakly interact with water and are generally nonpolar in nature. Such materials may strongly interact with nonpolar liquids such as petroleum solvents. In contrast, hydrophilic substances strongly interact with water through hydrogen bonding and are polar in nature. The degree to which a material is either hydrophobic or hydrophilic can be determined from measurements of the contact angle that water makes in air with the material surface. Soils are composed of minerals that are generally hydrophilic in character. Some degree of hydrophobicity is desirable in soils in that it promotes aggregation, enhances permeability, and retards the movement of pesticides. Soil organic matter is relatively hydrophobic and some components of it (e.g., humic acid) will adsorb to mineral surfaces and make the surface hydrophobic. Synthetic materials such as cationic, organic surfactants can displace inorganic cations from mineral surfaces and make the surfaces hydrophobic.

William F. Jaynes

Bibliography

Boyd, S.A., Lee, J.F., and Mortland, M.M., 1988a. Attenuating organic contaminant mobility by soil modification. *Nature*, **333**: 345–347.

Boyd, S.A., Mortland, M.M., and Chiou, C.T., 1988b. Sorption characteristics of organic compounds on hexadecyltrimethylammonium-smectite. *Soil Sci. Soc. Am. J.*, **52**: 652–657.

Chiou, C.T., Peters, L.J., and Freed, V.H., 1979. A physical concept of soil–water equilibrium for non-ionic organic compounds. *Science*, **206**: 831–832.

Giese, R.F., Costanzo, P.M., and van Oss, C.J., 1991. The surface free energies of talc and pyrophyllite. *Phys. Chem. Miner.*, **17**: 611–616.

Hassett, J.J., and Banwart, W.L., 1989. The sorption of nonpolar organics by soils and sediments. In *Reactions and movement of organic chemicals in soils.* Soil Science Society of America Special Publication #22, Madison, WI, pp. 31–44.

Hiemenz, P.C., and Rajagopalan, R., 1997. *Principles of Colloid and Surface Chemistry.* New York: Marcel Dekker, 650 pp.

Jaynes, W.F., and Boyd, S.A., 1990. Clay mineral type and organic compound sorption by hexadecyltrimethylammonium-exchanged clays. *Soil Sci. Soc. Am. J.*, **55**: 43–48.

Jaynes, W.F., and Boyd, S.A., 1991. Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. *Clays Clay Miner.*, **39**: 428–436.

Lewis, G.N., 1923. *Valence and Structure of Atoms and Molecules.* Reprint 1966 with a new introduction by K.S. Pitzer. New York: Dover, 172 pp.

Malik, M., Amrhein, C., and Letey, J., 1991. Polyacrylamide to improve water flow and salt removal in a high shrink-swell soil. *Soil Sci. Soc. Am. J.*, **55**: 1664–1667.

van Oss, C.J., Good, R.J., and Chaudhury, M.K., 1987. Determination of the hydrophobic interaction energy – application to separation processes. *Sep. Sci. Technol.*, **22**: 1–24.

Schrader, M.E., and Yariv, S., 1990. Wettability of clay minerals. *J. Colloid Interf. Sci.*, **136**: 85–94.

Sposito, G., 1984. *The Surface Chemistry of Soils.* Oxford: Oxford University Press, 234 pp.

Washburn, E.W., 1921. The dynamics of capillary flow. *Phys. Rev.*, **17**: 273–283.

Cross-reference

Wetting Front

HYGROSCOPICITY, HYGROSCOPIC CONSTANT

Hygroscopicity is the property of small-particle systems to take up moisture from the atmosphere (Gregorich et al., 2001) through strong sorption forces on the particle surfaces and through capillary condensation due to the lowering of the watervapor pressure above concave capillary menisci. Hygroscopicity differs from *deliquescence* in that it does not result in liquefaction even at relatively high atmospheric humidity.

Hygroscopic moisture, as defined by the soils engineer, is the water content of an air-dry soil as determined by oven-drying at 105–110 °C and expressed as a percentage of the oven-dry weight. This parameter is practically important for field and laboratory work; however, because of its dependence on environmental conditions, especially the relative humidity of the atmosphere, it cannot serve as a fundamental soil characteristic. For the latter role, the environmental influence must be either eliminated or standardized.

The *hygroscopic constant* (or coefficient) W_{hc} is defined as that moisture content of a soil material at which further addition of water will not release additional heat of wetting. This moisture content corresponds closely to that reached by an oven-dry soil sample at room temperature in the well-stirred atmosphere within a desiccator above a 10% aqueous solution of sulfuric acid. This moisture content corresponds to a relative humidity (*RH*) of about 95%. Because at this and lower relative humidities, the hygroscopic moisture is directly proportional to the *RH* value, tests may be performed at higher sulfuric-acid concentrations corresponding to lower relative humidities. This test is especially advantageous because at lower humidities the contribution by capillary condensation is minimized if not eliminated, and the hygroscopicity values obtained are significant soil parameters expressive of the specific surface and the physicochemical characteristics of the soil constituents. This significance is lessened or even destroyed by the presence of soluble salts. The close relationship between W_{hc} and heat of wetting is exemplified by the fact that the heat of wetting in calories per gram of oven-dry soil is about $0.5 \times W_{hc}$ (10% H_2SO_4) and $0.75 \times W_{hc}$ (30% H_2SO_4).

Capillary condensation, which can contribute significantly to water-vapor sorption at high relative humidities, may be understood from, but not calculated by, the expression $dp/p = 2\sigma M/(r\delta RT)$ where dp is the change in vapor pressure above a meniscus with radius of curvature r, p is the vapor pressure over a free-water surface, R is the gas constant, and T the absolute temperature in *K;* σ, M and δ are the surface tension, molecular weight, and density of the water. An approximate measure of the contribution of capillary condensation to total water sorption is the difference between hygroscopicity measured at or close to 100% *RH* and the value obtained for this *RH* by linear extrapolation from hygroscopicity data determined at less than 95% *RH*.

Hans F. Winterkorn

Bibliography

Anon., 1952. *Landolt-Börnstein: Zahlenwerte und Funktionen, Bodenkunde*, **3**(3237): 358–368.

Baver, L.D., and Winterkorn, H.F., 1935. Sorption of liquids by soil colloids. *Soil Sci.*, **40**: 403–419.

Gregorich, E.G., Turchenek, L.W., Carter, M.R., and Angers, D.A., 2001. *Soil and Environmental Science Dictionary.* Boca Raton, FL: CRC Press, 577 pp.

Winterkorn, H.F., and Fang, H.Y., 1975. Soil technology and engineering properties of soils. In Winterkorn, H.F., and Fang, H.Y., eds., *Foundation Engineering Handbook.* New York: Van Nostrand Reinhold, pp. 67–120.

Cross-references

Capillary Pressure
Heat Capacity
Water Content and Retention

HYPOGENE

Formed under the surface; applied to rocks otherwise called primary and metamorphic; also, subterranean, hypogean.

I

ICE EROSION

Glaciers are large perennial bodies of ice that move under gravity (Benn and Evans, 1998). The term was originally applied to bodies of ice moving in mountain valleys. Later, it was extended to ice sheets that cover sizeable regions including areas of continental dimensions. A distinction is made between polar (or cold) and temperate glaciers, with temperate glaciers being the ones that do most of the erosion. Both types move by internal flow, while temperate glaciers move also by basal sliding lubricated by water in the liquid state (Figure I1). Glaciers terminate along a margin where forward flow is balanced or exceeded by melting.

Erosion by ice has three important aspects in the context of soil science: *(a)* the effect on pre-glacial soils and surfaces, *(b)* the effect on the post-glacial landscape, and *(c)* the effect on post-glacial soil parent materials. In addition, it is also important to consider the near glacial, or periglacial environment in the same context.

Effect on pre-glacial soils and surfaces

The most obvious effect of glaciers on the pre-existing landscape is the scraping off of soils and regolith, commonly leaving exposed bedrock, especially in the shield areas of the northern hemisphere. The bedrock surfaces commonly (though not invariably) still retain evidence of grinding, polishing, scraping and plucking (for example, chatter marks, striae and striations) thousands of years after the ice has disappeared, indicating minimal weathering of the rock since the ice left.

The nature of pre-glacial weathering systems can be determined in regions where cold base glaciers (glaciers in which the basal layer was frozen to the substratum) have left remnants of ancient regolith or soil (paleosol). From these scattered remnants it is clear that even at high latitudes, weathering of the land surface had reached a stage of considerable maturity in Europe, and North America (Mellor and Wilson, 1989, Chesworth and Evans, 1982), the almost ubiquitous presence of gibbsite (Dejou et al., 1970) indicating a late stage of weathering (Jackson, 1968). Most probably this is a consequence of the fact that much of the Earth outside of volcanic and orogenic zones, had undergone tens of millions of years of essentially undisturbed weathering and pedogenesis during the Tertiary period (approximately 1.5 to 65 million years ago), before global cooling had given rise to the Pleistocene glaciations.

In terms of the pre-glacial landform, glaciers operate mainly by modifying pre-existing features formed by running water (Charlesworth, 1957). This is perhaps most obvious in the case of river valleys in alpine terrain – eroded into their characteristic U shape, with hanging valleys left high on the main valley walls, at points where tributary glaciers fed into the main glacier. Higher in the mountains cirques, tarns, horn peaks, and arêtes are characteristic.

Effect on the post-glacial landscape

Modification of pre-glacial landscapes by the destructive effects of ice erosion has already been noted. The principal constructive effects are seen where materials carried by ice are left on the landscape (usually modified by meltwater and wind) when the ice departs. The most characteristic feature of a post-glacial landscape is the moraine. In glaciated mountain valleys there are three types, lateral, medial, and end moraines, the qualifying adjective indicating their position with respect to the glacier. Similarly continental ice sheets leave several types of moraine as a prominent post-glacial landform (Figure I2). Moraines are usually hummocky, and as a consequence tend to have highly variable slopes over short distances. Water erosion during deglaciation flushes finer materials into the hollows between hummocks, leaving coarser materials upslope. Because of this, soils developed on moraines commonly show much local textural variation.

Ice also smooths prominences on the landscape into drumlins, while meltwater lays down eskers below ice, kames upon it, and various types of outwash deposit, including braided stream, deltaic, lacustrine and marine sediments beyond the ice front.

Isostatic rebound, well documented in Scandinavia and Canada, has also affected (and is still affecting) the post

Pleistocene landscape. This is responsible for the newly emergent wetland landscape of the James Bay Lowlands south of Hudson Bay, and for the exposure of marine clays in northern and eastern Canada, and northern Russia and Siberia.

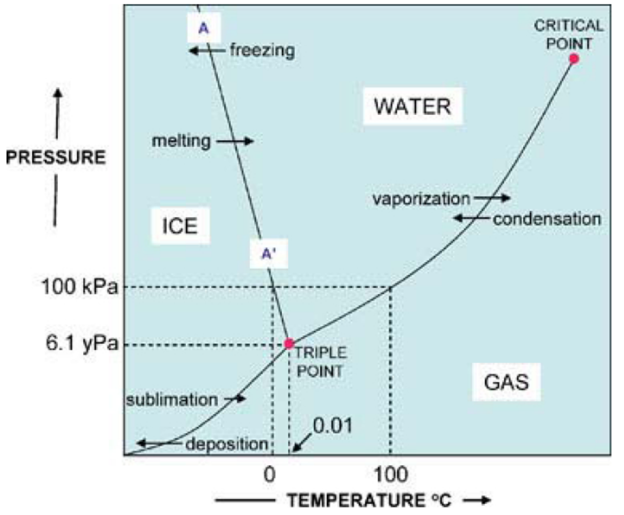


Figure I1 The system H_2O at low temperature and pressure. More than 10 polymorphs of ice are known, the ice field shown is for Ice *I*, the form stable at the surface of the Earth. Of particular significance in the context of glacier ice is the curve *A–A′*, which marks the univariant equilibrium between ice and water. The negative slope means that ice can melt, not only by an increase in temperature, but also isothermally, by an increase in pressure. This commonly leads to melting at the base of a glacier and consequent lubrication of the moving ice mass. See also Figure M2.

Effect on post-glacial soil parent materials

The principal soil parent material in glaciated terrain is till, an unsorted mixture of whatever the ice was carrying, left directly on the landscape when the glacier melted. The characteristic makeup of till is indicated by a term still used in Britain, boulder clay: a morainic deposit in which boulders, cobbles and gravel sized particles, not in contact with each other (as they would be in a water laid conglomerate), are embedded typically in a matrix of clay, though matrices of sand or silt are not uncommon. Pettijohn (1957) proposed the term paraconglomerate for deposits with this type of texture though most recent workers refer to them as diamicton.

For the most part, the constituents of till are derived from the bedrock overridden by the glacier or ice sheet, and are thus related to the solid geology of a glaciated region. The calcareous tills of southern Ontario for example are predominantly composed of materials derived from the Paleozoic bedrock with an admixture of Precambrian rocks transported from the Canadian Shield. The Precambrian component varies from 2 or 3% (Dreimanis, 1960) in the south to virtually 100% in central and northern Ontario, where the Shield itself is exposed.

The presence of material derived from the pre-glacial regolith has been inferred from the study of the cosmic-ray-produced radionuclide ^{10}Be, which is abundant in deeply weathered soils. Balco et al. (2003), discovered that ^{10}Be-rich till occurs twice in tills deposited by the Laurentide Ice Sheet in eastern North America. On that basis they conclude that regolithic materials were eroded first at the immediate onset of glaciation, as would be expected, but also later in the middle Pleistocene during an apparent expansion of either the size of the ice sheet, or of the area of thawed-bed conditions.

Extensive reworking of tills by meltwater is a major feature of glaciated terrain resulting in deltaic, braided stream, outwash

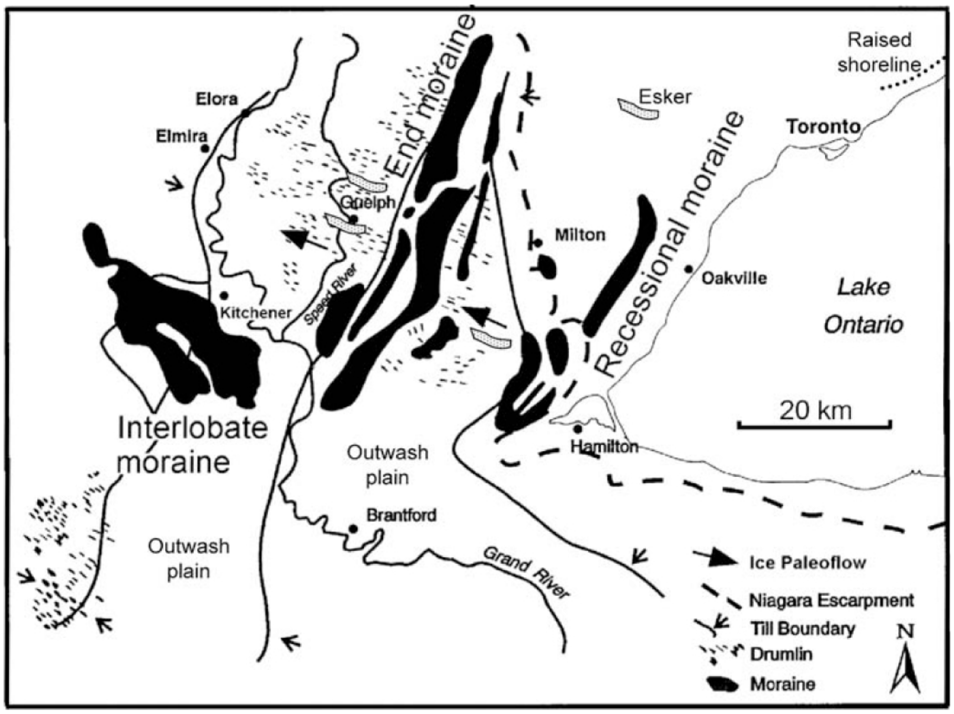


Figure I2 Glacial features of the landscape west of Lake Ontario, Canada (modified from Martini et al., 2001).

plain, lacustrine and marine deposits (Martini et al., 2001). These tend to be highly variable, relatively poorly sorted to well sorted sand and gravel admixtures close to the melting ice, with silts and clay further away from the active margin, where the meltwater has lost much of its energy. Discontinuous patches of silt and clay are also common where water became ponded behind a moraine or in the highly variable topography associated with stagnant ice margins.

Periglacial features

Beyond the ice front, freezing and thawing of the ground is active with an intensity that generally diminishes with distance from the glacier. This is the periglacial zone (French, 1996). Closest to the ice permanently frozen ground or permafrost is found. Further away, the permafrost becomes discontinuous until it disappears entirely as ambient conditions become warmer. Two processes are especially active in the periglacial zone: cryoturbation and wind erosion.

Cryoturbation is the collective term for geological and pedological disturbances associated with frost (Vandenberghe, 1992). The fundamental driving force is the expansion of water on freezing, and the growth of ice masses in surficial materials, and the contraction on thawing, and the wasting away of ice concentrations (Figure I1). Growth of ice bands, lenses and larger masses is important within the permanently frozen ground, and as climate ameliorates and the ice masses melt, collapse of the land surface into the vacated space, gives rise to the phenomenon of thermokarst. However, from a pedological point of view, the effects of cryoturbation are most obvious at the surface of permafrost, where a so-called active layer is subject to a yearly freeze-thaw cycle.

The principle effects of cryoturbation are the development of frost wedges in soil, the movement of active layer materials downslope (solifluxion), the formation of patterned ground (circular, polygonal and linear sortings of stones, brought about by frost heave and solifluxion), and the raising of hummocks of various kinds both within and without the zone of permafrost (van Vliet-Lanoe and Seppala, 2002, and Figure I3). The common adjective used for these features in geomorphology and soil science is cryogenic (see Valcarcel-Dıaz et al., 2006, for examples in the southern hemisphere).

Wind erosion has profound effects on the periglacial landscape principally because much of the region is only recently vacated by ice, contains loose sediments of various kinds, and does not yet have a well developed protective cover of vegetation. Clay and silt sized particles are winnowed from surficial deposits, transported over great distances, and have given rise to extensive loess deposits in the northern hemisphere and in South America.

Loess is a silty, quartz-rich sediment, transported by wind under periglacial conditions and deposited typically in cold steppic environments close to the edges of large ice-sheets (Antoine et al., 2003, and Figure I4). An important mineralogical component is calcite (approaching a maximum of 20%). Redistribution of loess by water transport has been important in extending the area of coverage of this material along the great river valleys such as the Mississippi, Huang and La Plata.

Liquefaction of sensitive clays is not uncommon in periglacial regions, though not restricted to them. The most susceptible clays are 2:1 type, and are found for example, in certain glaciomarine deposits such as those of the Champlain Sea now exposed along the St. Lawrence in eastern North America. Clay content, type of clay, and water content, are the principal factors that determine soil consistency. In terms of engineering properties the dry, fine grained soils developed on the clays of the Champlain Sea, behave as solids. As water content increases, they become plastic and eventually behave as liquids, when there is a high enough water-content to separate each soil particle from its neighbors. The change from solid to plastic behavior and from plastic to liquid behavior (in a standardized laboratory test), may be defined in terms of the water content at which a standard amount of applied energy causes a given transition. The water content for the solid-plastic transition is the plastic limit, and for the plastic-liquid transition is the liquid limit. Together, they are called Atterberg limits, after Albert Atterberg (1846–1916), the Swedish scientist who first defined them. On a landscape covered by water-saturated soils of this type, a sudden shock or earth tremor, may shake the soil particles apart causing liquefaction and the catastrophic failure of slopes. Major landslides have been caused in historical times in this way along the Ottawa and St. Lawrence Rivers in Eastern Canada.

Soils

A fundamental reference is Catt (1986) and see also Catt (1979). The main generalizations that can be made about the soils that occur in areas notably affected by the Pleistocene glaciations are:

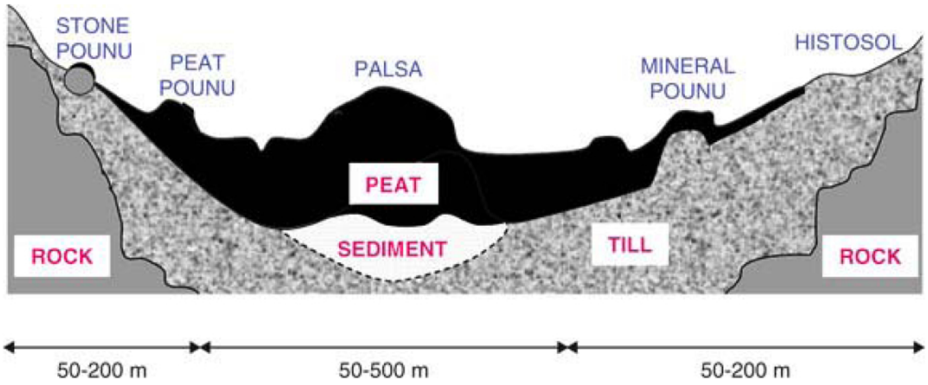


Figure I3 Hummocky landscape features in peat deposits, (adapted from Vliet-Lanoe and Seppala, 2002). For the terminology of the hummocks see the section on Useful Vocabulary at the end of this entry.

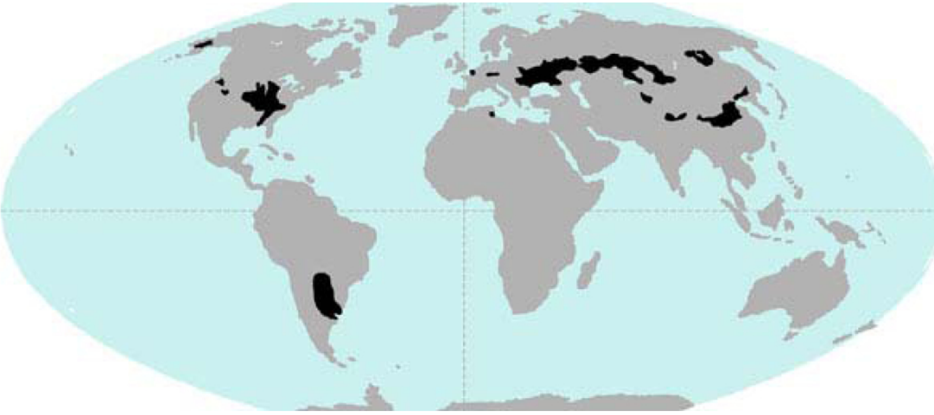


Figure I4 Major deposits of loess around the globe (adapted from Muhs and Bettis, 2003). The deposits are more or less coincident with major grasslands (with Chernozems and Kastanozems) in drier climates, and temperate, deciduous forest (with Luvisols and Cambisols) in wetter regions.

1. The soils are developed on a wide variety of parent materials. Tills may be any combination of boulders, cobbles, gravel, sand, silt and clay. The lithologies represented are those of bedrock passed over by ice, with lithologies of local provenance predominating. In the taiga and tundra, quartzo-feldspathic materials of cratonic regions are prominent. Further south, Phanerozoic sedimentary rocks abound. Concurrent and postglacial reworking of materials by water and wind produce parent materials ranging from the relatively poorly sorted gravels and sands of braided streams, to well sorted sands, silts and clays of outwash plains. Of immense economic significance is the extensive wind-deposited loess, particularly along the southern margin of the ice masses of the northern hemisphere.
2. Compared to unglaciated areas, the soils are inevitably young. For example, Protz et al. (1984) examined a transect of soils from the coast of Hudson Bay to about 70 km inland. The coast is emergent (isostatic rebound) and the soils ranged in age from about 100 years near the coast to more than 5 000 years at the further extreme. The parent materials are calcareous, and an Ah horizon required about 750 years to develop. Leaching of calcite from the upper part of the profile was sufficient to allow an Ae–Bh combination to develop in about 1 900 years, and an Ae–Bf sequence of horizons in 2 300 years. South of their area, Podzols continue through the boreal forest and the southern limit of the Canadian Shield, to landscapes between 11 000 and 12 000 years old. Older glaciated landscapes, (including extensions into the United States to a limit approaching 20 000 years old) include Cambisols and Luvisols (see Figure I5 where Cambisols are shown as Brunisols).
3. The emergent land around the coast of the Arctic Ocean is low-lying, commonly underlain by glaciomarine clays, and generally poorly drained and waterlogged due to persistent underlying permafrost. Wetland is the characteristic landform, with gleysols, sphagnum peats, peatlands and Histosols, all well developed (Tarnocai and Stolbovoy, 2006; Martini, 2006).
4. On deglaciation, the soils and surface materials have been subjected to periglacial processes. With increasing age soil–forming activities render the periglacial features more

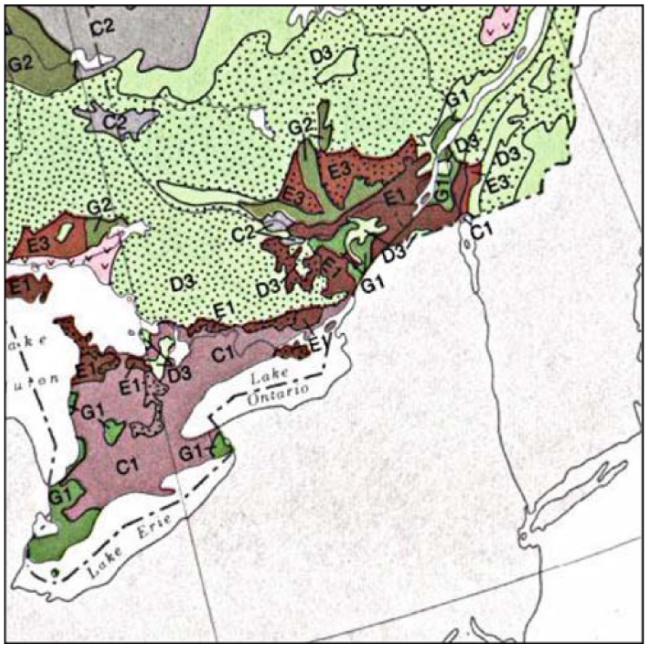


Figure I5 Soil distribution on glacial deposits of Quebec and Ontario, Eastern Canada (from Natural Resources Canada, 2002). Key: *D3* humo ferric Podzol; *G1* humic Gleysol; *G2* Gleysol; *C1* gray brown Luvisol; *C2* gray Luvisol; *E1* melanic Brunisol; *E3* dystric Brunisol. Areas marked with a *'v'* symbol are exposures of bedrock, with striae and chatter marks. Soils in the *dotted* region tend to be stony. There is a marked change in till composition from the Shield area (approximately the area dominantly podzolic, with quartzo-feldpathic materials prominent in the parent material), to the peninsula of southern Ontario (predominantly luvisolic with parent materials rich in carbonate materials). The Gleysols occur on poorly drained clays, mostly deposited in previous extensions of the Great Lakes, or of the Sea (in the St. Lawrence valley for example). Note that in this figure the terminology accords with a Canadian system of soil classification. Podzol, Gleysol and Luvisol are essentially as in the WRB system, whereas the Brunisol area would be labelled Cambisol in the WRB system.

and more occult, though soils on landscapes that have been free of ice for 14 000 years in southern Canada, still reveal evidence of frost wedging and patterned ground (Morgan et al., 1972; Karrow et al., 2001).

5. Because the Pleistocene ice sheets removed pre-glacial soils, the glacial and post–glacial deposits represent one of the significant ways by which the planetary surface is rejuvenated and the plant-nutrient content of the land surface is boosted (Chesworth, 1982). To begin with, this is potential rather than realized, and needs perhaps one to two thousand years of weathering to produce what might be recognized as a fertile soil. Generally, the most fertile soils are those that have developed on parent materials of largely Phanerozoic provenance, with 10 000 years or more of soil forming activity: the Luvisols of western Europe and southern Ontario for example in regions with annual rainfall of around 600 mm or more, and the Chernozems and Kastanozems of the Eurasian steppes and the North American prairies, in regions with annual rainfall between 200 and 500 mm.

Useful vocabulary

Accretionary soil: a soil buried slowly enough that pedological processes continue during burial.

Active layer: the uppermost layer of permafrost that thaws to depths of a few centimeters to 2–3 m, during the warm season. It is the site of the only significant biological activity in the soils of the tundra.

Alas: a steep sided, more or less circular depression with a flat floor created by the collapse of the land surface when ice below it melts. A kind of thermokarst.

Arete: Common in mountains as a sharp ascending ridge or ‘edge’, between adjacent cirques for example.

Boulder clay: used as the name of a formation (ground moraine) and of the material of which the formation is made – boulders and rock fragments, randomly embedded in clay, but with great variation in the matrix, which may be gravelly and sandy in places. The preferred usage is till.

Braided stream: a network of interwoven stream channels separated by sand and gravel bars, and characteristic of glacier fronts where copious amounts of high-energy meltwaters, are charged with a large sedimentary load.

Buried soil: a soil that is rapidly buried and prevented from further pedological development by being removed from interaction with the atmosphere.

Chatter mark: a curved, almost conchoidal fracture made on a surface by a fragment of rock on the under-surface of glacier ice, the name implying a jerky motion of the ice.

Cirque: A natural amphitheater, or rounded hollow or plain encircled by heights; esp. one high up in the mountains at the head of a stream or glacier. Designated glacial cirque (or amphitheater) when glacial derivation is known. Synonyms are corrie and cwm.

Crevasse infilling: the solid materials that fall into cracks on a glacier’s surface, and that are left as more or less linear mounds on the landscape when the ice melts.

Cryogenic: Of or pertaining to the production or use of very low temperatures.

Cryostatic pressure: pressure generated by the volumetric expansion of water on freezing. Responsible for frost heave and other forms of cryoturbation.

Cryoturbation: disturbance of soil or other materials of the land surface, by the freezing and thawing, solifluxion and other cryogenic processes.

Diamicton: term used for a deposit/material, composed of a poorly sorted mixture of gravel, sand, silt and clay. Diamicton can form as a result of a variety of glacial and non-glacial processes. The term is used to describe poorly sorted materials, with no genetic implication. This is in contrast to the term ‘till’, which requires direct deposition by ice. Diamictite is the lithified equivalent of diamicton.

Drift: A term applied to Pleistocene deposits of glacial and fluvioglacial detritus, also known as boulder-clay, and till. A term still used in Europe though dating from a period when such materials were believed to be deposited by Noah’s flood (whence also the synonym ‘diluvium’).

Drumlin: a lenticular or pear-shaped mound, molded beneath a glacier, and having a steep slope towards the upstream direction of the ice, and a gentler sloped tail downstream.

Esker: Sinuous, steep sided ridges of gravel and sand, laid down by meltwater beneath a glacier.

Fluvioglacial: formed by rivers and streams issuing from the melting front of a glacier, and laying down outwash materials in deltaic, braided stream, and ephemeral lake deposits.

Glaciation: The condition of being covered by an ice-sheet or by glaciers; glacial action or its result.

Glacier: A large accumulation or river of ice in a high mountain valley, formed by the gradual descent and consolidation of the snow that falls on the higher ground. The resulting mass is often many miles in length, and continues to move slowly downward until it reaches a point where the temperature is high enough to melt the ice as fast as it descends.

Hanging valley: a valley, which is abruptly cut across by the steep side of a larger valley or a sea-cliff.

Horn or horn peak: a steep sided, pyramidal mountain peak formed where a ring of three or four cirques join or coalesce.

Hummock: An equidimensional (i.e. non ridge-like), hill, knoll or protuberance, generally from about one to a few tens of square meters in plan. Hummocks rise above a more or less level surface of a moraine for example, where they represent the irregular pattern of deposition of debris from melting ice. When the core is silt and/or clay the term *earth hummock* is appropriate.

Ice sheet: A sheet or layer of ice covering an extensive tract of land; spec. That supposed to have covered a great part of the northern hemisphere during the glacial period.

Ice wedge: a narrow wedge of ice extending vertically through soil and subsoil in periglacial regions, for up to several meters. The result of repeated seasonal freeze-thaw cycles.

Liquefaction: the temporary transformation of a soil or sediment into a fluid mass. Brought about by a shock or strain, which destroys the internal cohesion of the individual particles of which the material is composed.

Lithalsas: mound of peat with a core of silty-sediment in an otherwise flat peatland.

Kame: Mounds of poorly sorted gravel and sand laid down in streams running on top of glacier ice, with disrupted stratification consequent upon melting of the ice that originally supported the materials.

Meltwater channel: a channel or valley cut by a river or stream of water issuing from the ice-front of a glacier.

Moraine: A mound, ridge, or other feature consisting of debris that has been carried and deposited by a glacier or ice sheet, usually at its sides or extremity; the till or similar material forming such a deposit. Types: ablation, end, ground, lateral moraine, etc.

Nunatak: from the Inuit for “lonely peak” a prominent landform surrounded by ice and projecting above it.

Outwash: The material carried out from a glacier by meltwater and deposited beyond the terminal moraine (chiefly sand and gravel, or, further away, silt and clay); a deposit formed by this. Delta, plain, deposit.

Palsas: circular or elongated mounds of peat, ice and mineral material, in an otherwise, flat peatland. The may reach 10 m in height and have a long axis of as much as 100 m.

Patterned ground: ground showing a definite pattern of stones, fissures, vegetation, etc. (commonly polygons, rings, or stripes), esp. as typical of periglacial regions.

Periglacial: adjective applied to areas marginal to ice sheets, to the cold climate prevailing there, and to the processes and features characteristic of such environments.

Permafrost: permanently frozen subsoil. Pergelisol is a less generally accepted word for permafrost.

Pingo: a large, perennial hill, commonly conical, with an ice core, the growth of which is the generative cause for the hill. From the Inuit pingok – conical hill.

Pounu: a Finnish word meaning a peaty hummock in the zone of discontinuous permafrost, that may have core of mineral soil, of several large stones or of a single large frost-heaved boulder, covered by peat. They are up to 1.2 m in height and 2 m in diameter.

Solifluxion: the movement downslope of water saturated soil and other surficial materials, under the influence of gravity. Terraces, slumps and salients form downslope, and are especially prevalent in the active layer of permafrost.

Striae or Striation: one of a series of grooves etched into a rock-surface. These are often sub-parallel and are formed as a result of erosion by debris-laden ice.

Tarn: a small mountain lake, having no significant tributaries.

Thermokarst: a landscape characterized by collapse structures, pits and depressions, caused by the melting of subsurface ice.

Thufur: a kind of unsorted stone circle raised as a hummock in the active layer of discontinuous permafrost.

Till: an unstratified glacial deposit containing (in no fixed proportions) gravel, sand, and clay, with embedded boulders and rock fragments. Tillite is the name of the rock formed when ancient till becomes indurated.

U shaped valley: a valley with steep sides and a flat bottom, formed or modified by a glacier that was originally present. Tributaries to the main glacier leave hanging valleys along the U-shaped valley, at points where the tributary glaciers joined the main one.

Ward Chesworth, Augusto Perez-Alberti, and
Emmanuelle Arnaud

Bibliography

Antoine, P., Catt, J.A., Lautridou, J.-P., and Sommé, J., 2003. The loess and coversands of northern France and southern England. *J. Quaternary Sci.*, **18**: 309–318.

Balco, G., Stone, J.O.H., and Jennings, C.J., 2003. The fate of preglacial regolith beneath the Laurentide Ice Sheet. Absracts with programs, XVI INQUA Congress, Abstract 64-4.

Catt, J.A., 1979. Soils and Quaternary geology in Britain. *J. Soil Sci.*, **30**: 607–642.

Catt, J.A., 1986. Soils and Quaternary Geology: A Handbook for Field Scientists. Oxford/New York: Clarendon Press/Oxford University Press, 267 pp.

Charlesworth, J.K., 1957. *The Quaternary Era, with Special Reference to its Glaciation*, 2 Vols. London: E. Arnold, 1700 pp.

Chesworth, W., 1982. Late Cenozoic geology and the second oldest profession. *Geosci. Can.*, **9**: 54–61.

Chesworth, W., and Evans, L.J., 1982. Weathering, soil formation and land use in south and central Ontario. Field Excursion 10a, Eleventh International Congress of Sedimentology, Hamilton, Ontario, Canada, 66 pp.

Dejou, J., Guyot, J., Pedro, G., Chaumont, C., and Antoine, H., 1970. Etude sur le probleme de l’origine de la gibbsite dans les arenes granitiques des pays temperes. *Sciences du Sol*, **2**: 15–25.

Dreimanis, A., 1960. Tills of southern Ontario. In *Soils of Canada*. Royal Society of Canada Special Publication No. 3, pp. 80–96.

French, H.M., 2007. *The Periglacial Environment*, 3rd edn. London: Addison & Wesley, 458 pp.

Jackson, M.L., 1968. Weathering of primary and secondary minerals in soil. *Trans. 9th Int. Congr. Soil Sci.*, **4**: 281–292.

Karrow, P.F., McAndrews, J.H., Miller, B.B., Morgan, A.V., Seymour, K.L., and White, O.L., 2001. Illinoian to Late Wisconsinan stratigraphy at Woodbridge, Ontario. *Can. J. Earth Sci.*, **38**: 921–942.

Martini, I.P., 2006. The cold climate peatland of the Hudson bay Lowland, Canada: brief overview of recent work, Chapter 3. In Martini, I.P., Martinez Cortizas, A., and Chesworth, W., eds., *Peatlands: Evolution and Records of Environmental and Climate Changes.* New York: Elsevier, pp. 53–84.

Martini, I.P., Brookfield, M.E., and Sadura, S., 2001. *Principles of Glacial Geomorphology and Geology.* Upper Saddle River, NJ: Prentice-Hall, 381 pp.

Mellor, A., and Wilson, M.J., 1989. Origin and significance of gibbsitic montane soils in Scotland, U.K. *Arctic Alpine Res.*, **21**: 417–424.

Morgan, A.V., 1972. Late Wisconsinan ice-wedge polygons near Kitchener, Ontario, Canada. *Can. J. Earth Sci.*, **9**: 607–617.

Muhs, D.R., and Bettis, E.A., III., 2003. Quaternary loess-paleosol sequences as examples of climate-driven sedimentary extremes. In *Extreme Depositional Environments*. Geological Society of America Special Paper 370, pp. 53–74.

Natural Resources Canada, 2002. *National Atlas of Canada Online*, 6th edn. Ottawa: accessed at http://atlas.nrcan.gc.ca/site/index.html.

Pettijohn, F.J., 1957. *Sedimentary Rocks*, 2nd edn. New York: Harper, 718 pp.

Protz, R., Ross, G.J., Martini, I.P., Terasmae, J., 1984. Rate of podzolic soil formation near Hudson Bay, Ontario. *Can. J. Soil Sci.* **64**(1): 31–49.

Tarnocai, C., and Stolbovoy, B., 2006. Northern peatlands: their characteristics, development and sensitivity to climate change, Chapter 2. In Martini, I.P., Martinez Cortizas, A., and Chesworth, W., eds., *Peatlands: Evolution and Records of Environmental and Climate Changes.* New York: Elsevier, pp. 17–51

Valcarcel-Dıaz, M., Carrera-Go’mez, P., Coronato, A., Castillo-Rodrıguez, F., Rabassa, J., and Perez-Alberti, A., 2006. Cryogenic Landforms in the Sierras de Alvear, Fuegian Andes, Subantarctic Argentina. *Permafrost Periglac. Process.*, **17**: 371–376.

Vandenberghe, J., 1992. Cryoturbations: a sediment structural analysis. *Permafrost Periglac. Process.*, **3**: 343–351.

Vandenberghe, J., Isarin, R.F.B., and van Huisstedenand, J., 1998. *Paleo-Periglacial Phenomena in Northwestern Europe.* Boulder, CO: National Snow and Ice Data Center/World Data Center for Glaciology, Digital Media.

van Vliet-Lanoe, B., and Seppala, M., 2002. Stratigraphy, age and formation of peaty earth hummocks (pounus), Finnish Lapland. *The Holocene*, **12**(2): 187–199.

ICE WEDGE AND POLYGON

Shrinkage cracks due to low temperatures may form in soils in periglacial regions. They become the site of wedge-shaped sheets of ice, thinning downwards, in permafrosted soil. They have dimensions of a few millimeters to several meters. On melting, the resulting fissure will normally fill with soil and sediment and is called a fossil ice wedge. This may retain the wedge-shape, or be irregular in form. In cross section they generally have a polygonal shape, and are one of the components of patterned ground common on landscapes of the permafrost.

Bibliography

Morgan, A.V., 1972. Late Wisconsinan ice wedge polygons near Kitchener, Ontario, Canada. *Can. J. Earth Sci.*, **9**: 607–617.

IGNEOUS

The family of rocks that are formed from magma (a mush of melt and crystals) that solidifies into volcanic rocks at the Earth's surface, hypabyssal rocks under near surface conditions, and plutonic rocks at great depth.

ILLUVIATION

The deposition in a lower horizon of material, particularly clay-sized particles (as in Luvisols, Acrisols and Alisols, for example) that have been transported by water from an upper horizon. The material may be transported in suspension or in solution. Illuviation is complementary to the process of eluviation.

IMBIBITION

The term *imbibition* has several meanings, sometimes being used as a synonym for *wetting* or *infiltration* (*q.v.*). Usage, however, seems to have attached to the word *imbibition* a more restricted meaning. Imbibition is, precisely, the phenomenon of water penetration into a relatively dry porous medium, which is therefore *wetted*, from a saturated source of water (e.g., a water container or a saturated porous medium such as a porous plate) in contact with the porous medium (soil) under the *sole* motor action of the *capillary* forces (see *Capillary pressure*). The thorough understanding of the reason why water at atmospheric pressure will penetrate a porous medium and displace another fluid such as air, also at atmospheric pressure, is of capital importance to gain a sound physical understanding of *water movement* (*q.v.*) in soils. To the extent that a porous medium, as a first rough approximation, can be visualized as a bundle of unconnected cylindrical tubes, some small, some large, there is merit to the study of imbibition in a tube. This over-simplified model of the porous medium is an obviously inaccurate picture of an extremely complex reality. Nevertheless, it provides a convenient and simple introduction to ulterior, more complicated developments.

If the water pressure in the source of water supply is equal to atmospheric pressure, the imbibition is said to be *free*. If that water pressure is greater than atmospheric, the imbibition is *forced;* if it is less than atmospheric, the imbibition is said to be *restrained*.

Free (capillary) imbibition in a tube

Consider a preferentially water-wet, small-diameter tube, initially filled with air. The tube is brought in contact with an ample supply of water at atmospheric pressure (Figure I6). The initial water-air interface may be considered to be the plane *ab*. For an infinitesimal amount of time, the force diagram will be as shown in Figure I6b. The interface will be in equilibrium except at the contact with the solid. There, a net impulse of magnitude proportional to $\sigma_{as}-\sigma_{ws}$ causes the point *a* of the interface to move into the tube. The term σ_{as} is the air-solid surface tension (see *Capillary pressure* for a definition of surface tension), and σ_{ws} is the water-solid surface tension. Because the other points of the interface are in equilibrium, the interface curves in, and it very quickly assumes the shape shown in Figure I6c, where α is the equilibrium wetting angle. The interface is now in equilibrium because the surface tension force and the capillary-pressure force balance one another. Because the pressure drop in the moving-air phase is essentially negligible compared to that in water, the pressure in the air just ahead of the interface is essentially atmospheric. Just behind the interface, the pressure in the water is less than atmospheric by an amount equal to the capillary pressure. At the inlet the pressure is atmospheric. As a result, there exists an unbalanced pressure gradient in the water phase, which causes the water to flow and which sustains the motion initially created by unbalanced surface-tension forces. Viscous shear (particle *A*, Figure I6) will resist the driving force tending to enforce a uniform flow. Actually,

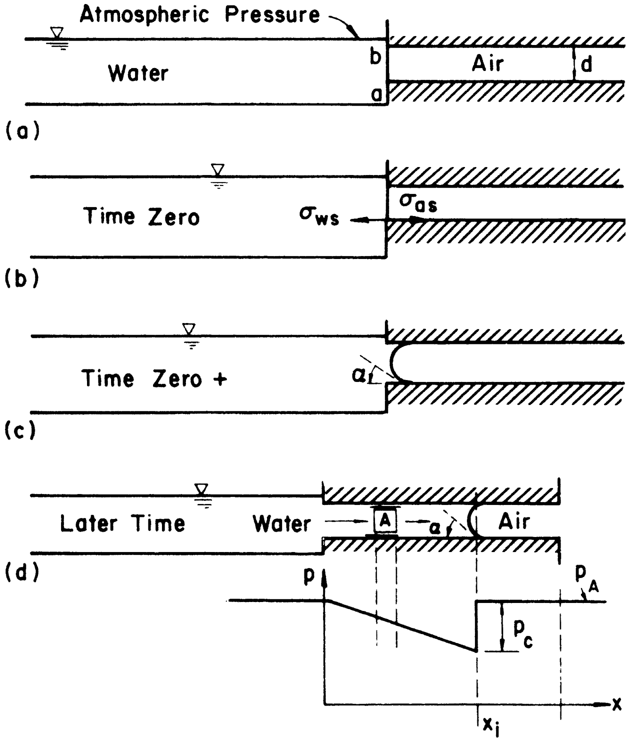


Figure I6 Initiation and evolution of imbibition in a capillary.

flow is constantly retarded because the pressure gradient in the water phase, p_c/x_i, itself decreases with time.

In summary, motion is originated by preferential wettability and later sustained by the induced pressure gradient in the wetting phase.

Entrapment of air

As water moves into the porous medium, it displaces most of the air ahead of its path, but it also manages to trap a fraction of it. How such entrapment takes place can be qualitatively understood by considering a system of interconnected tubes. Figure I7 illustrates the geometry of the simplest of such systems.

First consider an experiment of the same nature as that just described. Assume that atmospheric pressure prevails at both ends of the tubes (Figure I7). Assuming that the interface has the shape of a spherical cap, the capillary pressure at the interface in tube *i* is

$$p_{\mathrm{c}}^{\mathrm{i}} = \left(\frac{2\sigma}{R_{\mathrm{i}}}\right)\cos\alpha \tag{1}$$

Assuming again a negligible pressure drop in the gas phase, the pressure gradient in the water phase is

$$\left(\frac{2\sigma}{R_i}\right)\left(\frac{\cos\alpha}{x_i}\right)$$

where x_i is the location of the water-air interface in tube *i*. Application of *Poiseuille's Equation* for laminar flow in a cylindrical tube (Schlichting et al., 2000, p. 66) yields the velocity of the interface:

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = \frac{R_i\sigma\cos\alpha}{4\mu_{\mathrm{w}}x_i} \tag{2}$$

and after integration:

$$x_i^2 = \frac{R_i\sigma t\cos\alpha}{2\mu_{\mathrm{w}}} \tag{3}$$

where μ_{w} is the (dynamic) viscosity of water. Under free imbibition, it follows from Equation (2) that water flows more rapidly in the larger tube. Thus water will reach point *a* through tube 2 first. Immediately after the water has passed section *a* in tube 2, water imbibes tube 1 due to the rock's preferential wettability to water. An interface starts to propagate into tube 1. It will come to a stop at an equilibrium position somewhere within the constriction between tubes 1 and 2 where the radius is R_{a} such as to satisfy:

$$p_{\mathrm{c}}^{\mathrm{a}} = \frac{2\sigma\cos\alpha}{R_{\mathrm{a}}} \tag{4}$$

Air is then entrapped. Note that the existence of a constriction between tube 1 and tube 2 is a necessary condition for entrapment. Under free imbibition the maximum value for $p_{\mathrm{c}}^{\mathrm{a}}$ is $p_{\mathrm{c}}^1 + p_{\mathrm{c}}^2$. Thus at the point of maximum constriction, the radius must be somewhat less than $(R_1R_2)/(R_1 + R_2)$. Under such conditions, entrapment is stable. In the event of an external pressure gradient such as obtained by a column of water (Figure I8), the constriction must be more severe to constrain air within the smaller tube. The limiting value for R_{a} is the one that gives

$$p_{\mathrm{c}}^{\mathrm{a}} = p_{\mathrm{c}}^1 + p_{\mathrm{c}}^2 + \Delta p \tag{5}$$

Thus

$$R_{\mathrm{a}} < \left(\frac{1}{R_1} + \frac{1}{R_2} + \frac{\Delta p}{2\sigma\cos\alpha}\right)^{-1} \tag{6}$$

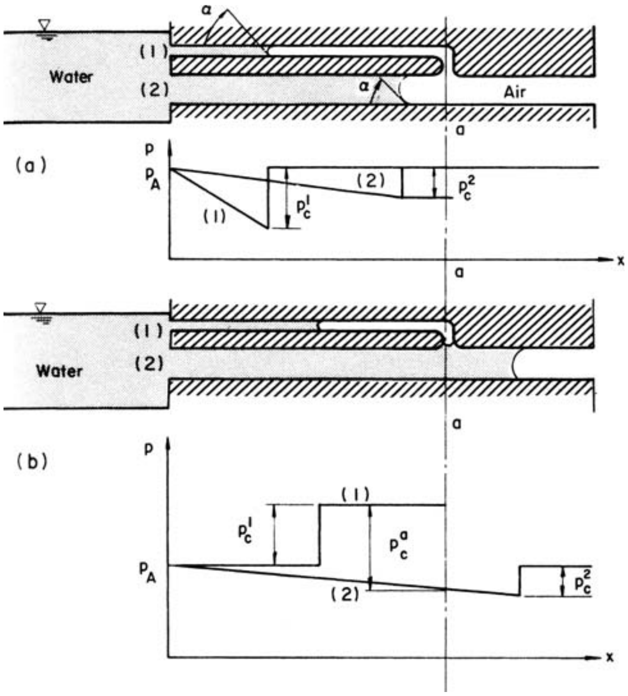


Figure I7 Mechanism of air entrapment in a wetting medium.

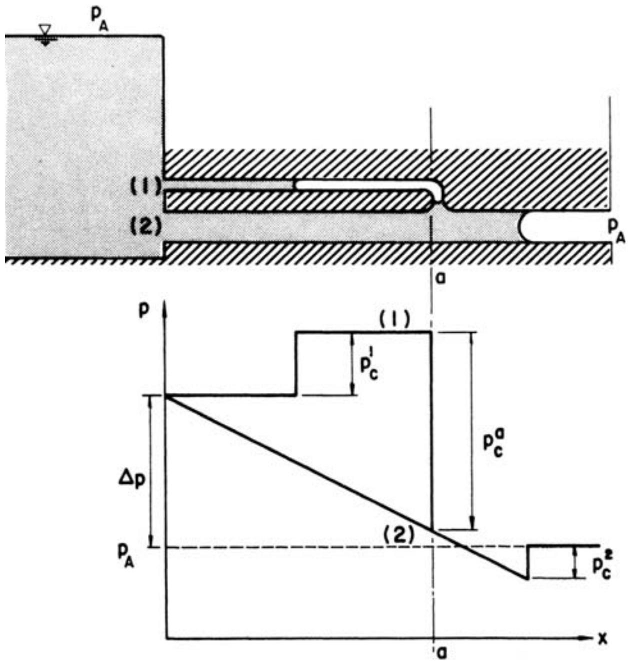


Figure I8 Mechanism of air entrapment under forced imbibition.

The larger the imposed pressure gradient, the less chance there is to entrap air. In the limit for an infinite pressure gradient, there would be no entrapment at all. Under restrained imbibition ($\Delta p < 0$) the opposite is true. It follows that the degree of air entrapment (or the residual air saturation, or the displacement efficiency) depends not only on the geometric characteristics of the medium but also on the rate at which the displacement proceeds.

Imbibition rate in a tube

Let the position of the water-air interface be located at x_f at time t. The pressure distribution in the tube is indicated in Figure I9. Application of Poiseuille's Equation in the water and in the air phases yields for the water and air velocities in the tube, respectively,

$$u_w = \frac{dx_f}{dt} = \frac{R^2}{8\mu_w} \frac{(p_A + \Delta p - p_w)}{x_f} \tag{7}$$

and

$$u_a = \frac{dx_f}{dt} = \frac{R^2}{8\mu_a} \frac{(p_a - p_A)}{(L - x_f)} \tag{8}$$

where L is the length of the tube. As the two velocities must be equal, it follows by equating u_w and u_a that the unknown p_w and p_a must be related by the equalities:

$$\begin{aligned} \frac{p_a - p_A}{\mu_a(L - x_f)} &= \frac{p_A + \Delta p - p_w}{\mu_w x_f} \\ &= \frac{p_c + \Delta p}{\mu_a(L - x_f) + \mu_w x_f} \end{aligned} \tag{9}$$

from which the velocity dx_f/dt can be obtained as a function of the interface position, namely,

$$\frac{dx_f}{dt} = \frac{R^2}{8} \left[\frac{p_c + \Delta p}{x_f(\mu_w - \mu_a) + \mu_a L} \right] \tag{10}$$

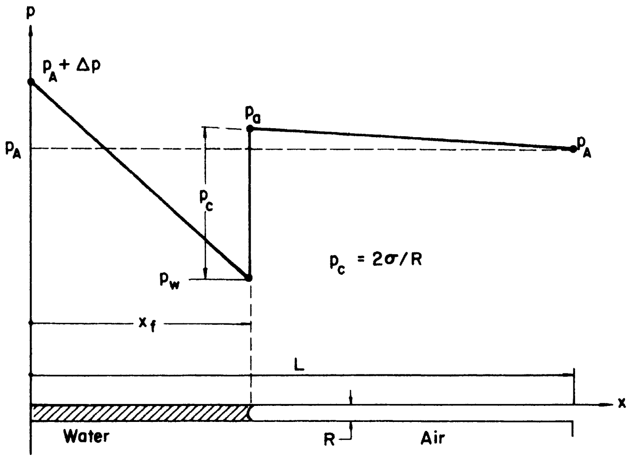


Figure I9 Pressure distribution in a capillary tube.

After integration, one obtains

$$x_f = \frac{\sqrt{(\mu_a L)^2 + (\mu_w - \mu_a)(R^2/4)(p_c + \Delta p)t} - \mu_a L}{\mu_w - \mu_a} \tag{11}$$

from which the imbibition rate $I = dx_f/dt$ can be deduced as a function of time:

$$I = \frac{1}{2} \frac{R^2/4(p_c + \Delta p)}{\sqrt{(\mu_a L)^2 + (\mu_w - \mu_a)(R^2/4)(p_c + \Delta p)t}} \tag{12}$$

If the viscosity of air is desregarded compared to that of water ($\mu_w/\mu_z \equiv 50$), Equation (12) reduces to the simpler form:

$$I = \frac{1}{2} \frac{S_P}{\sqrt{t}} \tag{13}$$

where

$$S_P = \sqrt{\frac{R^2}{4\mu_w}(p_c + \Delta p)} \tag{14}$$

can be called the "Poiseuille *sorptivity*." The sorptivity characterizes the ability of the *tube* to imbibe *water*. Under forced, free, or restrained imbibition, Δp is positive, zero, or negative, respectively. Equation (13) yields an infinite imbibition rate at time zero, which is not physically realistic. However, if the terms in μ_a are not disregarded, as in Equation (12), then the imbibition rate is not infinite (singular) at time zero. Equation (13) is a good approximation for Equation (12) for *large* values of *time*, and it shows that the (asymptotic) imbibition rate decreases like the *inverse of the square root of time*. On the other hand, for small times the Taylor expansion of Equation (12), truncated after the first-order term, yields

$$I = \frac{R^2(\Delta p + p_c)}{8\mu_a L} - \frac{R^4(\Delta p + p_c)^2(\mu_w - \mu_a)t}{64(\mu_a L)^3} \tag{15}$$

which shows that the imbibition rate *decreases linearly with time for small times* and is finite at time zero.

Free imbibition rate in a bundle of tubes

Let $n(r)dr$ represent the number of tubes of radius between r and dr. Defining

$$\delta(r) = \frac{n(r)}{N}, \ \delta(r)$$

is the density function of the number of tubes of size r. From its definition the integral of $\delta(r)$ between the limits of zero and infinity is one. For a bundle of tubes, the *average* imbibition rate (disregarding air viscosity) per unit bulk cross-section area is deduced from Equations (13) and (14) to be:

$$I = \frac{1}{2\sqrt{t}} \left\{ \phi \sqrt{\frac{\sigma}{2\mu_w}} \frac{\int_0^\infty r^2 \sqrt{r}\delta(r)\, dr}{\int_0^\infty r^2 \delta(r)\, dr} \right\} \tag{16}$$

where φ is the porosity of the tube system.

From the analogy of Poiseuille's and Darcy's law, the *conductivity* of a tube filled with water can be defined by the relation:

$$K(R) = \frac{R^2 \rho_w g}{8\mu} \tag{17}$$

Introducing this notation and that of the capillary-pressure head, Equation (16) takes the form:

$$I = \frac{1}{2\sqrt{t}} \left\{ \phi \frac{\int_0^\infty \sqrt{2K(r)h_c(r)}\; K(r)\delta(r)\,\mathrm{d}r}{\int_0^\infty K(r)\delta(r)\,\mathrm{d}r} \right\} \tag{18}$$

The application of the mean theorem to the integral in the numerator of Equation (18) yields:

$$I = \frac{1}{2}\phi\sqrt{\overline{2K(r)h_c(r)}}\frac{1}{\sqrt{t}} \tag{19}$$

where the bar over the term $2K(r)h_c(r)$ means the appropriate mean value of this quantity. Equation (19) suggests that there is a bundle of tubes of *uniform* size R, which is equivalent to the bundle of tubes of different sizes, such that,

$$\sqrt{K(R)h_c(R)} = \sqrt{\overline{K(r)h_c(r)}} \tag{20}$$

Imbibition rate in a porous medium

The results of the previous section are not of great practical interest because a porous medium is a far more complex system. Besides, the $\delta(r)$ distribution is unknown. Nevertheless, the equations have provided insight to the solution of the problem of predicting the imbibition rate in a *real* porous medium.

The water-content equation (without air effect)

Away from the water source the soil is dry; its *water content* (*q.v.*) is low. Close to the source it is high. At a fixed location x_0 (Figure I10), the soil gets wetter as time passes. In general, the water content θ is a function of x and t. The variation of θ in time at a fixed location x is related to the net inflow of water at that time through the principle of conservation of mass, which expressed in mathematical symbols, reads:

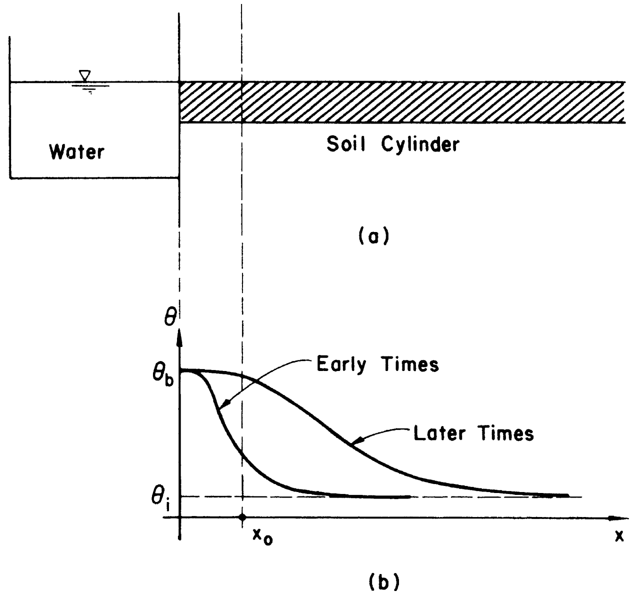


Figure I10 Water-content evolution in a horizontal soil slab.

$$\frac{\partial\theta}{\partial t} + \frac{\partial}{\partial x}(v_w) = 0 \tag{21}$$

where v_w is the water velocity in a Darcy sense (i.e., a volume flow rate per unit bulk cross-section area in a direction perpendicular to flow). The water velocity is given by Darcy's law, namely,

$$v_w = -K(\theta)\frac{\partial h_w}{\partial x} \tag{22}$$

or

$$v_w = K(\theta)\frac{\partial h_c}{\partial x} = \left[K(\theta)\frac{\partial h_c}{\partial\theta}\frac{\partial\theta}{\partial x}\right] \tag{23}$$

if one assumes that air pressure is atmospheric everywhere in the medium. The term $K(\theta)$ is the *unsaturated hydraulic conductivity*. It measures the conductivity of the medium to water at various water contents. Substitution of Equation (23) in Equation (21) yields the *water-content equation*, also called *Richard's Equation*:

$$\frac{\partial\theta}{\partial t} + \frac{\partial}{\partial x}\left[K(\theta)\frac{\partial h_c}{\partial x}\right] \tag{24}$$

Defining a new positive function of water content, the *diffusivity*, namely,

$$D(\theta) = -K(\theta)\frac{\partial h_c}{\partial\theta} \tag{25}$$

the water-content equation takes the form referred to as the *diffusivity equation*, namely,

$$\frac{\partial\theta}{\partial t} - \frac{\partial}{\partial x}\left[D(\theta)\frac{\partial\theta}{\partial x}\right] = 0 \tag{26}$$

Approximate solutions of the water-content equation

The Green and Ampt solution. It is assumed that the initial water content of the soil is uniform at value θ_i. At time zero, the soil is placed in contact with the water supply. Immediately the water content takes the value $\tilde{\theta}$, water content at *natural* saturation (that is, $\Phi - \theta_{ar}$, where θ_{ar} is the residual air content) at $x = 0$ and keeps this value there indefinitely thereafter. Green and Ampt assumed that there exists a wetting *front* that separates a fully saturated zone and a zone still at the initial water content. With this assumption, in the fully wetted zone, $\theta = \tilde{\theta}$ and does not vary with time. Application of Equation (24) in this zone yields $\partial h_c/\partial x =$ constant. In other words, the capillary pressure increases linearly with the distance x, which means that the water pressure decreases linearly with x as in the case of a capillary tube. The same reasoning therefore yields for the velocity of propagation of the front, V_f (see Figure I11):

$$V_f = \frac{\mathrm{d}x_f}{\mathrm{d}t} = \frac{\tilde{K}H_f}{x_f(\tilde{\theta} - \theta_i)} \tag{27}$$

where H_f is the capillary-pressure head at the front. After integration for x_f, one obtains:

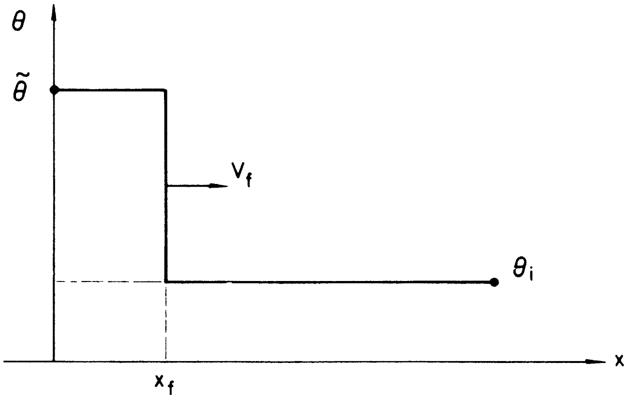


Figure I11 The Green and Ampt (piston) displacement model.

$$x_{\mathrm{f}} = \sqrt{\frac{2\tilde{K} H_{\mathrm{f}}\, t}{\tilde{\theta} - \theta_{\mathrm{i}}}} \tag{28}$$

and the imbibition rate is finally:

$$I = \frac{1}{2}\sqrt{2(\tilde{\theta} - \theta_{\mathrm{i}})\tilde{K} H_{\mathrm{f}}}\,\frac{1}{\sqrt{t}} \tag{29}$$

From Equation (29) one deduces the *Green and Ampt sorptivity:*

$$S_{\mathrm{f}} = \sqrt{2(\tilde{\theta} - \theta_{\mathrm{i}})\tilde{K} H_{\mathrm{f}}} \tag{30}$$

In a capillary tube the capillary pressure on the water side of the meniscus is well defined: $2\sigma/r$. Unfortunately, H_{f}, the capillary-pressure head at the wetting front, is not.

From the Green and Ampt model it is not possible to relate H_{f} to the soil characteristic curves. The term H_{f} is in a sense some sort of *average* capillary pressure. It can be determined for a given soil from experiments.

It has been suggested that a *weighted* average value of capillary-pressure head should be used with the relative permeability to water k_{rw}, which is a function of h_{c}, as the weight. Then one obtains an effective capillary drive, H_{b}, defined by the equation:

$$H_{\mathrm{b}} = \int_0^{h_{\mathrm{ci}}} k_{\mathrm{rw}}\, \mathrm{d}h_{\mathrm{c}} \tag{31}$$

where $h_{\mathrm{ci}} = h_{\mathrm{c}}(\theta_{\mathrm{i}})$, the initial capillary-pressure head, leading to the *Bouwer sorptivity*:

$$S_{\mathrm{b}} = \sqrt{2(\tilde{\theta} - \theta_{\mathrm{i}})\tilde{K} H_{\mathrm{b}}} \tag{32}$$

Experience has shown that this sorptivity led to quantitatively good predictions of the imbibition rate.

Gardner's solution. For a constant diffusivity $\bar{D}$, independent of water content, the diffusivity equation, Equation (26), is linear with constant coefficients. Its solution for a uniform initial water content θ_{i} and a fixed boundary value θ_{b} (Figure I10b) is:

$$\frac{\theta - \theta_{\mathrm{i}}}{\theta_{\mathrm{b}} - \theta_{\mathrm{i}}} = \mathrm{erfc}\left(\frac{x}{\sqrt{4\bar{D}t}}\right) \tag{33}$$

where erf*c*( ) is the complementary error function defined as:

$$erfc(u) = 1 - \frac{2}{\sqrt{\pi}} \int_0^u \mathrm{e}^{-\xi^2}\, \mathrm{d}\xi \tag{34}$$

From Equation (33) one can deduce the imbibition rate:

$$I = \frac{1}{2}(\theta_{\mathrm{b}} - \theta_{\mathrm{i}})\sqrt{\frac{4\bar{D}}{\pi}}\,\frac{1}{\sqrt{t}} \tag{35}$$

from which one deduces the *Gardner sorptivity:*

$$S_{\mathrm{G}} = (\theta_{\mathrm{b}} - \theta_{\mathrm{i}})\sqrt{\frac{4\bar{D}}{\pi}} \tag{36}$$

The solution is exact in the sense that Equation (33) is an exact solution of Equation (26) when D is constant, but in reality, it is a very approximate one because the diffusivity varies tremendously with water content. Defining the average diffusivity $\bar{D}$ as

$$\bar{D} = \frac{\int_{\theta_1}^{\theta_{\mathrm{b}}} w(\theta)\, D(\theta)\, \mathrm{d}\theta}{\theta_{\mathrm{b}} - \theta_{\mathrm{i}}} = \frac{\tilde{K} \int_{\theta_{\mathrm{i}}}^{\theta_{\mathrm{b}}} w\, k_{\mathrm{rw}}\, \mathrm{d}h_{\mathrm{c}}}{\theta_{\mathrm{b}} - \theta_{\mathrm{i}}} \tag{37}$$

where *w*( ) is an appropriate weight function, Equation (36) takes the form:

$$S_{\mathrm{G}} = \sqrt{\frac{4}{\pi}(\theta_{\mathrm{b}} - \theta_{\mathrm{i}})\tilde{K} \int_{h_{\mathrm{cb}}}^{h_{\mathrm{ci}}} w\, k_{\mathrm{rw}}\, \mathrm{d}h_{\mathrm{c}}} \tag{38}$$

As with the Green and Ampt approach, the problem is the choice of the weight *w*.

Parlange's solution. Figure I12 indicates that as imbibition proceeds, there is a region near the water-entry (boundary) face where the water content no longer changes value significantly with time. In that region, $\partial\theta/\partial t$ is essentially zero. From Equation (21) one concludes that in this region $\partial v_{\mathrm{w}}/\partial x$ is essentially zero or in other words, that the water flux is constant with distance in this region. Symbolically,

$$v_{\mathrm{w}} = -D\frac{\partial\theta}{\partial x} = v_{\mathrm{w}}|_{x=0} = I \tag{39}$$

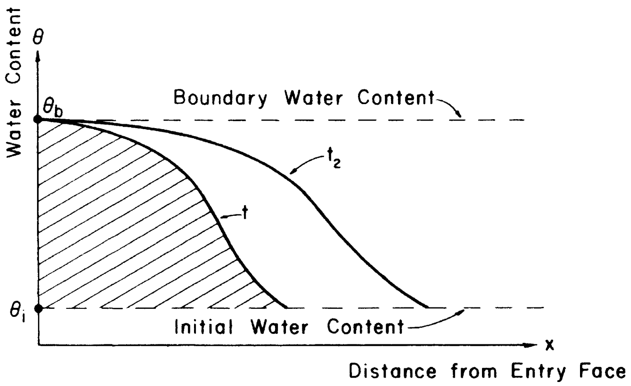


Figure I12 Time evolution of water-content profile in a horizontal soil.

Naturally the imbibition rate I still varies with time. Equation (39) for a fixed t is an ordinary differential Equation in θ and x that can be integrated with the result:

$$x = \frac{1}{I(t)} \int_{\theta}^{\theta_b} D(\alpha)\,d\alpha = \frac{1}{I(t)} \int_{h_{cb}}^{h_c} k_{rw}\,dh_c \tag{40}$$

Equation (40) provides the position x of a given water content θ at a given time t. It is a good approximation to the exact profile near the water-entry face, away from the wetting front region.

The cumulative infiltration from time 0 to time t, W, is the cross-hatched area shown on Figure I12, or,

$$W = \int_0^{\infty} (\theta - \theta_i)dx \tag{41}$$

Integration by parts of Equation (41) yields

$$W = x(\theta - \theta_i)|_0^{\infty} - \int_{\theta_b}^{\theta_i} x\,d\theta = \int_{\theta_i}^{\theta_b} x d\theta \tag{42}$$

Substitution of Equation (40) for x in Equation (42) gives

$$W = \frac{1}{I} \int_{\theta_i}^{\theta_b} \left(\int_{\theta}^{\theta_b} D(\alpha)\,d\alpha \right) d\theta \tag{43}$$

Integration by parts of the definite integral in Equation (43) yields

$$IW = \int_{\theta_i}^{\theta_b} (\theta - \theta_i) D(\theta) d\theta \tag{44}$$

and since $I = dW/dt$, Equation (44) can be integrated for $W(t)$ with the result

$$W = \sqrt{2 \int_{\theta_i}^{\theta_b} (\theta - \theta_i) D(\theta) d\theta} \ \sqrt{t} \tag{45}$$

from which the infiltration rate is deduced:

$$I = \frac{1}{2} \frac{S_p}{\sqrt{t}} \tag{46}$$

where the *Parlange sorptivity* is

$$S_p = \sqrt{2 \int_{\theta_i}^{\theta_b} (\theta - \theta_i) D(\theta) d\theta} \tag{47}$$

From the definition of the diffusivity, Equation (25), and of the relative permeability Equation (47) can be rewritten in the form,

$$S_p = \sqrt{2(\theta_b - \theta_i)\tilde{K} \int_{h_{cb}}^{h_{ci}} \left(\frac{\theta - \theta_i}{\theta_b - \theta_i} \right) k_{rw}\,dh_c} \tag{48}$$

In particular, for $\theta_b = \bar{\theta}$ (case of free imbibition), the Parlange sorptivity takes the form

$$S_p = \sqrt{2(\bar{\theta} - \theta_i)\bar{K} \int_0^{h_{ci}} \left(\frac{\theta - \theta_i}{\bar{\theta} - \theta_i} \right) k_{rw}\,dh_c} \tag{49}$$

which is interesting to compare to the Bouwer sorptivity:

$$S_b = \sqrt{2(\tilde{\theta} - \theta_i)\tilde{K} \int_0^{h_{ci}} k_{rw}\,dh_c} \tag{50}$$

If $D(\theta)$ decreases rapidly with θ (which is generally the case) or if, equivalently, k_{rw} decreases rapidly with h_c, then the low values of θ (or high values of h_c) contribute little to the value of the integral

$$\int_0^{h_{ci}} (\theta - \theta_i) k_{rw}\,dh_c$$

which can be well approximated by the expression

$$(\tilde{\theta} - \theta_i) \int_0^{h_{ci}} k_{rw}\,dh_c$$

Thus generally the Bouwer and the Parlange sorptivities will differ little. Both will lead to fair prediction of infiltration rates. It should be pointed out that Parlange sorptivity is more general than Bouwer's since it applies for arbitrary values of water content at the entry face θ_b (restrained imbibition), whereas Bouwer's sorptivity applies only for $\theta_b = \tilde{\theta}$, that is, for the case when the entry face is saturated. Similarly, Equation (48) is more general than Equation (47) as it applies also for h_{cb} in the capillary fringe, whereas Equation (47) applies only for a boundary capillary pressure in excess or equal to the imbibition entry pressure (see *Capillary pressure* for definitions).

Numerical solution of the water-content equation

It can be readily verified that the assumed special relation between x, θ, and t, given by the equation,

$$x(\theta, t) = u(\theta)\sqrt{t} \tag{51}$$

will transform the partial differential equation, Equation (26), into the ordinary differential equation for the unknown function of θ, $u(\theta)$:

$$-\frac{u}{2} = \frac{d}{d\theta} \left(D \frac{d\theta}{du} \right) \tag{52}$$

with boundary conditions $u = 0$ for $\theta = \theta_b$ $(= \theta_N)$ and $u = \infty$ for $\theta = \theta_i$ $(= \theta_0)$. Equation (52) can be rewritten by integrating with respect to θ in the form,

$$\int_{\theta_0}^{\theta} u\,d\theta = -2D \frac{d\theta}{du} \tag{53}$$

This equation can be solved by an efficient finite-difference technique introduced by Philip (1955). The nomenclature associated with this scheme is displayed in Figure I13. The cross-hatched area represents the discretized form of the integral

$$\int_{\theta_0}^{\theta_{n+0.5}} u d\theta$$

and for convenience, one defines:

$$I_{n+0.5} = \frac{\int_{\theta_0}^{\theta_{n+0.5}} u d\theta}{\Delta\theta} \tag{54}$$

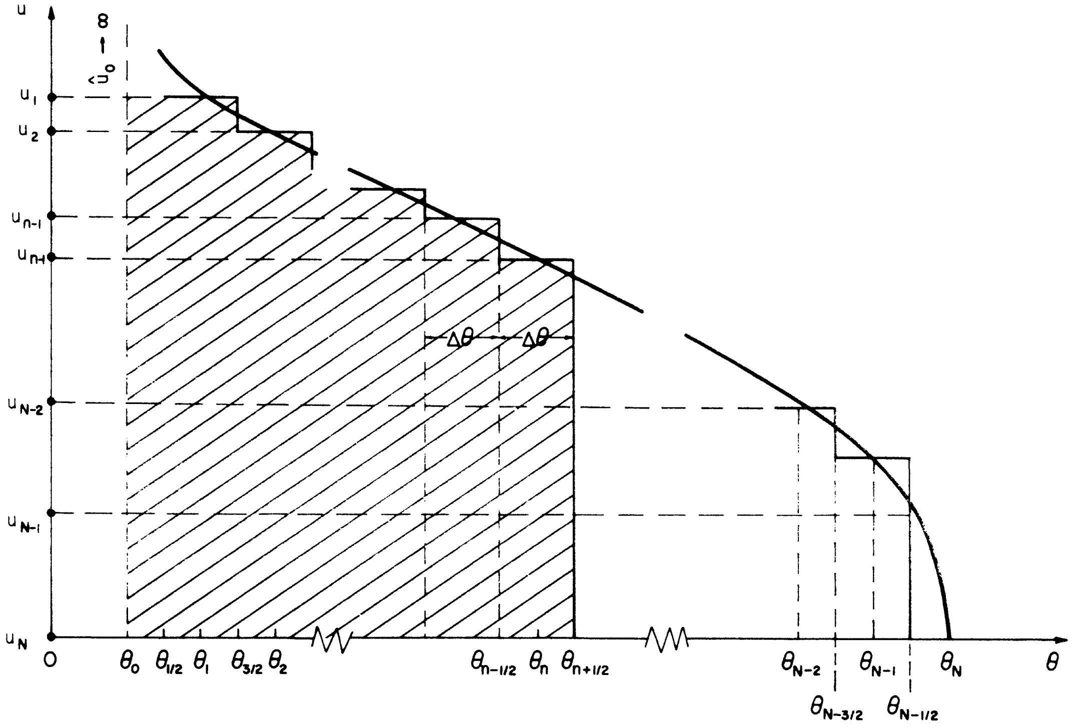


Figure I13 Finite difference nomenclature in numerical solution of the diffusivity equation.

Defining an average diffusivity in an interval as

$$\bar{D}_{n+0.5} = \frac{\int_{\theta_n}^{\theta_{n+1}} D(\theta)\mathrm{d}\theta}{\Delta\theta} \tag{55}$$

then the finite-difference form of Equation (53) leads to the equations:

$$u_n = u_{n+1} + \frac{2\bar{D}_{n+0.5}}{I_{n+0.5}} \quad n = N-1,\ N-2\ \ldots\ 2,\ 1 \tag{56}$$

and from the very definition of the integral,

$$I_{n-0.5} = I_{n+0.5} - u_n \quad n = N-1,\ N-2\ \ldots\ 3,\ 2,\ 1 \tag{57}$$

The iterative procedure is to *assume* a value for $I_{N-\frac{1}{2}}$, say $I^{u}_{N-\frac{1}{2}}$, calculate u_{N-1} from Equation (56), then $I_{N-\frac{3}{2}}$ from Equation (57), then u_{N-2} again from Equation (56), etc., until u_1 and $I_{\frac{1}{2}}$ are obtained. In the range θ_0, θ_1 because $u_0 = \infty$, one cannot proceed with the finite-difference method, but rather one calculates a value of I_1 from an approximate analytical solution, assuming D constant in that interval (thus similar to Gardner's solution). This solution is

$$\frac{\theta - \theta_0}{\Delta\theta} = \frac{\mathrm{erfc}\left(\frac{u}{\sqrt{4\hat{D}}}\right)}{\mathrm{erfc}\left(\frac{u_1}{\sqrt{4\hat{D}}}\right)} = \frac{\mathrm{erfc}\left(\frac{u}{\sqrt{4\hat{D}}}\right)}{E_1} \tag{58}$$

where

$$\hat{D} = \frac{\int_{\theta_0}^{\theta_1} D(\theta)\mathrm{d}\theta}{\Delta\theta} \tag{59}$$

From Equation (58) one can calculate I_1 by integration with the result:

$$I_1 = u_1 + \frac{2\hat{D}}{u_1} A\left(\frac{u_1}{\sqrt{4\hat{D}}}\right) \tag{60}$$

where $A(v)$ is the special function $2v$ (i erf $c(v)$/erf $c(v)$), which has been tabulated by Philip. From I_1 a second value of $I_{\frac{1}{2}}$ denoted $\hat{I}_{\frac{1}{2}}$ could be calculated:

$$\hat{I}_{0.5} = I_1 - \frac{u_1}{2} \tag{61}$$

Thus two values of the integral

$$\int_{\theta_0}^{\theta_1} u\,\mathrm{d}\theta$$

are calculated. If $I_{\frac{1}{2}}$ and $I_{\frac{1}{2}}$ agree, then the assumed value of $I_{N-\frac{1}{2}}$ was correct. If not, a new value of $I_{N-\frac{1}{2}}$ is assumed, etc., until the two values agree. Then Philip's sorptivity has been obtained:

$$S = I_{N-0.5}\,\Delta\theta = \int_{\theta_0}^{\theta_b} u\mathrm{d}\theta \tag{62}$$

Though the procedure can be made as accurate as desired with small enough $\Delta\theta$, the strictly numerical aspect of Equation (62) is a drawback. Equation (62) reveals nothing of the factors that contribute to make S small or large. It is exact but *silent*. By contrast, the Bouwer and Parlange sorptivities display explicitly, tellingly, the physical factors that constitute the sorptivity and naturally are easier to compute. This latter advantage is not significant because Philip's procedure can be programmed easily for even the smallest computers and run at the cost of a few cents.

For the first estimate of $I_{N-½}$, Philip suggested the use of Gardner's solution with an average D value, D_a defined as:

$$D_a = \frac{2\int_{\theta_0}^{\theta_N} (\theta - \theta_0) D(\theta) \mathrm{d}\theta}{(\theta_N - \theta_0)^2} \qquad (63)$$

From Gardner's solution one obtains Philip's *initial sorptivity:*

$$S_\mathrm{i} = \sqrt{\frac{8}{\pi} \int_{\theta_\mathrm{i}}^{\theta_\mathrm{b}} (\theta - \theta_\mathrm{i}) D(\theta) \mathrm{d}\theta} \qquad (64)$$

or

$$S_\mathrm{i} = \sqrt{\frac{8}{\pi} (\theta_\mathrm{b} - \theta_\mathrm{i}) \tilde{K} \int_{h_\mathrm{cb}}^{h_\mathrm{ci}} \frac{\theta - \theta_\mathrm{i}}{\theta_\mathrm{b} - \theta_\mathrm{i}} k_\mathrm{rw} \, \mathrm{d}h_\mathrm{c}} \qquad (65)$$

Comparison of Philip's initial sorptivity to Parlange's sorptivity shows that the two are in a constant ratio, namely,

$$\frac{S_\mathrm{i}}{S_\mathrm{p}} = \sqrt{\frac{4}{\pi}} = 1.13 \qquad (66)$$

The water-content equations with air effect

As water penetrates soil, it displaces air. The problem of water movement is therefore also a problem of air movement. Traditionally, the description of the air movement has been neglected. The resulting mathematical simplification is secured at the expense of physical significance.

Darcy's law in the horizontal direction for two immiscible fluids such as air and water can be written in the form:

$$v_\mathrm{w} = -\tilde{K} k_\mathrm{rw} \frac{\partial h_\mathrm{w}}{\partial x} \qquad (67)$$

$$v_\mathrm{a} = -\tilde{K} \frac{\mu_\mathrm{w}}{\mu_\mathrm{a}} k_\mathrm{ra} \frac{\partial h_\mathrm{a}}{\partial x} \qquad (68)$$

where k_rw and k_ra are the relative permeabilities to water and air, respectively, and h_w and h_a are water and air pressures expressed both as equivalent water heights. Typical relative permeability curves are shown in Figure I14.

It is convenient to define the *total* velocity v as the *algebraic* sum of the water and air velocities. By adding Equations (67) and (68) and using the fact that $h_\mathrm{a} - h_\mathrm{w} = h_\mathrm{c}$ one obtains the relation,

$$v = -\tilde{K}\left(k_\mathrm{rw} + \frac{\mu_\mathrm{w}}{\mu_\mathrm{a}} k_\mathrm{ra}\right) \frac{\partial h_\mathrm{a}}{\partial x} + \tilde{K} k_\mathrm{rw} \frac{\partial h_\mathrm{c}}{\partial x} \qquad (69)$$

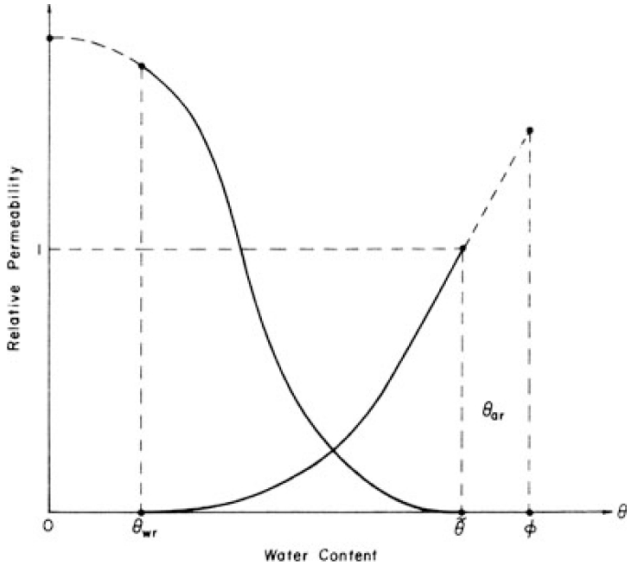


Figure I14 Typical relative permeability curves.

or multiplying through by

$$\mu_\mathrm{rT} = \left[k_\mathrm{rw} + \frac{\mu_\mathrm{w}}{\mu_\mathrm{a}} k_\mathrm{ra}\right]^{-1}$$

(the *total* relative viscosity),

$$\mu_\mathrm{rT} \, v = -\tilde{K} \frac{\partial h_\mathrm{a}}{\partial x} + \tilde{K} f_\mathrm{w} \frac{\partial h_\mathrm{c}}{\partial x} \qquad (70)$$

where the *little* f_w function of water content is defined by the relation

$$f_\mathrm{w} = \frac{k_\mathrm{rw}}{k_\mathrm{rw} + (\mu_\mathrm{w}/\mu_\mathrm{a}) k_\mathrm{ra}} = \frac{1}{1 + (\mu_\mathrm{w}/\mu_\mathrm{a})(k_\mathrm{rw}/k_\mathrm{ra})} \qquad (71)$$

A typical f_w curve is shown on Figure I15, and a typical $\mu_{r\mathrm{T}} = ((f_\mathrm{w}/k_\mathrm{rw}))$ curve is shown on Figure I16. Disregarding air compressibility, assuming that air can escape readily ahead of the wetting front, the expression of mass conservation for water and air yields the equations:

$$\frac{\partial \theta}{\partial t} + \frac{\partial v_\mathrm{w}}{\partial x} = 0 \qquad (72)$$

$$\frac{\partial \theta_\mathrm{a}}{\partial t} + \frac{\partial v_\mathrm{a}}{\partial x} = 0 \qquad (73)$$

where θ_a is the air content. Adding these two last equations yields the result,

$$\frac{\partial (\theta + \theta_\mathrm{a})}{\partial t} + \frac{\partial v}{\partial x} = 0 \qquad (74)$$

For a nondeforming soil (ϕ = constant), Equation (74) reduces to the result,

$$\frac{\partial v}{\partial x} = 0 \qquad (75)$$

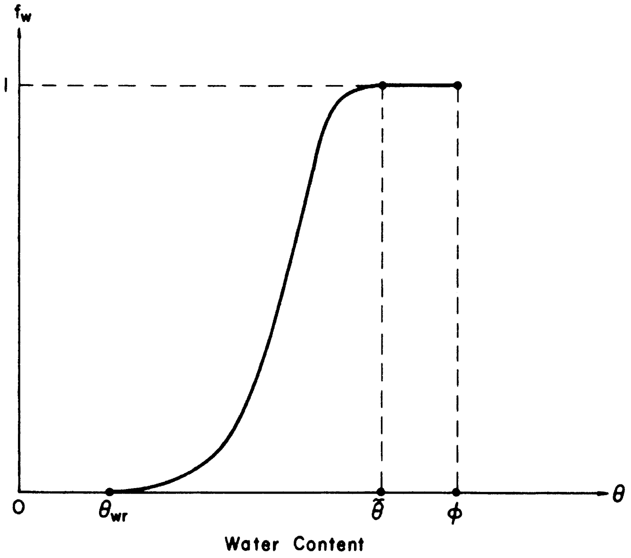


Figure I15 Typical *little-*f_w curve.

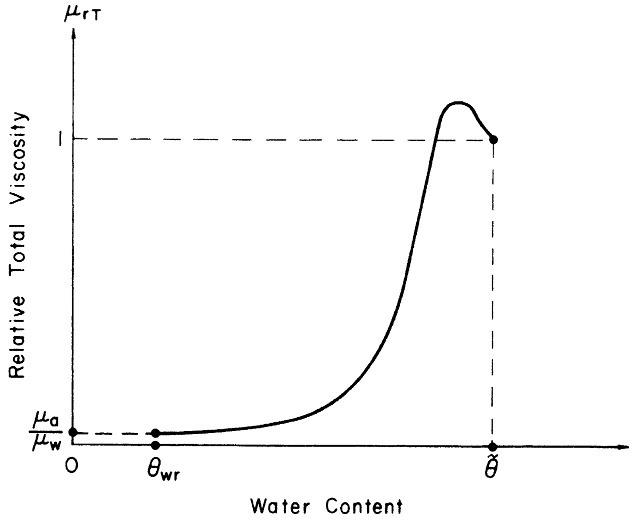


Figure I16 Typical relative total viscosity.

In other words, the total velocity is space invariant. This result is important because it means that v is only a function of time, whereas θ and v_w are functions of both time and x coordinate. Thus it is *easier to work with* v *than either* θ *or* v_w.

Equation (70) is exact. No assumptions of air incompressibility or porous medium deformability were made in its derivation. Integration of the two sides of Equation (70) with respect to x between the water-entry face and just ahead of the wetting front at position x_2 yields:

$$v = \frac{\tilde{K} \int_{h_{cb}}^{h_{ci}} f_w \, dh_c}{\int_0^{x_2} \mu_{rT} \, dx} \tag{76}$$

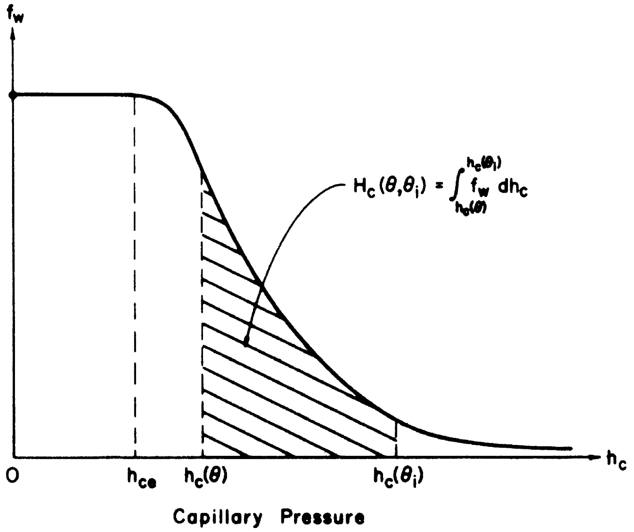


Figure I17 Typical curve of *little-*f_w versus capillary pressure.

or defining the *effective capillary drive* as

$$H_c(\theta, \theta_i) = \int_{h_c(\theta)}^{h_c(\theta_i)} f_w \, dh_c \tag{77}$$

v takes the form,

$$v = \frac{\tilde{K} H_c(\theta_b, \theta_i)}{\int_0^{x_2} \mu_{rT} \, dx} = I \tag{78}$$

A typical curve of f_w versus h_c is shown in Figure I17. Equation (78) provides the imbibition rate into the soil. It must be noted that the numerator can be calculated exactly without the prior determination of a water-content profile. In fact, if one assumes a piston displacement (i.e., a Green and Ampt model for the wetting front), Equation (78) immediately yields,

$$I = \frac{\tilde{K} H_c}{x_f} \tag{79}$$

where

$$H_c = \int_0^{h_{ci}} f_w \, dh_c \tag{80}$$

Noting the complete similarity between Equation (79) and the Green and Ampt one,

$$I = \frac{\tilde{K} H_f}{x_f} \tag{81}$$

deduced from Equation (27), one can write immediately the *correct wetting front suction* sorptivity:

$$S_c = \sqrt{2(\tilde{\theta} - \theta_i)\tilde{K} \int_0^{h_{ci}} f_w \, dh_c} \tag{82}$$

We are quick to point out that this sorptivity is *not* exact. It is only a Green and Ampt sorptivity using a correct wetting front suction rather than the empirical H_f or the Bouwer estimate H_b. It is still not an exact sorptivity because the denominator of Equation (78), the relative viscous resistance, was calculated using an assumed crude profile, a piston profile, rather than the correct profile.

To determine the correct profile, the derivation of the water-content equations must be completed. It is convenient to define the ratio of water velocity to total velocity as the fractional-flow function:

$$F_w = \frac{v_w}{v} \tag{83}$$

An explicit form of F is obtained from Equations (67) and (68), rewritten in the form

$$\frac{v_w}{\tilde{K}k_{rw}} = -\frac{\partial h_w}{\partial x} \tag{84}$$

$$\frac{v_a}{\tilde{K}(\mu_w/\mu_a)k_{ra}} = -\frac{\partial h_a}{\partial x} \tag{85}$$

Subtracting yields

$$\frac{v_w}{\tilde{K}k_{rw}} = \frac{v - v_w}{\tilde{K}(\mu_w/\mu_a)k_{ra}} = \frac{\partial h_c}{\partial x} \tag{86}$$

Collecting terms in v_w and dividing by v yields

$$F_w = \frac{v_w}{v} = f_w + \frac{\tilde{K}}{v}(1 - f_w)k_{rw}\frac{\partial h_c}{\partial x} \tag{87}$$

Defining the nonnegative function of water content

$$E = -\tilde{K}k_{rw}(1 - f_w)\frac{\partial h_c}{\partial x} \tag{88}$$

a final expression for F_w is obtained:

$$F_w = f_w - \frac{E}{v}\frac{\partial \theta}{\partial x} \tag{89}$$

In this last equation, f_w represents the external pressure effect, and the term with E represents the capillary effect. A typical curve for E is shown in Figure I18. The term E has the dimension of a diffusivity.

The water-conservation equation, Equation (72), can be rewritten in the form,

$$\begin{aligned}\frac{\partial \theta}{\partial t} + v\frac{\partial F}{\partial \theta}\frac{\partial \theta}{\partial x} &= \frac{\partial \theta}{\partial t} + vf'\frac{\partial \theta}{\partial x}\\ &\quad - E'\left(\frac{\partial \theta}{\partial x}\right)^2 - E\frac{\partial^2 \theta}{\partial x^2} = 0\end{aligned} \tag{90}$$

This nonlinear equation contains two unknowns, θ and v, and a second equation is required for solution, namely, Equation (76). To summarize, with inclusion of air effects two equations must be solved simultaneously:

$$\frac{\partial \theta}{\partial t} + vF'\frac{\partial \theta}{\partial x} = \frac{\partial \theta}{\partial t} - \frac{\partial}{\partial x}\left(E - \frac{\partial \theta}{\partial x} - vf\right) = 0 \tag{91}$$

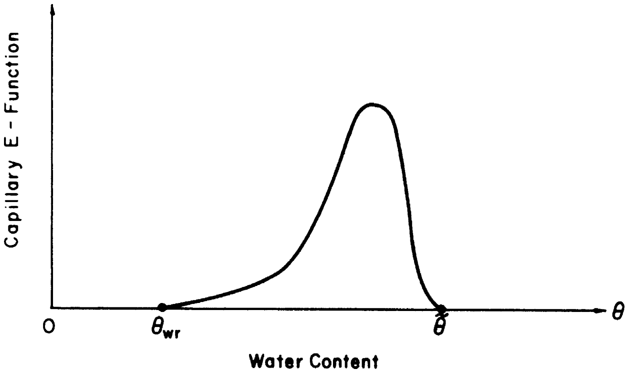


Figure I18 Typical curve of the capillary E function of water content.

and

$$v = \frac{\tilde{K}H_c}{\int_0^L \mu_{rT}\,\mathrm{d}x} \tag{92}$$

one partial differential equation, and one ordinary differential equation. (The prime indicates differentiation with respect to θ at a fixed time.) It can be verified readily that the assumed special relation

$$x(\theta,\ t) = u(\theta)\sqrt{t} \tag{93}$$

will transform the partial differential Equation (91) into the ordinary differential equation for the unknown function of θ, $u(\theta)$:

$$-\frac{u}{2} = \frac{\mathrm{d}}{\mathrm{d}\theta}\left(E\frac{\mathrm{d}\theta}{\mathrm{d}u} - \frac{S}{2}f\right) \tag{94}$$

with boundary conditions $u = 0$ for $\theta = \theta_b$, and $u = \infty$ for $\theta = \theta_i$, and the ordinary differential Equation (92) into the algebraic relation,

$$S = \frac{2\tilde{K}H_c}{\int_0^\infty \mu_{rT}\,\mathrm{d}u} \tag{95}$$

A procedure similar to that of Philip for the Richards Equation can be followed leading to the system of equations:

$$\int_{\theta_0}^{\theta} u\,\mathrm{d}\theta = -2E(\theta)\frac{\mathrm{d}\theta}{\mathrm{d}u} + Sf(\theta) \tag{96}$$

$$\int_{\theta_0}^{\theta_b} -\mu_{rT}\left(\frac{\mathrm{d}u}{\mathrm{d}\theta}\right)\mathrm{d}\theta = 2\tilde{K}H_cS \tag{97}$$

The finite-difference forms of Equation (96) analogous to Equations (56) and (57) are

$$\begin{gathered}u_n = u_{n+1} + \frac{2\bar{E}_{n+0.5}}{I_{n+0.5} - (S/\Delta\theta)\bar{f}_{n+0.5}}\\ n = N-1,\ N-2,\ \ldots\ 2,\ 1\end{gathered} \tag{98}$$

$$I_{n-0.5} = I_{n+0.5} - u_n \quad n = N-1,\ N-2,\ \ldots\ 2,\ 1 \tag{99}$$

Again this procedure is strictly numerical. An approximate but more practical solution can be obtained.

From Equation (91) it follows that the velocity of propagation of given water content is

$$\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_\theta = vF'_\mathrm{w} \tag{100}$$

In other words, the velocity is proportional to the slope of the curve F. Since the profile deforms strictly by stretching (see Equation (93)), the curve F does not change with time, and the solution for x is

$$x(\theta, t) = F'(\theta)\, W(t) \tag{101}$$

where $W(t)$ is the cumulative infiltration. Since the low water contents must travel faster than the high ones, the F curve must be concave towards the θ axis. By definition of F (Equation (89)), F is always greater than f since the term $-(E/v)(\partial\theta/\partial x)$ is positive. Thus a lower limit for the F curve is the curve f_w for $\theta > \theta_{\bar{\mathrm{f}}}$, and the tangent line shown in Figure I19 in the range $\theta_\mathrm{i} \leq \theta \leq \theta_{\bar{\mathrm{f}}}$. Using this lower limit for F as an approximation, one obtains the continuous solution for x:

$$x = Wf' \quad \theta_{\bar{\mathrm{f}}} < \theta < \tilde{\theta} \tag{102}$$

and a front of size $\theta_{\bar{\mathrm{f}}} - \theta_\mathrm{i}$ located at $xf = Wf'(\theta_{\bar{\mathrm{f}}})$. In other words, we use the following approximations for F_w:

$$F_\mathrm{w} = f_\mathrm{w} \quad \theta_{\bar{\mathrm{f}}} < \theta < \tilde{\theta} \tag{103}$$

$$F_\mathrm{w} = f_\mathrm{i} + \left[\frac{f_\mathrm{w}(\theta_{\bar{\mathrm{f}}}) - f_\mathrm{i}}{\theta_{\bar{\mathrm{f}}} - \theta_\mathrm{i}}\right](\theta - \theta_\mathrm{i}) \tag{104}$$

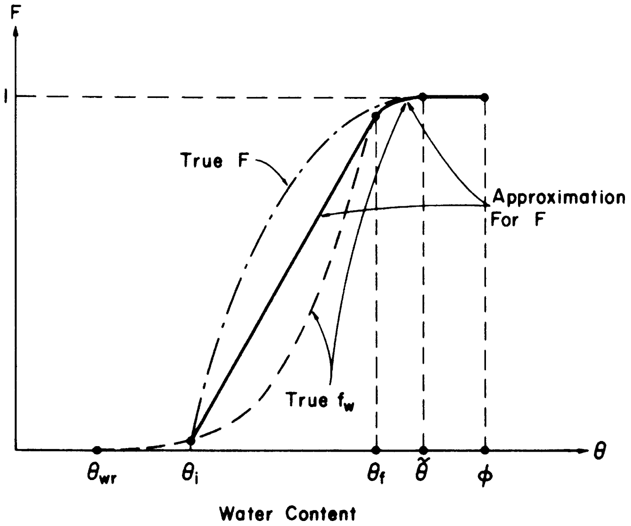


Figure I19 Fractional flow function of water content and its time evolution during imbibition.

Table I1 Values of critical pressure head H_b, effective capillary drive H_c, viscous resistance correction β, and derived quantities

Soil type	H_b (cm)	H_c (cm)	$\frac{H_\mathrm{c}}{H_\mathrm{b}}$	β	$\frac{1}{\beta}$	$\frac{1}{\beta}\frac{H_\mathrm{c}}{H_\mathrm{b}}$
Plainfield Sand	11.7	14.7	1.26	1.4	0.7	0.9
Columbia Sandy Loam	23.8	25.0	1.05	1.4	0.7	0.75
Guelph Loam	31.4	32.1	1.02	1.3	0.8	0.8
Ida Silt Loam	7.4	5.0	0.7	1.1	0.9	0.65
Yolo Light Clay	22.4	23.1	1.03	1.7	0.6	0.6

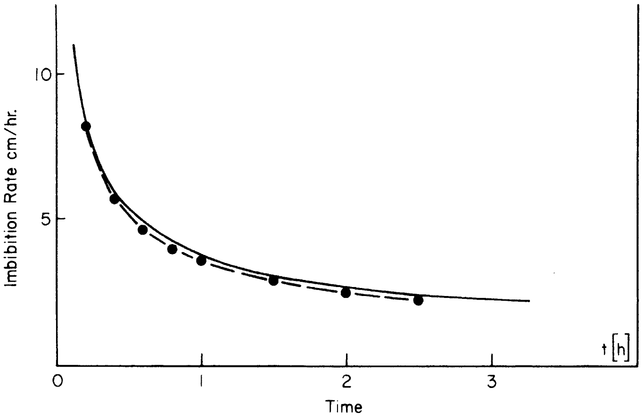


Figure I20 Comparison of observed (– ● –) and predicted (*solid line*) imbibition rates as a function of time.

Because the effective capillary drive is already known exactly, this approximate profile is necessary only to calculate the viscous resistance term. This term, the denominator of Equation (92), takes the form

$$W\int_0^{x_{\bar{\mathrm{f}}}} \mu_\mathrm{rT} f''\,\mathrm{d}\theta = W\int_{\theta_{\bar{\mathrm{f}}}}^{\tilde{\theta}} -f''\mu_\mathrm{rT}\,\mathrm{d}\theta \tag{105}$$

$$\beta = (\tilde{\theta} - \theta_\mathrm{i})\int_{\theta_{\bar{\mathrm{f}}}}^{\tilde{\theta}} -\frac{ff''}{k_\mathrm{rw}}\,\mathrm{d}\theta \tag{106}$$

then Equation (92) takes the form

$$W\frac{\mathrm{d}w}{\mathrm{d}t} = \frac{(\tilde{\theta} - \theta_\mathrm{i})\tilde{K}H_\mathrm{c}}{\beta} \tag{107}$$

or

$$W = \sqrt{\frac{2(\tilde{\theta} - \theta_\mathrm{i})\tilde{K}H_\mathrm{c}}{\beta}}\sqrt{t} \tag{108}$$

from which we deduce a new sorptivity:

$$S_\beta = \sqrt{\frac{2(\tilde{\theta} - \theta_\mathrm{i})\tilde{K}H_\mathrm{c}}{\beta}} \tag{109}$$

where β is a viscous correction factor. Table I1 lists values of β for various soils. Figure I20 shows a comparison of predictions of imbibition rate using the sorptivity S_β and of experimental observations.

H. J. Morel-Seytoux

Bibliography

Bouwer, H., 1964. Unsaturated flow in ground water hydraulics. *J. Hydraul. Div. Proc. ASCE*, **90**: 121–144.

Gardner, H.R., 1959. Solution of the flow equation for the drying of soils and other porous media. *Soil Sci. Soc. Am. Proc.*, **23**: 183–187.

Green, W.H., and Ampt, C.A., 1911. Studies on soil physics: 1. Flow of air and water through soils. *J. Agric. Sci.*, **4**: 1–24.

Morel-Seytoux, H.J., and Khanji, J., 1974. Derivation of an equation of infiltration. *Water Resour. Res. J.*, **10**(4): 795–800.

Morel-Seytoux, H.J., and Khanji, J., 1975. Prediction of imbibition in a horizontal column. *Soil Sci. Soc. Am. Proc.* **39**(4): 613–617.

Parlange, J.Y., 1971. Theory of water movement in soils: I. One-dimension 1 absorption. *Soil Sci. J.*, **111**: 134–137.

Philip, J.R., 1955. Numerical solution of equations of the diffusion type with diffusivity concentration dependent. *Farad. Soc. Trans.*, **51**: 885–892.

Schlichting, H., Gersten, K., Krause, E., and Oertel, H., 2000. *Boundary Layer Theory.* New York: Springer, 799 pp.

Cross-references

Capillary Pressure
Conductivity, Hydraulic
Field Water Cycle
Infiltration
Percolation
Permeability
Soil Pores
Soil Solution
Soil Water
Thermodynamics of Soil Water
Water Budget in Soil
Water Content and Retention
Wetting Front

IMOGOLITE

An aluminosilicate with an approximate stoichiometry $Al_2SiO_3(OH)_4$ and a short range order of a tubular nature (2 nm diameter). Commonly associated with allophane in soils. Discovered first in soils developed on volcanic ash or glass. The redox–pH diagram (Figure I21) shows the approximate conditions in andosolic soils where imogolite is most common. A represents the most oxidizing conditions, where organic matter is absent or weakly developed. B represents the more usual case was organic matter is well developed. The dotted line is the envelope that encloses the conditions of formation of the common mineral soils. Imogolite is also found in the B horizon of Podzols.

Bibliography

Wada, K., 1989. Allophane and imogolite. In Dixon, J.B., and Weed, S.B., eds., *Minerals in Soil Environments.* Madison, WI: Soil Science Society of America, pp. 1051–1088.

Cross-reference

Andosols

IMPERMEABLE

A soil that does not permit the passage of water or fluids generally is said to be impermeable. It may be so because of high clay content, the presence of a pan or indurated layer, or because of a high state of compaction.

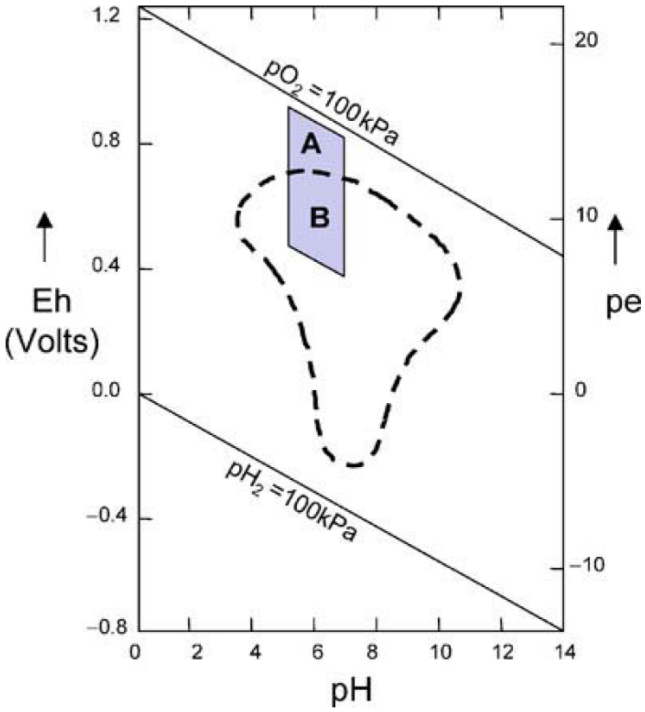


Figure I21 Redox–pH diagram of conditions in of andosolic soils, and considered to be conducive to the formation of imogolite. Area B represents the most likely conditions. Area A represents possible conditions if organic activity is low and partial pressure of O_2 approaches atmospheric value. The dashed envelope encloses the redox-pH conditions found in common mineral soils.

IMPERVIOUS

An impervious soil is one that not only affords no passage for water or other fluids, but is also impenetrable to plant roots.

INDURATION

See *Hardening*.

INFILTRATION

The term *infiltration* has several meanings, sometimes being used as a synonym for *wetting*, *imbibition* (*q.v.*), or *percolation* (*q.v.*). However, the concept of infiltration specifically relates to the phenomenon of water penetration from the surface of the ground into the subjacent soil. As water penetrates the soil, its distribution in space and time varies. The description of the evolution of the water (see Water Content and Retention) in the soil resulting from the occurrence of a rain or of a pond of water at the surface is also sometimes considered part of the infiltration phenomenon. Mostly, however, infiltration is thought of as the phenomenon of water crossing from the air side to the soil side of the air–soil interface. Certainly, it is this aspect of infiltration that is of greatest concern in hydrology, and thus it is the aspect discussed here.

Significance in the hydrologic cycle

If water has a choice, so to speak, it will infiltrate rather than run off on the land surface. Rain will infiltrate until it exceeds the so-called *infiltration capacity* of the soil. Infiltration capacity is the maximum rainfall rate the soil can fully absorb at a given time, given the previous history of soil moisture and rainfall pattern. A number of factors affect infiltration capacity, which varies greatly among soils depending on their permeability and capillary characteristics. For a given soil, the infiltration capacity will vary according to whether the soil was initially dry when the rainfall started or already fairly wet from a relatively recent rain. The ability to predict the infiltration capacity of the soil and the actual infiltration rates is a prerequisite to the prediction of surface runoff and therefore streamflow. Depending on the infiltration capacity of the soil at the time of rainfall, a storm may lead to an inoffensive streamflow change or on the contrary, to a devastating flood.

Infiltration in a capillary tube

Consider the highly simplified situation shown in Figure I22. Due to intense rain, water is continuously available at the surface. Water covers the surface with a film of thickness H. At time zero the tube is dry, and immediately as water becomes available at the soil surface, a meniscus forms in the tube and propagates in the tube under the action of the capillary-pressure forces (for a detailed discussion of this phenomenon, see *Imbibition*). Later the distribution of pressure (*expressed as a water height*) in the two phases, h_w and h_a, is as shown in Figure I22.

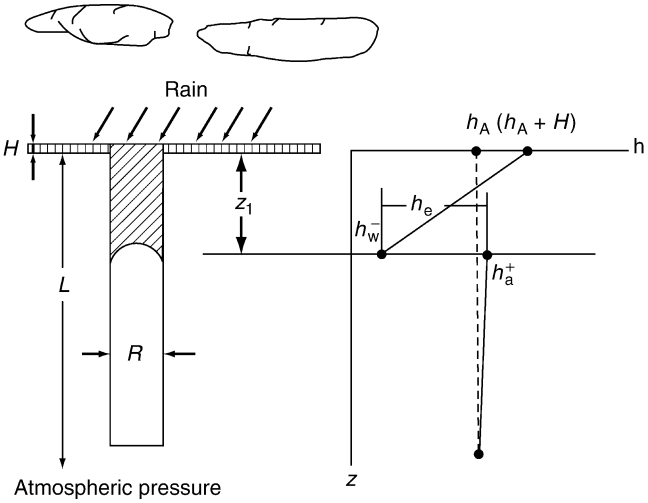


Figure I22 Infiltration in a capillary tube.

The term h_w^- is the water pressure on the water side of the interface, h_a^+ is the air pressure on the air side of the interface, and h_A is the atmospheric pressure. The velocity of water (or air) in a vertical tube of length L is given by *Poiseuille's law*:

$$u_w = \frac{R^2}{8\mu_w}\frac{\Delta\Phi}{L} \tag{1}$$

where $\Delta\Phi$ is the drop in total head Φ, and μ_w is the viscosity of water. The total head is defined as

$$\Phi = h_w - z \tag{2}$$

where z is the vertical coordinate oriented positive downward. Application of Poiseuille's law for the water phase yields

$$\begin{aligned} u_w &= \frac{R^2}{8\mu_w}\frac{h_A + H - (h_w^- - z_f)}{z_f} \\ &= \frac{R^2}{8\mu_w}\frac{h_A + H + z_f - h_w^-}{z_f} \end{aligned} \tag{3}$$

since $z = 0$ at the entrance to the tube and there the water pressure is hydrostatic, i.e., equal to H. Similarly, one obtains for u_a (neglecting the small gravity effect on air),

$$u_a = \frac{R^2}{8\mu_a}\frac{h_a^+ - h_A}{L - z_f} \tag{4}$$

Since the velocities of water and air are both equal to dz_f/dt, equating Equations (3) and (4) yields

$$\begin{aligned} \frac{dz_f}{dt} &= \frac{R^2}{8}\frac{h_A + H + z_f - h_w^-}{\mu_w z_f} \\ &= \frac{R^2}{8}\frac{h_a^+ - h_A}{\mu_a(L - z_f)} \end{aligned} \tag{5}$$

or

$$\begin{aligned} \frac{dz_f}{dt} &= \frac{R^2}{8}\frac{H + (h_a^+ - h_w^-) + z_f}{\mu_w z_f + \mu_a(L - z_f)} \\ &= \frac{R^2}{8}\frac{H + h_c + z_f}{z_f(\mu_w - \mu_a) + \mu_a L} \end{aligned} \tag{6}$$

since the pressure difference across the meniscus is the capillary pressure h_c. Equation (6) can be integrated for z_f with the result:

$$\begin{aligned} \frac{R^2 t}{8(\mu_w - \mu_a)} = z_f - \left(H + h_c - \frac{\mu_a L}{\mu_w - \mu_a}\right) \\ \ln\left(\frac{H + h_c + z_f}{H_f}\right) \end{aligned} \tag{7}$$

From Equation (6) the infiltration rate is obtained, namely;

$$I = \frac{R^2}{8}\frac{H + h_c + z_f}{z_f(\mu_w - \mu_a) + \mu_a L} \tag{8}$$

In Equation (8) the infiltration rate is defined in terms of the position of the meniscus (the *wetting front*). The infiltration rate at a given time is obtained by calculating z_f from Equation (7) for a given value of t and then evaluating I from Equation (8) for this value of z_f.

Infiltration in a soil

The water-content equation (without air effect)

Away from the water source the soil is dry; its *water content* (*q.v.*) is low. Close to the source it is high. At a fixed location z_0 (Figure I23), the soil gets wetter as time passes. In general, the water content θ is a function of z and t. The variation of θ in time at a fixed location z is related to the net inflow of water at that time through the principle of conservation of mass, which expressed in mathematical symbols, reads

$$\frac{\partial\theta}{\partial t}+\frac{\partial}{\partial z}(v_{\mathrm{w}})=0 \tag{9}$$

where v_{w} is the water velocity in a Darcy sense (i.e., a volume flow rate per unit bulk cross-section area in a direction perpendicular to flow). The water velocity is given by *Darcy's law*, namely,

$$v_{\mathrm{w}}=-K(\theta)\frac{\partial h_{\mathrm{w}}}{\partial z}+K(\theta) \tag{10}$$

or

$$v_{\mathrm{w}}=K(\theta)\frac{\partial h_{\mathrm{c}}}{\partial z}+K(\theta)=\left[K(\theta)\frac{\mathrm{d}h_{\mathrm{c}}}{\mathrm{d}\theta}\right]\frac{\partial\theta}{\partial z} \tag{11}$$

if one *assumes* that air pressure is atmospheric everywhere and for all times in the medium. The term $K(\theta)$ is the *unsaturated hydraulic conductivity*. It measures the conductivity of the medium to water at various water contents. Substitution of Equation (11) in Equation (9) yields the *water-content equation*, also called *Richard's Equation*:

$$\frac{\partial\theta}{\partial t}+\frac{\partial}{\partial z}\left(K(\theta)\frac{\partial h_{\mathrm{c}}}{\partial z}\right)+\frac{\partial K(\theta)}{\partial z}=0 \tag{12}$$

Defining a new positive function of water content, the *diffusivity*, namely,

$$D(\theta)=-K(\theta)\frac{\mathrm{d}h_{\mathrm{c}}}{\mathrm{d}\theta} \tag{13}$$

the water-content equation takes the form

$$\frac{\partial\theta}{\partial t}-\frac{\partial}{\partial z}\left(D(\theta)\frac{\partial\theta}{\partial z}\right)+\frac{\partial K(\theta)}{\partial z}=0 \tag{14}$$

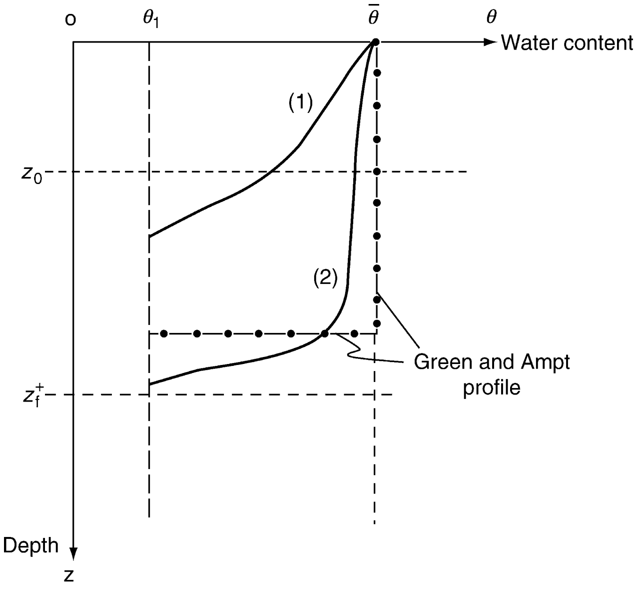


Figure I23 Evolution of water contents in a soil during infiltration.

Approximate solutions of the water-content equation

The Green and Ampt solution. It is assumed that the initial water content of the soil is uniform at value θ_{i}. At time zero the soil is placed in contact with an ample water supply. Immediately the water content takes the value $\tilde{\theta}$, water content at *natural* saturation (that is, θ–θ_{ar}, where θ_{ar} is the residual air content) at $z=0$ and keeps this value there indefinitely thereafter. Green and Ampt (1911) assumed that there exists a *wetting front* (*q.v.*) that separates a fully saturated zone and a zone still at the initial water content. With this assumption, in the fully wetted zone, $\theta=\tilde{\theta}$ and does not vary with time.

The same reasoning discussed in the section *Imbition* leads to the velocity of propagation of the front V_{f}:

$$V_{\mathrm{f}}=\frac{\mathrm{d}z_{\mathrm{f}}}{\mathrm{d}t}=K\frac{H+H_{\mathrm{f}}+z_{\mathrm{f}}}{z_{\mathrm{f}}(\theta-\theta_{\mathrm{i}})} \tag{15}$$

The infiltration rate is

$$I=\bar{K}\frac{H+H_{\mathrm{f}}+z_{\mathrm{f}}}{z_{\mathrm{f}}} \tag{16}$$

where H_{f} is the capillary-pressure head at the front. After integration for z_{f}, one obtains

$$\frac{\tilde{K}t}{\tilde{\theta}-\theta_{\mathrm{i}}}=z_{\mathrm{f}}-(H+H_{\mathrm{f}})\ln\left(1+\frac{z_{\mathrm{f}}}{H+H_{\mathrm{f}}}\right) \tag{17}$$

which is the well-known Green and Ampt Equation. Equation (17) can be rewritten in terms of the cumulative infiltration up to time t, W, since $W=z_{\mathrm{f}}(\tilde{\theta}-\theta_{\mathrm{i}})$, namely,

$$\tilde{K}t=W-(H+H_{\mathrm{f}})(\tilde{\theta}-\theta_{\mathrm{i}})\ln\left[1+\frac{\mathrm{W}}{(H+H_{\mathrm{f}})(\tilde{\theta}-\theta_{\mathrm{i}})}\right] \tag{18}$$

In a capillary tube the capillary pressure on the water side of the meniscus is well defined: $2\sigma/r$. Unfortunately, H_{f}, the capillary-pressure head at the wetting front, is not (see *Wetting front*).

From the Green and Ampt model, it is not possible to relate H_{f} to the soil characteristic curves. In a sense, H_{f} is some sort of *average* capillary pressure. If can be determined for a given soil from experiments.

It has been suggested that a *weighted* average value of capillary-pressure head should be used with the relative permeability to water, k_{rw}, which is a function of h_{c}, as the weight. Then one obtains an effective capillary drive, H_{b}, defined by the equation

$$H_{\mathrm{b}}=\int_0^{h_{\mathrm{ci}}}k_{\mathrm{rw}}\,\mathrm{d}h_{\mathrm{c}} \tag{19}$$

where $h_{\mathrm{ci}}=h_{\mathrm{c}}(\theta_{\mathrm{i}})$, the initial capillary-pressure head. This estimated value of the effective capillary drive leads to relatively good predictions of the infiltration rates.

Philip's solution. Philip (1957) recognized that in the case of imbition (i.e., horizontal water penetration), the water-content equation, which reduces then to the diffusivity equation,

$$\frac{\partial\theta}{\partial t}-\frac{\partial}{\partial z}\left[D(\theta)\frac{\partial\theta}{\partial z}\right]=0 \tag{20}$$

could be reduced to an ordinary differential equation,

$$\frac{u_0}{2}+\frac{\mathrm{d}}{\mathrm{d}\theta}\left(D\frac{\mathrm{d}\theta}{\mathrm{d}u_0}\right)=0 \tag{21}$$

by the similarity transformation,

$$z=u_0(\theta)\sqrt{t} \tag{22}$$

This approach and the numerical method of solution of Equation (21) are discussed in detail in the section *Imbibition*.

The next step is to view Equation (14) as a combination of Equation (20) and a perturbation term: $\partial K(\theta)/\partial z$. One then expects that the solution of Equation (14) can be fruitfully put in the form $z=z_0+z$. Naturally, no gain is achieved if Δz is not a separable function of θ and t. Thus the procedure is to look for a solution of Equation (14) in the form

$$z=u_0(\theta)\sqrt{t}+u_1(\theta)g(t)+\varepsilon(\theta,\ t)$$

After substitution in Equation (14), one obtains an equation for u_1, one disregards the terms in ε, and one selects the function $g(t)$, which reduces the approximate remaining equation to an ordinary differential equation. Repeating the operation several times, one obtains a solution in the form,

$$z(\theta,t)=u_0(\theta)\,t^{1/2}+u_1(\theta)t+u^2(\theta)\,t^{3/2}+\ldots \tag{23}$$

From this solution one can deduce an equation for the rate of infiltration I as a function of time:

$$I=\frac{C}{\sqrt{t}}+A+D\sqrt{t}+Et+\mathrm{F}t^{3/2}+\ldots \tag{24}$$

where the constants C, K, …, depend on the soil characteristics and the boundary conditions θ_i and $\tilde{\theta}$.

Equation (24) predicts that at small times the infiltration rate is high, which is appropriate. For large times the infiltration rate increases indefinitely. As this result is totally contradictory to experimental evidence, this indicates that the method of solution does not converge for large times, which is clear from Equation (23). It is accepted practice now to truncate Equation (24) after the constant term A and to interpret A to be the saturated hydraulic conductivity at natural saturation.

The inconsistency of the results arises from the implicit assumption of the perturbation procedure that gravity is small compared to capillarity. At large times (of the order of only one hour in some instances), the gravity force will actually become the dominant one. Nevertheless, Philip's method has given good predictions of infiltration using three terms in the series of Equation (22) particularly, as one would expect, for tight soils with low conductivity and high capillary drive.

The water-content equations (with air effect)

As water penetrates the soil, it displaces air. The problem of water movement is also a problem of air movement. The treatment of the air movement is parallel to that of water. Indeed, Darcy's law for water and air can be written very *symmetrically* in the form,

$$v_\mathrm{w}=-\frac{k\,k_\mathrm{rw}}{\mu_\mathrm{w}}\left(\frac{\partial p_\mathrm{w}}{\partial z}-\rho_\mathrm{w}\mathrm{g}\right) \tag{25}$$

$$v_\mathrm{a}=-\frac{k\,k_\mathrm{ra}}{\mu_\mathrm{a}}\left(\frac{\partial p_\mathrm{a}}{\partial z}-\rho_\mathrm{a}\mathrm{g}\right) \tag{26}$$

where v_w and v_a are the fluid velocities (in the Darcy sense); k is the intrinsic permeability; k_rw and k_ra are the fluid relative permeabilities; p_w and p_a are the fluid pressures; ρ_w and ρ_a are their specific masses; and g is the acceleration of gravity. If *both* water and air pressures are expressed as equivalent *water* heights, the expressions for the fluid velocities become,

$$v_\mathrm{w}=-\tilde{K}\,k_\mathrm{rw}\frac{\partial h_\mathrm{w}}{\partial z}+\tilde{K}\,k_\mathrm{rw} \tag{27}$$

$$v_\mathrm{a}=-\tilde{K}\frac{\mu_\mathrm{w}}{\mu_\mathrm{a}}k_\mathrm{ra}\frac{\partial h_\mathrm{a}}{\partial z}+\tilde{K}\frac{\mu_\mathrm{w}}{\mu_\mathrm{a}}\frac{\rho_\mathrm{a}}{\rho_\mathrm{w}}k_\mathrm{ra} \tag{28}$$

where the relative permeabilities are relative to $\tilde{K}$ or, in other words,

$$k_\mathrm{rw}=\frac{K(\theta)}{\tilde{K}} \tag{29}$$

It is convenient to define the *total* velocity v as the *algebraic* sum of the water and air velocities. By adding Equations (27) and (28) and using the fact that $h_\mathrm{c}=h_\mathrm{a}-h_\mathrm{w}$, one obtains the *exact* relation,

$$v=\frac{\tilde{K}\left(-\dfrac{\partial h_\mathrm{a}}{\partial z}+f_\mathrm{w}\dfrac{\partial h_\mathrm{c}}{\partial z}+f_w\right)}{\mu_\mathrm{rT}} \tag{30}$$

where f_w is the *little-f* function of water content, defined as

$$f_\mathrm{w}=\frac{1}{1+(k_\mathrm{ra}/k_\mathrm{rw})(\mu_\mathrm{w}/\mu_\mathrm{a})} \tag{31}$$

and μ_rT is the *total relative* viscosity (a function of water content) defined as

$$\mu_\mathrm{rT}=\frac{f_\mathrm{w}}{k_\mathrm{rw}} \tag{32}$$

Typical curves of f_w and μ_rT are given in the section on *Imbibition*.

The equations of conservation for water and air are, very symmetrically,

$$\frac{\partial\theta}{\partial t}+\frac{\partial v_\mathrm{w}}{\partial z}=0 \tag{33}$$

$$\frac{\partial\theta_\mathrm{a}}{\partial t}+\frac{\partial v_\mathrm{a}}{\partial z}=0 \tag{34}$$

where θ_a is the air content in the soil. Adding Equations (33) and (34) yields the result

$$\frac{\partial(\theta+\theta_\mathrm{a})}{\partial t}+\frac{\partial v}{\partial z}=0 \tag{35}$$

For a nondeforming soil (ϕ, porosity = constant), Equation (35) reduces to the result

$$\frac{\partial v}{\partial z} = 0 \tag{36}$$

In other words, the total velocity is *invariant* in *space*. This result is important because it means that v is a function only of time, whereas θ and v_w are functions of both time and z coordinate. Thus it is *easier* to work with v than with either θ or v_w. Taking advantage of the fact that v is not a function of z, the integration of Equation (30) between any two levels 1 and 2 yields the *v-integral* equation

$$v = \frac{\tilde{K}\left(h_{a1} - h_{a2} + \int_1^2 f_w \, dh_c + \int_{z_1}^{z_2} f_w \, dz\right)}{\int_{z_1}^{z_2} \mu_{rT} \, dz} \tag{37}$$

With air effects, the water-content equations are *two:* the partial differential Equation (33) and the Equation (37). In the case of infiltration into a dry soil with a constant head of water on the soil surface (*ponded* infiltration), application of Equation (37) between the soil surface and a position z_2 just downstream from the wetting front yields the infiltration rate I, as

$$I = \frac{\tilde{K}\left(H + H_c \int_0^{z_2} f_w \, dz\right)}{\int_0^{z_2} \mu_{rT} \, dz} \tag{38}$$

where

$$H_c = \int_0^{h_{ci}} f_w \, dh_c \tag{39}$$

is the *effective capillary drive* (see *Wetting front*). Naturally, the exploitation of Equation (38) requires knowledge of the water-content profile. With the Green and Ampt assumption (Figure I23), the profile shape is assumed to be known a priori. For this assumed profile, Equation (38) reduces to a formula derived previously, namely, Equation (16), which can be rewritten as

$$I = \frac{\tilde{K}[H + H_c + (W)/(\tilde{\theta} - \theta_i)]}{(W)/(\tilde{\theta} - \theta_i)} \tag{40}$$

because in a saturated zone, $f_w = 1$, and $\mu_{rT} = 1$. Equation (40) can be integrated to yield an equation identical to Equation (18) except that H_f, then unknown, is now replaced by the known quantity H_c. Naturally, the Green and Ampt assumed profile does not account for any *simultaneous* flow of water and air. One may legitimately ask whether that profile is not too crude to accurately represent the phenomenon. The problem is to find an approximate water-content profile that accounts correctly for the viscous interaction of the two flowing phases. To answer this question, it is convenient to discuss first the *fractional-flow* concept.

The fractional-flow function

The *total* velocity is defined as the *algebraic* sum of the water and air velocities:

$$v = v_w + v_a \tag{41}$$

In the total volumetric stream of fluids, only a fraction of the stream is water, and *by definition*, the *fractional-flow* function is

$$F_w = \frac{v_w}{v} \tag{42}$$

In this form Equation (42) is not too useful, but using Equations (27), (28), and (41), one can eliminate the water and air pressures and obtain the more explicit result:

$$F_w = f_w + \frac{G_w}{v} - \frac{E_w}{v}\frac{\partial\theta}{\partial z} \tag{43}$$

where the two nonnegative functions of water content

$$G_w = \tilde{K}\, k_{rw}(1 - f_w) \tag{44}$$

and

$$E_w = -G_w \frac{dh_c}{d\theta} \tag{45}$$

are defined. In Equation (43) the term f_w represents an external pressure effect, the term with G_w represents the gravity effect, and the term with E_w represents the capillary effect. A typical curve for E_w is given in the section *Imbibition*, and the curve of G_w is very similar. The term G_w has the dimension of a *velocity*, whereas E_w has the dimension of diffusivity. The F_w curve depends on the water-content profile since it depends on $\partial\theta/\partial z$. For the two typical water-content profiles of Figure I23, the corresponding F_w curves are shown in Figure I24.

Movement of water contents

The water-content equation can be rewritten in the form

$$\frac{\partial\theta}{\partial t} + \frac{\partial}{\partial z}(vF_w) = 0 \tag{46}$$

or

$$\frac{\partial\theta}{\partial t} + vF_w'\frac{\partial\theta}{\partial z} = 0 \tag{47}$$

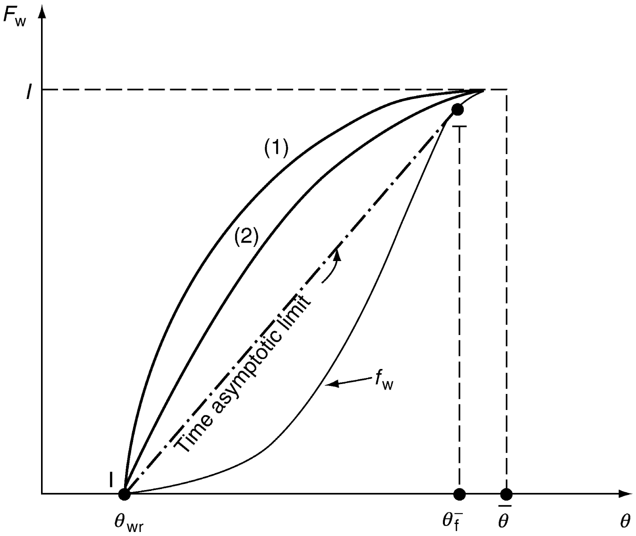


Figure I24 Fractional-flow functions corresponding to water-content profiles at various times.

where F'_w means the derivative of F_w with respect to θ at a *fixed time* and graphically is the *slope* of the curve of F_w versus θ at a given time. It follows from Equation (47) that the *velocity of propagation* of a given water content is

$$\left(\frac{dz}{dt}\right)_\theta = v\left.\frac{\partial F_w}{\partial\theta}\right|_t = vF'_w \tag{48}$$

It follows that if the water-content profile evolves strictly by translation, all water contents move at the same speed, and F'_w must be constant, that is, the curve F_w must be straight. As shown in Figure I24, as time proceeds, the curve F_w tends to straighten up. In fact, as F_w is always greater than f_w during infiltration – since all terms in Equation (43) are positive and must be convex because otherwise the water-content profiles would exhibit multiple values – one concludes that for large times, F_w tends to a limit shown in Figure I24. This limit is the tangent from point I to the curve f_w, namely, line *IT*, and beyond *T* it is the curve f_w itself. With this approximate choice for F_w, namely,

$$F_w = \left[\frac{f_w(\theta_f^-) - f_w(\theta_i)}{\theta_f^- - \theta_i}\right](\theta - \theta_i) + f_w(\theta_i) \quad \theta < \theta < \theta_f^- \tag{49}$$

and

$$F_w = f_w \quad \theta_f^- < \theta < \tilde{\theta} \tag{50}$$

Equation (48) can be integrated to yield the profile

$$z(\theta, t) = f'_w(\theta)\int_0^t v(\tau)\,d\tau = f'_w(\theta)\,W(t) \tag{51}$$

where $W(t)$ is the cumulative infiltration up to time t. Substitution of Equation (41) in the denominator of Equation (38) plus the assumption that $f_w = 1$ behind the wetting front leads to the equation

$$I = \frac{\bar{K}\,[H + H_c + W/(\bar{\theta} - \theta_i)]}{\beta\,[W/(\bar{\theta} - \theta_i)]} \tag{52}$$

where β (dimensionless), the *viscous correction* factor, is (like H_c) solely a function of the soil and fluid characteristics and defined by the relation

$$\beta = (\tilde{\theta} - \theta_i)\int_{\theta_f^-}^{\tilde{\theta}} -f''_w(\theta)\,\mu_{rT}(\theta)\,d\theta \tag{53}$$

Equation (52) can be integrated to yield

$$\frac{\tilde{K}t}{\beta} = W - (H + H_c)(\tilde{\theta} - \theta_i) \ln\left[1 + \frac{W}{(H + H_c)(\tilde{\theta} - \theta_i)}\right] \tag{54}$$

which is the same as Equation (18) except for the substitution of H_c for H_f and the presence of the viscous correction factor β. (Values of β for various soils are given in the section on *Imbibition*). Though β is not much larger than 1, it averages around 1.3 and is not negligible.

Effect of air compression

The previous results were derived for the situation when air can escape freely ahead of the wetting front. If, on the other hand, the soil column is of limited depth D to an impervious stratum or to a water table, air compression will result. A similar analysis to that discussed in the previous section (Morel-Seytoux and Khanji, 1975) leads to the result for cumulative infiltration:

$$\frac{\tilde{K}t}{\beta} = \frac{W}{1 - H_A/D} - \frac{(\tilde{\theta} - \theta_i)(H + H_c)}{(1 - H_A/D)^2} \ln\left[1 + \frac{(1 - H_A/D)\,W}{(\tilde{\theta} - \theta_i)(H + H_c)}\right] \tag{55}$$

where H_A is atmospheric pressure expressed as a water depth. Equation (55) has the same structure as the Green and Ampt Equation with an additional two correction terms: β for the total viscous-resistance effect and $(1 - (H_A)/(D))$ for the compression effect. Equation (55) can be used only as long as W does not exceed the value

$$\frac{D(H + H_c)(\tilde{\theta} - \theta_i)}{H_A + D(\beta - 1)}$$

due to the appearance of the *counterflow* phenomenon. At high infiltration rates both water and air flow downward, but as the infiltration rates starts to decrease, air starts to flow upward, that is, in a direction opposite to the water flow.

Effect of air counterflow

In an infiltration process, $\partial\theta/\partial z$ is negative everywhere in the medium (see Figure I23). From the expression of the *fractional-flow* function, given by Equation (43), it is clear that $F_w \geq F_w = f_w + (G_w)/(v) \geq f_w$. In particular, at a fixed value of θ, F_w increases as v decreases. Figure I25 displays several F_w curves for two values of v: one large, v_1, and one small, v_2. For large v (case 1), the F_w and F'_w curves do not cross the horizontal line of ordinate 1. However, for small values of v (case 2), the quantity G_w/v can become quite large, and F_w will exceed 1 in the range of high water contents. Because, by definition, $v_w = F_w v$ and $v_a = v - v_w$, it follows that $v_a = (1 - F_w)v$ is negative in the range of the high water contents. This means that in the vicinity of the soil surface, air is moving *upward*.

It is of interest to find out for which value of v counterflow will start. In the water-invaded zone near the surface (see Figure I23), when infiltration has proceeded for a relatively long time (curve 2), f_w is essentially 1, and the capillary-pressure gradient is negligible. Thus Equation (30) reduces to

$$v = \frac{\tilde{K}}{\mu_{rT}}\left(1 - \frac{\partial h_a}{\partial z}\right) = \frac{\tilde{K}}{\mu_{rT}}\left(1 - \frac{\partial h_w}{\partial z}\right) = K_T\left(1 - \frac{\partial h_w}{\partial z}\right) \tag{56}$$

Equation (56) can be interpreted as Darcy's Equation for the instantaneous velocity of a single fictitious fluid (the *total* fluid) in a heterogeneous column of conductivity $K_T(z)$, which varies with z since μ_{rT}, the total relative velocity, varies with θ (see *Imbibition*). Because at the surface $\theta = \tilde{\theta}$ then $K_T(0) = \tilde{K}$. The curve $K_T(z)$ has a minimum since μ_{rT} has a maximum for a value of $\theta < \tilde{\theta}$. Let us suppose now that v $(= I)$ drops below the value $\tilde{K}$, which will happen even in the case of an infinite

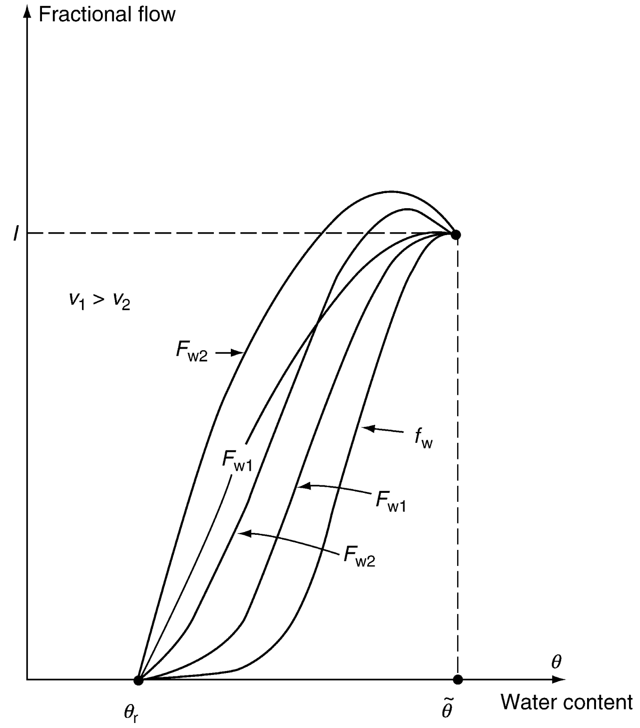


Figure I25 Fractional-flow functions for various values of total velocity.

column because $\beta > 1$. As soon as I becomes less than $\tilde{K}$, it follows that at the surface $\partial h_w/\partial z > 0$. The water-pressure gradient will be zero at a depth z_c below the surface where $K_T(z_c) = I$. In this zone ($0 \le z \le z_c$), water pressure increases with depth. Water still flows downward in spite of it due to its weight. On the other hand, in this same zone the increase of air pressure with depth (approximately the same as for water since the capillary pressure gradient is negligible in this zone) cannot be counteracted by the weight of air. Consequently, in this zone air flows upward. The air counterflow starts as soon as the infiltration rate drops below the value $\tilde{K}$. This does not mean that the buoyancy force is not felt until I dips below $\tilde{K}$. In fact, its effect on the infiltration rate is felt significantly before this moment. When the counterflow effect is included in the analysis (Morel-Seytoux and Khanji, 1975), the equation for cumulative infiltration versus time is

$$\ln\left[1 - \frac{\gamma W}{(\tilde{\theta} - \theta_i)(H + H_c)} + \frac{\gamma(\gamma+1)\tilde{K}t}{(\tilde{\theta} - \theta_i)(H + H_c)\beta}\right] = -\gamma \ln\left[1 + \frac{W}{(\tilde{\theta} - \theta_i)(H + H_c)}\right] \tag{57}$$

or

$$\frac{\tilde{K}t}{\beta} = \frac{W}{\gamma + 1} + \frac{(\tilde{\theta} - \theta_i)(H + H_c)}{\gamma(\gamma + 1)} \left\{\left[1 + \frac{W}{(\tilde{\theta} - \theta_i)(H + H_c)}\right]^{-\gamma} - 1\right\} \tag{58}$$

where γ (a dimensionless parameter) is given by the expression

$$\gamma = (\tilde{\theta} - \theta_i) \int_{\theta_f^-}^{\tilde{\theta}} \frac{G''}{\tilde{K}} \mu_{rT} \, d\theta \tag{59}$$

From Equation (58) one can deduce that the limiting value of the infiltration rate for large times is $[(\gamma + 1)/(\beta)](\tilde{K})$. As one would expect, the counterflow effect tends to compensate for the total viscous effect.

Joint effect of air compression and counter-flow

The equation for cumulative infiltration versus time is

$$\frac{\tilde{K}t}{\beta} = \frac{W}{\gamma + 1 - (H_A/D)} + \frac{(\tilde{\theta} - \theta_i)(H + H_c)}{\gamma[\gamma + 1 - (H_A/D)]} \left\{\left[1 - \frac{W[(H_A/D) - 1}{(\tilde{\theta} - \theta_i)(H + H_c)}\right]^{\frac{\gamma}{(H_A/D)-1}} - 1\right\} \tag{60}$$

The infiltration will come to a halt when the cumulative infiltration reaches the critical value

$$W_c = \frac{(\tilde{\theta} - \theta_i)(H + H_c)}{(H_A/D) - 1} \tag{61}$$

The corresponding critical time is

$$t_c = \frac{\beta(\tilde{\theta} - \theta_i)(H + H_c)}{\gamma\tilde{K}(H_A/D) - 1} \tag{62}$$

This is possible only if $D < H_A$. Otherwise, the infiltration will proceed. Its limiting value is then

$$\left(\gamma + 1 - \frac{H_A}{D}\right)\frac{\tilde{K}}{\beta}$$

Rainfall infiltration in a soil

In the previous section immediate ponding at the surface under a very intensive rain was assumed. This assumption is very restrictive. Indeed, for the hydrologist the practical problem is to predict the time at which ponding first occurs and only thereafter to predict the infiltration under a ponding condition.

Under natural rainfall, usually of relatively low intensity, the water content at the soil surface θ_u does not immediately take the saturated value (except for residual air content) $\tilde{\theta}$. Thus, in general, the hydrologic problem of the determination of the time at which a ponding condition first develops, in short, the *ponding time*, is equivalent to the mathematical problem of finding the unknown function $\theta_u(t)$. The "ponding" time is the solution of the equation

$$\theta_u(t_p) = \tilde{\theta} \tag{63}$$

The problem is difficult and an exact solution not possible. Mein and Larson (1973), assuming that the water displacement of air is piston-like from the beginning of rainfall, derived an equation for t_p, namely,

$$t_p = \frac{(\tilde{\theta} - \theta_i)H_b}{r(r/\tilde{K} - 1)} \tag{64}$$

where r is the (constant) rainfall rate, $\tilde{K}$ the hydraulic conductivity at natural saturation, and H_b is Bouwer's estimate of the effective capillary drive.

Smith (1972), using a computer model as a theoretical infiltrometer, ran many experiments. He then attempted to correlate the calculated (observed) ponding times with the rainfall intensity. Based on the data generated, he concluded that for a given soil and a given initial water content, t_p could be "well described by a power decay curve such that"

$$t_p = a_1 r^{-a_2} \tag{65}$$

where a_1 and a_2 are constants, characteristic of the soil and dependent on θ_i. If Equation (64) is valid, then without going into details, it is clear that a_2 should have a value on the order of 2. Indeed, the least-square values Smith obtained do not deviate too much from 2.

The integration of the total velocity between the surface ($z = 0$) and a depth z_2 just below the wetting zone yields

$$v = \frac{\tilde{K}\left[H_c(\theta_u,\ \theta_i) + \int_0^{z_2} f_w \, dz\right]}{\int_0^{z_2} \mu_{rT} \, dz} \tag{66}$$

where H_c (θ_u, θ_i) is the generalized *effective capillary drive* defined as

$$H_c(\theta_u, \theta_i) = \int_{h_{cu}}^{h_{ci}} f_w \, dh_c = \int_{h_{cu}}^{\infty} f_w \, dh_c - \int_{h_{ci}}^{\infty} f_w \, dh_c \tag{67}$$

Since the curve of f_w versus h_c (see Figure I26) is known for a given soil, the term H_c (θ_u, θ_i) depends only on the unknown θ_u and *not on the shape of the moisture profile between* θ_i *and* θ_u. Thus the capillary term is known exactly if θ_u is known. On the other hand, the gravity term, that is, $\int_0^{z_2} f_w dz$ depends on the shape of the profile. This term can be approximated using a piston profile and takes therefore the form $[W(1 - f_i)]/[\tilde{\theta} - \theta_i]$, where f_i is abbreviated notation for $f_w(\theta_i)$ and W is cumulative infiltration (expressed as a water height.) Equation (66) takes the more explicit form,

$$v = \frac{\tilde{K}\left[H_c(\theta_u,\ \theta_i) + W(1 - f_i)/(\tilde{\theta} - \theta_i)\right]}{\int_0^{z_2} \mu_{rT} \, dz} \tag{68}$$

Figure I27 displays the shape of the total relative viscosity as a function of water content for an actual soil. The determination of the denominator, the viscous-resistance term, is the big problem. To evaluate it, one must know the water-content profile or at least a good approximation for it.

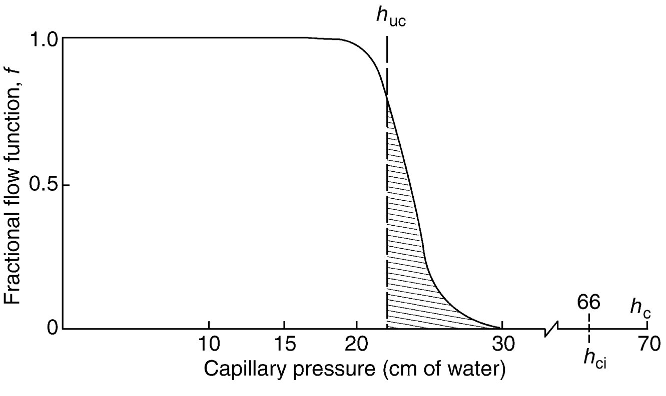


Figure I26 Curve of little-*f* function versus capillary pressure.

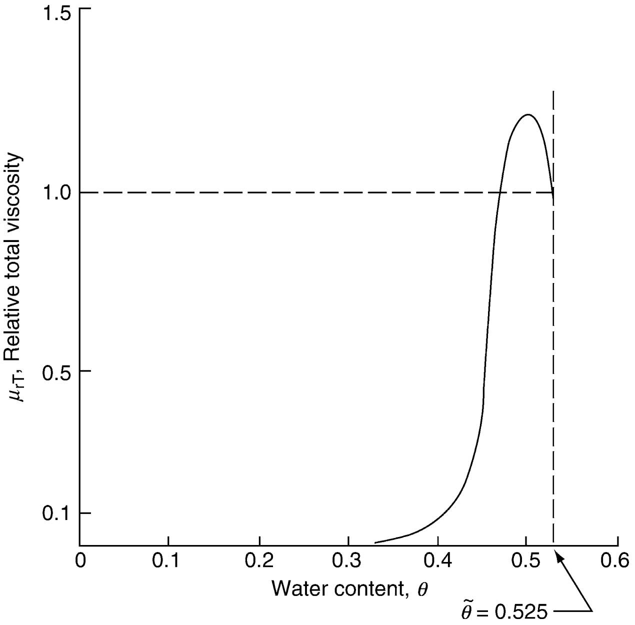


Figure I27 Curve of total relative viscosity versus water content.

Water-content profile approximation

The solution of Equation (48) is difficult in the general case. However, in the case of a given rainfall rate, the value of the total velocity is approximately known. Figure I28 shows a water-content profile and an air-pressure profile for a given time. For a column open at its bottom, the air pressure is atmospheric at both ends, and the air-pressure distribution must be as shown in Figure I28. The implication is that some air flows downward and some upward. From the definition of the total velocity, it follows that

$$v = r + v_a|_{z} = 0 \tag{69}$$

Since $v_a|_z = 0$ is negative, it follows that v is less than r and equal to r only if the air velocity at the surface is zero. By definition, $v_w = vF$, and in particular, at the soil surface,

$$r = vF(\theta_u) = vF_u \tag{70}$$

If one assumes that $v = r$, then $F_u = 1$. If $v < r$, the $F_u = (r)/(v) > 1$. The implication is that an error in v in one direction is compensated by an error in F_u in the other direction and the product vF_u remains "exact." For simplicity, it will be assumed that $v = r$, and consequently that $F_u = 1$. The exact shape of F is not known (see Figure I29), but the two end points of the curve are known. It can be shown, as was done in a previous section in the case of ponded infiltration, that for a fixed θ_u the time asymptotic limit of F is the secant approximation shown in Figure I29 and denoted F_∞. Since this approximation satisfies the condition of material balance, is correct for large times, and has provided excellent results when compared to actual experiments, it will be used, namely,

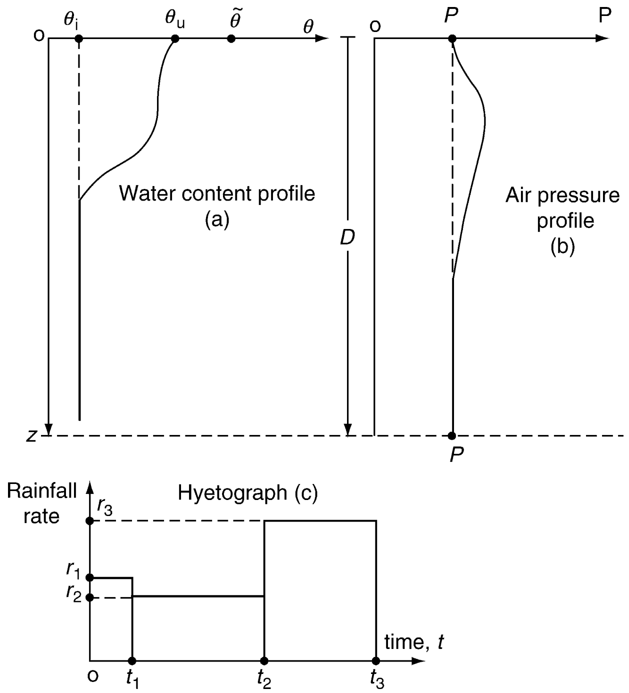


Figure I28 Water-content and air-pressure profiles during rain infiltration.

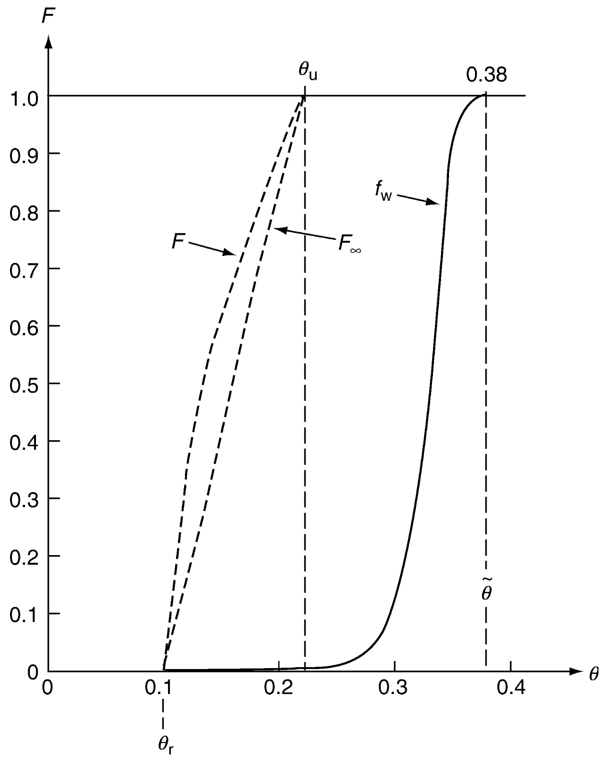


Figure I29 Fractional-flow function during rain infiltration.

$$F = \frac{1-f_i}{\theta_u - \theta_i}(\theta - \theta_i) + f_i \tag{71}$$

For this F and since $v = r$, Equation (68) can be integrated readily with the result

$$z_\theta = \int_{T(\theta)}^{t} \frac{1-f_i}{\theta_u - \theta_i} r(\tau)\,d\tau \tag{72}$$

where $T(\theta)$ is the time of the first appearance of the water content θ at the soil surface. Since θ_u is water content at time t at the surface, it follows by definition that

$$T(\theta_u) = t \tag{73}$$

Using Equation (72) to calculate $(\partial z)/(\partial \theta)|_t$, one obtains for the viscous-resistance term

$$\begin{aligned} \int_0^{z_2} \mu_{rT}(\theta)\,dz &= \int_{\theta_u}^{\theta_i} \mu_{rT}(\theta) \frac{\partial z}{\partial \theta}\bigg|_t d\theta \\ &= \frac{r(1-f_i)}{\theta_u - \theta_i} \int_{\theta_u}^{\theta_i} \mu_{rT} \frac{dT}{d\theta} d\theta \end{aligned} \tag{74}$$

Substitution of this result into Equation (68) leads to the fundamental equation for the unknown θ_u at a given time:

$$\frac{(\theta_u - \theta_i) H_c(\theta_u, \theta_i)}{1 - f_i} + \frac{(\theta_u - \theta_i) W}{\tilde{\theta} - \theta_i} = \frac{r2}{\tilde{K}} \int_{\theta_i}^{\theta_u} \mu_{rT} \frac{dT}{d\theta} d\theta \tag{75}$$

Differentiating Equation (75) with respect to time yields

$$\begin{aligned} \frac{d\theta_u}{dt} &= \left\{ \frac{H_c(\theta_u,\ \theta_i)}{1 - f_i} + \frac{\theta_u - \theta_i}{1 - f_i} \frac{d}{d\theta_u} [H_c(\theta_u,\ \theta_i)] + \frac{W}{\tilde{\theta} - \theta_i} \right\} \\ &= r \left[\frac{r}{\tilde{K}} \mu_{rT}(\theta_u) - \frac{\theta_u - \theta_i}{\tilde{\theta} - \theta_i} + \frac{2}{\tilde{K}} \frac{dr}{dt} \int_{\theta_i}^{\theta_u} \mu_{rT}\,dT \right] \end{aligned} \tag{76}$$

which is a nonlinear ordinary differential equation for the unknown $\theta_u(t)$. Equation (76) looks rather formidable, and for brevity H_c will be written for $H_c(\theta_u, \theta_i)$. Note, however, that the coefficient of $(d\theta_u)/(dt)$ is a linear function of W, say, $a(\theta_u) + b(\theta_u)W$ where $a(\theta)$ and $b(\theta)$ are deduced from the basic soil characteristics. Similarly, the right-hand side is an explicit function of r and θ_u except for the last integral.

Solution for constant rainfall rate

In this solution method the bothersome integral on the right-hand side of Equation (76) disappears. The remaining equation could then be solved numerically without too much difficulty. More insight, however, is obtained by integrating it approximately but analytically.

As long as rain infiltrates totally, that is, until ponding time, $v = I = r =$ constant. The denominator of Equation (68) will increase linearly with time. To maintain a constant ratio between the numerator and the denominator, it is necessary for $H_c(\theta_u, \theta_i)$ to also increase with time. From Figure I26 and a general knowledge of the shape of the capillary-pressure curve (see *Capillary pressure*), one can infer that in the range of intermediate water contents, $H_c(\theta_u, \theta_i)$ does not vary linearly with θ_u but is a much slower function of θ_u. Consequently, θ_u must vary with time more rapidly than linearly. Thus θ_u will of necessity rise quickly to values near $\tilde{\theta}$. Thus except for very early and very late times, it is legitimate to evaluate the *coefficients* in Equation (76) in the neighborhood of $\theta_\mathrm{u} = \tilde{\theta}$, and for simplicity at $\theta_\mathrm{u} = \tilde{\theta}$. The resulting simplified equation takes the form

$$\left(\frac{H_\mathrm{c}}{1-f_\mathrm{i}} + \frac{W}{\tilde{\theta}-\theta_\mathrm{i}}\right)\frac{\mathrm{d}\theta_\mathrm{u}}{\mathrm{d}t} = r\left(\frac{r\bar{\mu}_\mathrm{rT}}{\tilde{K}} - 1\right) \tag{77}$$

where $\bar{\mu}_\mathrm{rT}$ is an average value of μ_rT in the high range of water contents. Equation (77) is linear and can be integrated readily (Morel-Seytoux, 1975). Ultimately one obtains the ponding time

$$t_\mathrm{p} = \frac{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}}{(1-f_\mathrm{i})r}\left[\mathrm{e}^{\frac{\tilde{K}}{\bar{\beta}r-\tilde{K}}} - 1\right] \tag{78}$$

where $\bar{\beta}$ is an average between 1 and β defined previously (Equation (53)). The simple arithmetic average $\bar{\beta} = (1+\beta)/2$ agreement with experimental results (Figure I30). Predictions of ponding times (or equivalently of cumulative infiltration at ponding time) by Equation (78) compare favorably with experimental results (Figure I31).

After ponding, the infiltration rate is given by the relation

$$I = \frac{\mathrm{d}W}{\mathrm{d}t} = \frac{\dfrac{\tilde{K}}{\beta}\left[H_\mathrm{c}(\tilde{\theta},\theta_\mathrm{i}) + \dfrac{(1-f_\mathrm{i})W}{\tilde{\theta}-\theta_\mathrm{i}}\right]}{\dfrac{W(1-f_\mathrm{i})}{\tilde{\theta}-\theta_\mathrm{i}} - \dfrac{W_\mathrm{p}(1-f_\mathrm{i})}{\tilde{\theta}-\theta_\mathrm{i}}\left(1-\dfrac{1}{\beta}\right)} \tag{79}$$

or in integrated form,

$$\frac{\tilde{K}}{\beta}(t-t_\mathrm{p}) = W - W_\mathrm{p} - \left[\frac{\tilde{\theta}-\theta_\mathrm{i}}{1-f_\mathrm{i}}H_\mathrm{c}(\tilde{\theta},\theta_\mathrm{i}) + W_\mathrm{p}\left(1-\frac{1}{\beta}\right)\right] \ln\left[\frac{1+\dfrac{(1-f_\mathrm{i})W}{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}(\tilde{\theta},\theta_\mathrm{i})}}{1+\dfrac{(1-f_\mathrm{i})W_\mathrm{p}}{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}(\tilde{\theta},\theta_\mathrm{i})}}\right]$$

where W_p is the cumulative infiltration at ponding. Naturally, the preceding formula is valid only for $t > t_\mathrm{p}$.

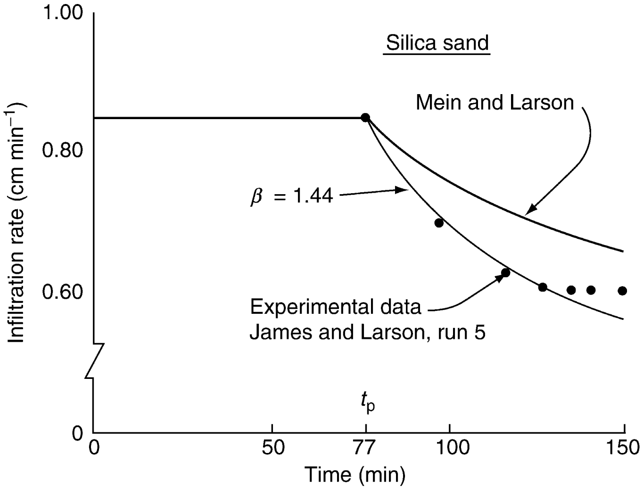


Figure I30 Comparison of observations and predictions of infiltration rates after ponding.

Solution for variable rainfall rate

For a succession of rainfall intensities such as shown in Figure I28, a ponding-time formula can be derived, namely,

$$t_\mathrm{p} = t_{j-1} + \frac{1}{r_j}\left[\frac{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}}{1-f_\mathrm{i}} + W_{j-1}\right] \left\{\mathrm{e}^{\frac{\tilde{K}}{\bar{\beta}r_j-\tilde{K}}}\left[\frac{j-1}{v=1}\left(\frac{1+\dfrac{W(1-f_\mathrm{i})}{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}}}{1+\dfrac{(1-f_\mathrm{i})W_{v-1}}{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}}}\right)^{-\left(\frac{\bar{\beta}r_v-\tilde{K}}{\bar{\beta}r_j-\tilde{K}}\right)}\right] - 1\right\} \tag{81}$$

where t_{j-1} is the beginning time of the rainfall intensity r_j, and W_{j-1} is the cumulative infiltration up to time t_{j-1}. Equation (81) applies if the ponding time occurs in the time interval (t_{j-1}, t_j).

For unsteady rainfall with various rates r_j, in order to determine the ponding time, one uses Equation (81) for the case $j = 1$, namely,

$$t_\mathrm{p}^1 = \frac{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}}{r_1(1-f_\mathrm{i})}\left(\mathrm{e}^{\frac{1}{\bar{\beta}r_1^*-1}} - 1\right) \tag{82}$$

If $t_\mathrm{p}^1 < t_1$, then the ponding time is given by Equation (82). If $t_\mathrm{p}^1 > t_1$, then ponding does not occur during the first constant rainfall rate time interval. One then recalculates t_p from Equation (81) for $j = 2$, namely,

$$t_\mathrm{p}^2 = t_1 + \frac{1}{r_2}\left[\frac{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}}{1-f_\mathrm{i}} + W_1\right] \left\{\mathrm{e}^{\frac{1}{\bar{\beta}r_2^*-1}}\left[\left(1+\frac{(1-f_\mathrm{i})W_1}{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}}\right)^{-\left(\frac{\bar{\beta}r_1^*-1}{\bar{\beta}r_2^*-1}\right)}\right] - 1\right\} \tag{83}$$

If $t_p^2 < t_2$ then the ponding time is given by Equation (83). If $t_p^2 > t_2$, then ponding does not occur during the second constant rainfall rate time interval. One then recalculates t_p from Equation (81) for $j = 3$, namely,

$$t_\mathrm{p}^3 = t_2 + \frac{1}{r_3}\left[\frac{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}}{1-f_\mathrm{i}} + W_2\right] \left\{\mathrm{e}^{\frac{1}{\bar{\beta}r_3^*-1}}\left[\left(1+\frac{(1-f_\mathrm{i})W_1}{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}}\right)^{-\left(\frac{\bar{\beta}r_2^*-1}{\bar{\beta}r_3^*-1}\right)} \left(1+\frac{(1-f_\mathrm{i})W_2}{(\tilde{\theta}-\theta_\mathrm{i})H_\mathrm{c}}\right)^{-\left(\frac{\bar{\beta}r_2^*-1}{\bar{\beta}r_3^*-1}\right)}\right] - 1\right\} \tag{84}$$

In this form it is clear that if $r_2 = r_1$ and thus $t_2 = t_1$, Equation (84) reduces to Equation (83) as it should. This also shows

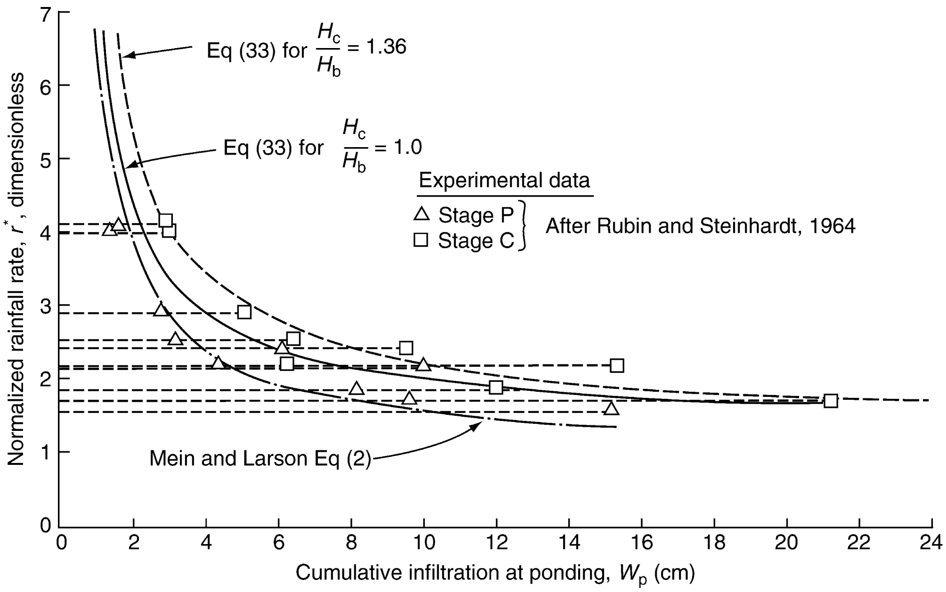


Figure I31 Comparison of observations and predictions of ponding times.

that successive rainfall rates need not be different. The process is repeated until the ponding moment is located in the proper interval. Once $t_{j-1} < t_p \leq t_j$ is known, then the cumulative infiltration up to ponding is

$$W_p = \sum_{i=1}^{j-1} r_i(t_i - t_{i-1}) + r_j(t_p - t_{j-1}) \tag{85}$$

and W can be obtained from Equation (80) for $W \geq W_p$ as a function of time. At a given time, the infiltration rate is given by Equation (79).

From a theoretical standpoint, Equation (81) should be particularly good if the rainfall intensities are high due to the assumptions made in its derivation that the coefficients in the differential equation for $\theta_u(t)$, water content at the soil surface, are evaluated at $\theta = \tilde{\theta}$. The variable θ_u will rise quickly to values close to $\tilde{\theta}$ for high rainfall rates, but its rise may be slow for low rainfall rates. In the latter case, Equation (81) may be in serious error. For r^* slightly $>1/\beta$, the rise of θ_u with time is probably underestimated. This fact is confirmed when using Equation (82) for a single rain of intensity r and Equation (83) for two intensities: one of value $\tilde{K}/\bar{\beta}$ and duration t_1 and a later one of value r. From Equation (82) one obtains

$$t_p^1 = \frac{a}{r}\left(e^{\frac{1}{\bar{\beta}r^*-1}} - 1\right) \quad \text{where} \quad a = \frac{(\tilde{\theta} - \theta_i)H_c}{1 - f_i} \tag{86}$$

and from Equation (83) one obtains

$$t_p^2 - t_1 = \frac{1}{r}(a + W_1)\left(e^{\frac{1}{\bar{\beta}r^*-1}} - 1\right) \tag{87}$$

or

$$t_p^2 - t_1 = \frac{W_1}{r}\left(e^{\frac{1}{\bar{\beta}r^*-1}} - 1\right) + t_p^1 \tag{88}$$

From a physical standpoint, one expects $t_p^2 - t_1$ to be $<t_p^1$, but clearly from Equation (88) it is predicted otherwise. Thus for low antecedent rainfall intensities, that is, for r^* greater than $1/\bar{\beta}$ and close to $1/\bar{\beta}$, Equation (81) is in error, and possibly in serious error if r^* is itself small and W_1 is large. However, once r^* significantly exceeds $\tilde{K}\bar{\beta}$, the compensating factor

$$\left(1 + \frac{W_1}{a}\right)^{-\frac{\bar{\beta}r_1^*-1}{\bar{\beta}r_2^*-1}}$$

comes into play, and results are in the correct direction, though they may still not be very accurate.

The basis for the improvement of Equation (81) naturally lies in a reexamination of the assumptions leading to it, namely, the steps leading from Equation (76) to (77). For constant rainfall rate the use of a time-average for $\mu_{rT}(\theta_u)$, namely, $\bar{\beta}$, is justified. However, for a succession of rainfall rates, in the interval of time when ponding occurs, the value of $\mu_{rT}(\theta_u)$ is on the average closer to β than to $\bar{\beta}$. Thus formula 81 tends to overestimate t_p. An obvious correction to Equation (81) in the right direction is

$$t_p = t_{j-1} + \frac{1}{r_j}\left[\frac{(\tilde{\theta} - \theta_i)H_c}{1 - f_i} + W_{j-1}\right]$$
$$\left\{e^{\frac{\tilde{K}}{\beta r_j - \tilde{K}}}\left[\frac{j-1}{v=1}\left(\frac{1 + \frac{W_v(1-f_i)}{(\tilde{\theta}-\theta_i)H_c}}{1 + \frac{(1-f_i)W_{v-1}}{(\tilde{\theta}-\theta_i)H_c}}\right)^{-\left(\frac{\bar{\beta}r_v - \tilde{K}}{\beta r_j - \tilde{K}}\right)}\right] - 1\right\} \tag{89}$$

Infiltration formulas in hydrologic practice

Naturally, practical hydrology could not wait for the fully mature development of scientific hydrology to solve hydrologic problems. This is particularly true since the birth of scientific hydrology as a discipline was only recent as compared to other disciplines. The International Association of Hydrological Sciences is less than a quarter century old.

There are two types of practical infiltration formulas: (1) those whose functional form was derived from solutions (albeit approximate) of the basic equations and (2) those whose functional form was selected a priori to perform in qualitative agreement with the known observational facts. In the first category are the formulas of Green and Ampt, Morel-Seytoux, and Philip. The Green and Ampt formula for cumulative infiltration is

$$W - (H + H_{\mathrm{f}})(\tilde{\theta} - \theta_{\mathrm{i}}) \ln\left[1 + \frac{W}{(\tilde{\theta} - \theta_{\mathrm{i}})(H + H_{\mathrm{f}})}\right] = \tilde{K}t \tag{90}$$

The parameters H_{f}, $\tilde{K}$, and $\bar{\beta}$ are characteristics of the soil, whereas H is a ponding depth variable and θ_{i} describes the initial moisture state of the system. Under natural conditions H can be taken as zero because H is usually negligible compared to H_{f}. Morel-Seytoux's Formula

$$W - (H + H_{\mathrm{c}})(\tilde{\theta} - \theta_{\mathrm{i}}) \ln\left[1 + \frac{W}{(\tilde{\theta} - \theta_{\mathrm{i}})(H + H_{\mathrm{c}})}\right] = \frac{\tilde{K}}{\beta}t \tag{91}$$

differs from the Green and Ampt formula only in the introduction of the viscous correction factor β. Philip's formula is:

$$W = \tilde{K}t + S\sqrt{t} \tag{92}$$

The parameters $\tilde{K}$ and S are characteristics of the soil.

In the second category belong the formulas of Kostiakov, Horton, and Holtan, namely, and in that order,

$$W = At^{n} \qquad 0 < n < 1 \tag{93}$$

where A and n are empirical parameters,

$$W = \tilde{K}t + \frac{1}{k}(I_0 - \tilde{K})\left(1 - \mathrm{e}^{-kt}\right) \tag{94}$$

where I_0 and k are parameters, and *Holtan's formula* for the infiltration rate:

$$I = I_{\mathrm{c}} + a(W_{\mathrm{M}} - W)^{m} \tag{95}$$

where W_{M}, I_{c}, and a are parameters. In Holtan's formula, W_{M} is interpreted as a maximum available storage quantity.

Most of the formulas listed behave similarly for small and large times. For large times Equations (90)–(94) and (and even (95) if we interpret to mean by large times $W = W_{\mathrm{M}}$) all lead to a constant infiltration rate: $\tilde{K}$, $\tilde{K}/\beta$, or I_{c}. In the case of Holtan's Equation, I_{c} is interpreted to mean the hydraulic conductivity at natural saturation of a deeper, less pervious stratum. Thus I_{c} is only a fraction of $\tilde{K}$. We note from Equation (55) that the limiting infiltration rate is $(\tilde{K})/(\beta)[1 - (H_{\mathrm{A}})/(D)]$, which can be any fraction of $\tilde{K}/\beta$ with a proper choice of D. Thus the low value of I_{c} compared to $\tilde{K}$ in Holtan's formula could be interpreted just as well to be due to air compression rather than due to the existence of a less pervious, deep stratum. From the remark that follows Equation (56), it is clear that the extension of the simplistic Green and Ampt approach has been validated by the more rigorous two-phase approach so that simple formulas to account for air effect, air compression, and the presence of a deeper, less pervious stratum can be derived.

For small times again Equations (90), (91), and (92) indicate that the infiltration decreases like $t^{-\frac{1}{2}}$. Essentially all the information in Equation (92) is contained in Equations (90) and (91), but Equations (90) and (91) provide information regarding the *intermediate* times. Equation (92) assumes without justification that the addition of the small-time and large-time behaviors provide the intermediate time behavior. Equation (91) makes no such assumption and has a sounder physical basis. It is also an experimental fact that the Green and Ampt formula gives better fit to experimental observations than Philip's formula.

Strictly speaking, the preceding equations apply only for ponded infiltration. Except Equations (92) and (93), all equations generalize to the case of rainfall infiltration. In Equation (94), t then is time since ponding, W is cumulative infiltration since ponding, and $I_0 = r$. The generalization of Equation (91) after ponding is given by Equation (80) and that of Equation (90) by the same equation with $\beta = 1$. Theoretically, Equations (94) and (95) could be used to calculate a ponding time. The *Hortan ponding time* would be the solution of the equation

$$\left(\frac{r - \tilde{K}}{I_0 - \tilde{K}}\right)t_{\mathrm{p}} = \frac{1}{k}\left(1 - \mathrm{e}^{-kt_{\mathrm{p}}}\right) \tag{96}$$

This ponding time shows the influence of rainfall intensity in agreement with experimental evidence. From Equation (95) one deduces a ponding time:

$$t_{\mathrm{p}} = \frac{W_{\mathrm{M}}}{r} - \left(\frac{r - I_{\mathrm{c}}}{a}\right)^{1/m} \tag{97}$$

This ponding time shows the proper decrease of t_{p} with r, but it does not indicate that ponding will not occur if r is less than $\tilde{K}$.

Two simple formulas for ponding time have been proposed for constant rainfall: the *Mein and Larson (1973) formula:*

$$t_{\mathrm{p}} = \frac{(\tilde{\theta} - \theta_{\mathrm{i}})H_{\mathrm{b}}}{r\left(\frac{r}{\tilde{K}} - 1\right)} \tag{98}$$

and Morel-Seytoux' formula:

$$t_{\mathrm{p}} = \frac{(\tilde{\theta} - \theta_{\mathrm{i}})H_{\mathrm{c}}}{r}\left[\mathrm{e}^{\frac{\tilde{K}}{\beta r - \tilde{K}}} - 1\right] \tag{99}$$

Both formulas show the proper dependence of t_{p} with r and give similar results. The Green and Ampt assumptions used to derive Equation (98) do not permit generalization of variable rainfall rates. With the two-phase approach (Morel-Seytoux, 1975), Equation (99) can be generalized with the result given in Equation (89). Though Equation (89) looks rather formidable, it requires no more parameters than Equation (99) since $\bar{\beta} = (1 + \beta)/2$. The result is limited to the situation when the rainfall intensities vary but nevertheless exceed the limiting value $\tilde{K}/\beta$. Extensions, which remove this limitation, have appeared in the literature (Morel-Seytoux, 1978) since this article was written.

H. J. Morel-Seytoux

Bibliography

Bouwer, H., 1969. Theory of seepage from open channels. In Chow, V.T., ed., *Advances in Hydroscience*, 5: 121–172.

Green, W.H., and Ampt, C.A., 1911. Studies on soil physics. I. Flow of air and water through soils. *J. Agric. Sci.*, **4**: 1–24.

James, L.G., and Larson, C.L., 1974. Modeling infiltration and redistribution of soil water during intermittent applications. Paper presented at the 1974 Winter Meeting of the Am. Soc. Agric. Eng., Chicago, Dec. 10–13, 1974, 26 pp.

Mein, R.G., and Larson, C.L., 1973. Modeling infiltration during a steady rain. *Water Res. Res. J.* **9**(2): 384–394.

Morel-Seytoux, H.J., 1973. Two-phase flows in porous media. In Chow, V.T., ed., *Adv. Hydrosci.,* 9: 119–202.

Morel-Seytoux, H.J., 1976. Derivation of equations for rainfall infiltration. *J. Hydrol.*, **31**(3/4): 203–219.

Morel-Seytoux, H.J., 1978. Derivation of equations for variable rainfall infiltration. *Water Res. Res. J.*, **14**(4): 561–568.

Morel-Seytoux, H.J., and Khanji, J., 1975. Equation of infiltration with compression and counterflow effects. *Bull. Int. Assoc. Hydrol. Sci.* **20**(4): 505–517.

Philip, J.R., 1957. The theory of infiltration. I. The infiltration equation and its solution. *J. Soil Sci.*, **83**: 345–357.

Rubin, J., and Steinhardt, R., 1964. Soil water relations during rain infiltration. III. Water uptake at incipient ponding, *Soil Sci. Soc. Am. Proc.*, **28**(5): 614–619.

Smith, R.E., 1972. The infiltration envelope: results from a theoretical infiltrometer. *J. Hydrol.*, **17**: 1–21.

Whisler, F.D., and Bouwer, H., 1970. Comparison of methods for calculating vertical drainage and infiltration for soils. *J. Hydrol.*, **10**(1): 1–19.

Cross-references

Capillary Pressure
Conductivity, Hydraulic
Flow Theory
Imbibition
Percolation
Puddling
Soil Pores
Soil Water
Water Budget in Soil
Water Content and Retention
Wetting Front

INHERITANCE

The acquisition by a soil of minerals, structures, textures and other qualities or characteristics from the parent material. Applied especially to 2 : 1 clay minerals that have inherited their basic structure from a pre-existing sheet silicate such as mica, chlorite of vermiculite.

Cross-reference

Clay Mineral Formation

INORGANIC FERTILIZERS

See *Fertilizers*, *Inorganic*.

INORGANIC SOIL

A soil composed mainly of minerals, with organic matter playing only a minor role in determining the properties of the soil. A less precise term than mineral soil.

INSOLATION

Exposure to the radiation of the sun and the action of the sun's rays on soils or other materials or bodies exposed to such. Applied particularly to the effect of temperature change on mechanical weathering.

INTENSIVE AGRICULTURE

A form of agriculture in which the optimal use of land is promoted by utilizing as much of a given area as possible, commonly as small holdings especially in underdeveloped countries, and employing such techniques as multiple cropping, and intercropping, to maximize production.

INTERFLUVE

An upland or ridge separating streams flowing in the same direction, but into two different, adjacent river systems.

INTERGRADE

An intermediate grade or stage having properties and characteristics that lie between those of two separate taxons in a system of soil classification. Also applied to sheet silicates with structures that have characteristics intermediate between two end-members e.g., illite-smectite, smectite-vermiculite.

Cross-references

Clay Mineral Formation
Soil Classification: Soil Taxonomy

ION

An *ion* is a charged particle obtained when an atom or group of atoms loses or gains an electron. If the electrons outnumber the protons the ion is negatively charged and is referred to as an anion since it is attracted to an anode. If the protons outnumber the electrons the ion is positively charged and is referred to as a cation (attracted to a cathode). An ion that has both a positive and a negative charge (a amino acid in neutral solution for example) is called a zwitterion, from the German for twin. Glycine is an example, containing a basic amino group (NH_2) and an acidic carboxyl group (COOH) at opposite ends of the molecule. In aqueous solution H^+ may be transferred from the acid group to the amino group so that the molecule is positively charged at one end and negatively charged at the other. Zwitter ions are also referred to as inner salts and (erroneously) as dipolar ions.

ION EXCHANGE

The interchange of ions of like charge between a solid and an aqueous solution in contact with it. In cation exchange the ions are positively charged, in anion exchange they are negatively charged.

Bibliography

Sposito, G., 1989. *The Chemistry of Soils* (Chaps. 8 and 9). New York: Oxford University Press, 277 pp.

Cross-references

Adsorption
Exchange Phenomena
Soil Chemistry
Soil Fertility
Soil Mineralogy

IONIC ACTIVITIES

See *Soil solution*.

IRON OXIDES

Basic reactions

With 5.1 mass-%, iron is the fourth most abundant element of the Earth's crust. It exists predominantly in the divalent state and is located in silicates such as pyroxene, amphibole, biotite and olivine as well as in sulfides (e.g., pyrite, FeS_2).

Once exposed to aerobic weathering, Fe^{2+} will be readily oxidized to Fe^{3+} which, in the common pH range of soils, will immediately hydrolyze and form sparingly soluble Fe^{III} oxides (in the following used as a group term embracing all compounds in the system Fe–O–H). The overall weathering reaction is schematically represented by:

$$\underset{Fe^{II}\ \text{silicate}}{Si{-}O{-}Fe^{II}{-}} + H_2O = \underset{Fe^{III}\ \text{oxide}}{-Fe^{III}{-}OH} + HO{-}Si{-} + e^-$$

The electron e^- is transferred to oxygen ($O_2 + 4e^- = 2O^{2-}$), readily available in aerobic soils. The proportion of the Fe in the parent rock "weathered" into Fe^{III} oxides through this reaction can be taken as one measure of the degree of weathering. It ranges between a few percent for young to almost 100% for highly matured soils.

Once formed, the sparingly soluble Fe^{III} oxides can not be redissolved by the reversal of hydrolysis (protonation), but complexation (mainly with organic ligands) or, more importantly, biotic reduction may bring about redissolution. Biotic reduction takes place in those parts of a soil where biological metabolism of biomass causes O_2 deficiency i.e., at a redox potential (Eh) of <0.1 V. In this case, immobile Fe^{3+} in oxides is reduced to mobile Fe^{2+} ions by electrons from the oxidation of biomass (represented by CH_2O):

$$4Fe^{III}OOH + CH_2O + 8H^+ = 4Fe^{2+} + CO_2 + 7H_2O$$

Thus, one C supplies 4 electrons to reduce four Fe^{3+}. The corollary is that Fe^{III} oxides are an important oxidant of organic matter (including xenobiotics) if oxygen is lacking. Conditions for microbial reduction in a soil are water saturation and the presence of metabolizable organic matter, e.g., biomass. The Fe^{2+}, once mobilized, may migrate in the profile, eventually being reoxidized on reaching a zone of higher Eh. New Fe^{III} oxides are then formed. The reoxidation is usually abiotic except at very low pH (e.g., in acid sulfate soils and in ARD) where the kinetic hindrance is surmounted by specific bacteria, e.g., *Thiobacillus ferrooxidans.* This redox process occurs repeatedly during pedogenesis and leads to or turns a homogeneous into a heterogeneous distribution of Fe^{III} oxides in so-called redoximorphic soils, thereby reflecting the mosaic of aeration, visually expressed as differential staining. It is also responsible for the redistribution of Fe in whole landscapes in almost any climatic region. Local concentrations vary in shape and hardness. Spherical forms can be soft (e.g., mottles), or hard (e.g., nodules, glaebules and concretions). Hardening of a complete horizon produces the commonly very hard accumulations of Fe^{III} oxide called ferricrete.

Iron oxide minerals of soil

The intensive yellow, brown and red colors of Fe^{III} oxides make their nature and spatial distribution in soils easily recognizable, and these colors often form the basis for naming (Red Earth, Terra rossa, Brunizem etc.) and classifying soils. The color variations are caused by different Fe oxide minerals in the system Fe–O–OH (or Fe_2O_3–H_2O). The mineralogical, physical and chemical characteristics of those oxides, which are repeatedly found in soils – and only these are treated here – are listed in Table I2.

Minerals are defined by their crystal structure and by their chemical composition. Only a brief description of the structure is given here. The Fe-oxides consist of layers of the (large) O and OH ions which are either hexagonally close packed (hcp), as in goethite and hematite, or cubically closed packed (ccp), as in lepidocrocite and maghemite. The small Fe^{III} cations ($r = 0.067$ nm) occupy the interstices between the O anions ($r = 0.14$ nm), thus forming an octahedron having as immediate neighbors either 6O i.e., $-[FeO_6]-$ as in hematite, or 3O and 3OH i.e., $-[FeO_3(OH)_3]-$ as in goethite (Figure I32). In addition, $-[FeO_4]-$ tetrahedra with four O neighbors occur e.g., in magnetite and maghemite. Thus, the Fe may be either 6- or 4-coordinated with O (^{vi}Fe or ^{iv}Fe). The octaedra may be connected to each other via faces, edges or corners leading to different Fe–O bond lengths. In the OH-containing forms the octahedra arrays are bridged by H-bonds.

The Fe^{III} in the octahedral position may be partially replaced by other trivalent metal cations of similar size, such as Al^{III}, Mn^{III}, Cr^{III} and V^{III}, but divalent metals (Ni, Co, Cu, Zn, Ti) may also be incorporated. This is called *isomorphous* substitution, because the structure itself is not modified. It leads to partial solid solutions, which are common in soils between goethite (named after the famous German poet), α-FeOOH, and diaspore, α-AlOOH, and between hematite, α-Fe_2O_3, and corundum, α-Al_2O_3, which have the same structure. Substitution modifies the properties of the Fe-oxides such as unit cell size, spectrographic behavior, magnetic properties, color, solubility and dissolution kinetics.

Table I2 General physical and chemical characteristics of iron-oxide minerals occurring in soils (see Cornell and Schwertmann, 2003)

Mineral name: Formula:	Hematite α-Fe_2O_3	Maghemite γ-Fe_2O_3	Magnetite Fe_3O_4	Goethite α-FeOOH	Lepidocrocite γ-FeOOH	Ferrihydrite (6-line) $Fe_{1.55}O_{1.66}(OH)_{1.34}$
Crystal system	Trigonal	Cubic or tetragonal	Cubic	Orthorhombic	Orthorhombic	Hexagonal
Cell dimensions (nm)	$a = 0.50340$	$a = 0.834$	$a = 0.839$	$a = 0.388$	$a = 0.4608$	$a = 0.296$
				$b = 0.9956$	$b = 1.254$	
	$c = 1.3752$	$c = 2.5014$		$c = 0.30215$	$c = 0.307$	$c = 0.949$
Usual crystal shape	Hexagonal plates Rhombohedra	Cubes	Cubes	Needles, laths	Laths, needles	Spheres
Density (g cm^{-3})	5.26	4.87	5.18	4.26	4.09	3.96
Color	Red	Reddish-brown	Black	Yellow-brown	Orange	Red-brown
Solubility product[§§] (pFe + 3 pOH)	42.2–43.3	40.5	43.4–44.0	40–44	~42	38–39.5
Most intense XRD Spacings (nm)	0.269, 0.251 0.366	0.251, 0.295 0.147	0.253, 0.297 0.1485	0.418, 0.245 0.269	0.626, 0.329 0.247	0.250, 0.221 0.196, 0.148
Type of magnetism*	*wfm* or *efm*	*fim*	*fim*	*afm*	*afm*	*sp*
Neel (Curie) temperature (K)	956	(820–986)	(850)	400	77	25–115[#]

[#] Blocking temperature.
[*] *wfm*: weekly ferromagnetic; *afm*: antiferromagnetic; *fim*: ferrimagnetic; *sp*: speromagnetic.
[§] Changes with substitution for Fe by cations for different radii.
[§§] Depends on particle size.

The various Fe oxide minerals differ mainly in the arrangement of the octahedra in space (Figure I32). The FeOOH forms consist of double bands of edge-sharing $FeO_3(OH)_3$ octahedra running along the crystallographic *b*-direction in goethite and the *c*-direction in lepidocrocite. In *goethite*, the double bands are linked by corner-sharing oxygens forming 2 × 1 octahedral arrangements and hydrogen bonds run across the bands. In *lepidocrocite* the double bands of octahedra share edges to form zig-zag layers which are connected by hydrogen bonds. In *schwertmannite* four double chains of octahedra form a 2 × 2 tunnel in which sulfate anions are supposed to be located. In all these FeOOH minerals only half of the octahedral interstices are occupied by Fe^{III}. *Hematite* consists of layers of FeO_6-octahedra, which are linked by edge- and face-sharing, and are stacked parallel to the *c*-direction. Two-thirds of the octahedral interstices are filled with Fe^{III}. Some distortion of the octahedra, and the absence of H bonds, yield a more compact structure than the FeOOH form. This is responsible for the high density (5.26 g cm^{-3}) of the mineral.

The crystallinity of ferrihydrite may vary considerably, as evidenced by the number (between 2 and 6–7) of broad X-ray diffraction peaks, which are used to further differentiate them. After Drits et al. (1993) the best ordered form (6-line) contains three intergrown structural components: (1) a defect-free one consisting of ABACA... anion close packing with the Fe-atoms (50% occupancy) only at octahedral sites, and a hexagonal unit cell with $a = 0.296$ nm and $c = 0.949$ nm and a space group P-31c; (2) a defective one with ABA and ACA structural fragments occurring with equal probability in a random sequence and with the Fe-atoms within each fragment being identically ordered in a hexagonal super-cell with $a = 0.5126$ nm, space group P3, and (3) about 25% ultradispersed 1–2 nm hematite. A general formula is $Fe_5O_5(OH)$. The main difference between 6- and 2-line ferrihydrite is in the size of their crystal domains. The formula for synthetic 6L sample $Fe_{1.55}O_{1.66}(OH)_{1.34}$ and $Fe_{1.42}O_{1.26}(OH)_{1.74}$ for synthetic 2L ferrihydrite.

Magnetite and *maghemite* differ from the foregoing Fe-oxides by having two types of metal-O-arrangements in their cubic structures: $^1/_3$ of the Fe is Fe^{IV} and 2/3 is Fe^{VI}. In magnetite all metal sites are filled with Fe with the tetrahedral positions being completely occupied by Fe^{3+}, while the octahedral sites contain equal amounts of Fe^{3+} and Fe^{2+}. This results in a unit cell formula of ${}^{iv}Fe_8^{3+}\ {}^{vi}(Fe_8^{3+}Fe_8^{2+})O_{32}$. In maghemite only 5/6 ($21^1/_3$ instead of 24) of the total available metal sites are filled by Fe^{3+}; the remaining sites being vacant. The vacancies may be ordered tetragonally to give superstructure XRD peaks and the formula is $Fe_{2.67}?_{0.33}O_4$, where ? signifies vacancy. *Limonite* and *hydrated ferric oxide* (HFO) are obsolete mineral names.

Properties of soil Fe^{III} oxides

1. They are strong pigments and give many soils their red, yellow, orange or brown color even at low concentrations (a few percent). The mineral-specific color results from their interaction with visible light and depends on both the crystal structure and particle size. It can be characterized by reflectance spectra in the visible range, by chromaticity parameters or simply by the Munsell color notation (hue, chroma, value).
2. They occur as minute crystals, often poorly ordered, ranging between about 5 and 100 nm in size. The crystal shape may be characteristic of a specific oxide (see Table I2) but equant, poorly defined particles often occur. Due to the small size, the oxides have a very large specific surface area between about 50 and 300 m^2 g^{-1} and contribute substantially to the surface area of soils even at low concentrations.
3. Their surface is covered with OH ions attached to Fe^{III} atoms. These are called surface functional groups and contribute substantially to the specific adsorption of various anions as inner sphere complexes. Common sorbates are phosphate, silicate, arsenate and humic compounds, as well as cations such as heavy metals. This adsorption makes the soil mantle act as an efficient sink for these ions and molecules thereby restricting their mobility in terrestrial ecosystems.
4. They have a very low *solubility* ($pFe^{3+} + 3pOH = 38$–44; Table 12) so that free Fe^{3+} ions only occur in extremely acid soils. The solubility increases with decreasing crystal size. It also increases if reduction to Fe^{2+} occurs (i.e., at Eh $\ll$ 0.1V), and if ligands forming strong Fe complexes are present (e.g., citrate, humics).

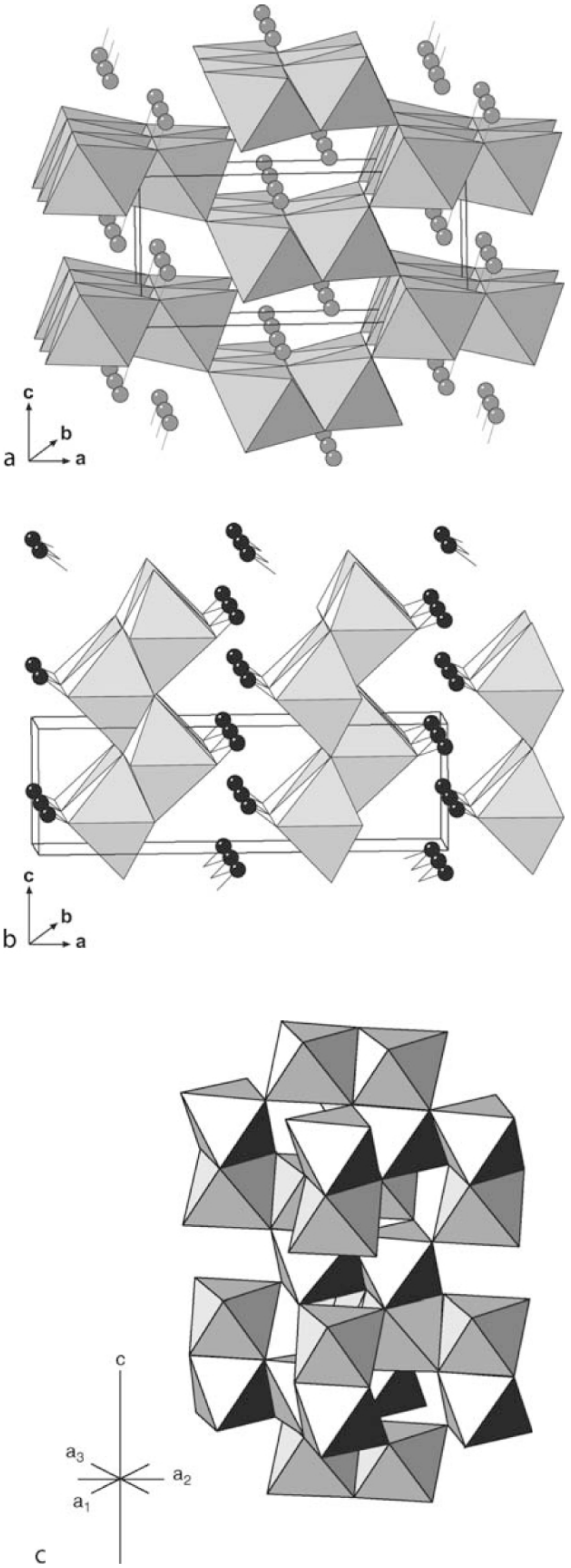


Figure I32 Idealized structural models of goethite (a), lepidocrocite (b) and hematite (c). The *small circles* indicate hydrogen bonds (H. Stanjek, unpubl.).

5. With respect to *isomorphous substitution* (see above), Al-for-Fe substitution is very common in soils. Up to $^1/_3$ of the Fe positions in goethite and up to $^1/_6$ in hematite may be occupied by Al. This substitution stabilizes the Fe-oxides, as shown by a decrease in the rate of dissolution by protonation and by reduction.
6. Due to their poor crystallinity (small crystal size and structural disorder), unspecific particle shape and low concentration in soils, their *identification* (e.g., by X-ray diffraction) is often difficult and requires Fe-specific methods, such as Mössbauer spectroscopy.

Occurrence and formation

All Fe oxide minerals listed in Table I2 have been identified in soils or similar earth-surface environments and can be readily synthesized in the laboratory under ambient conditions. The close link between the occurrence of Fe^{III} oxides and their mechanism of formation facilitates correlating their presence with pedogenetic conditions. This has been shown by a survey of Fe^{III} oxides in various soils around the world.

Goethite and *hematite* are by far the most common Fe-oxides in soils. This is partly due to their high thermodynamic stability (see Table I2). The much higher stability (lower solubility) of goethite relative to ferrihydrite is shown by the Eh–pH diagram in Figure I33 (see also below). At a given pH, goethite produces the same Fe concentration in solution, as ferrihydrite only at a much lower Eh. Lepidocrocite is intermediate in stability. However, in spite of their lower stability, metastable forms such as lepidocrocite and ferrihydrite often occur in soils, particularly in younger soils characterizing the non-equilibrium state in the pedoenvironment. This is because the formation of these oxides is kinetically favored and their transformation to the stable forms is kinetically hindered, e.g., by an association with adsorbed ions or molecules, such as phosphate and organics. Nonetheless, the Fe-oxides of older soils, e.g., ultisols and oxisols, are mostly goethite or goethite and hematite.

With respect to their global distribution, soils of the subtropics and tropics often contain hematite in addition to goethite, in widely varying ratios and are therefore red, whereas soils in temperate regions are usually free of hematite and are dominated by goethite, which makes them yellow-brown. In view of

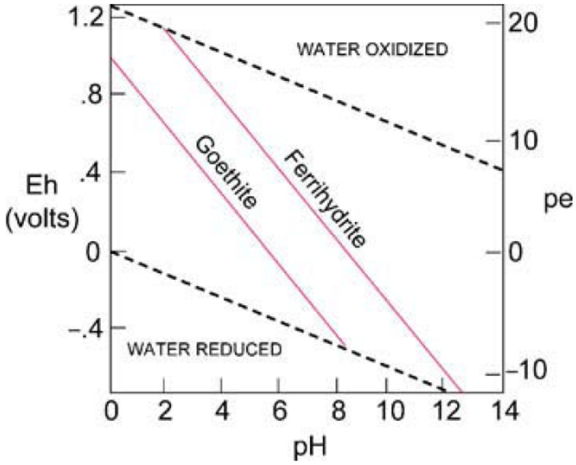


Figure I33 Eh–pH relation for goethite and ferrihydrite at a Fe^{2+} activity of 10^{-4} M l^{-1} and at 100 kPa and 25 °C.

their similar thermodynamic stability, it is essential to understand their mechanisms of formation in order to interpret the widely varying ratios of these two oxides. To this effect, numerous synthesis experiments have been conducted to simulate goethite and hematite formation under soil conditions, and their results may be very briefly summarized as follows: Goethite either forms through slow oxidation of Fe^{II} ions or solid Fe^{II} compounds such as pyrite or siderite or, alternatively from ferrihydrite. When ferrihydrite is the precursor, goethite formation competes with that of hematite (Figure I34), which, in contrast to goethite, needs ferrihydrite as a precursor. Whereas goethite forms *via solution* from dissolved, partly

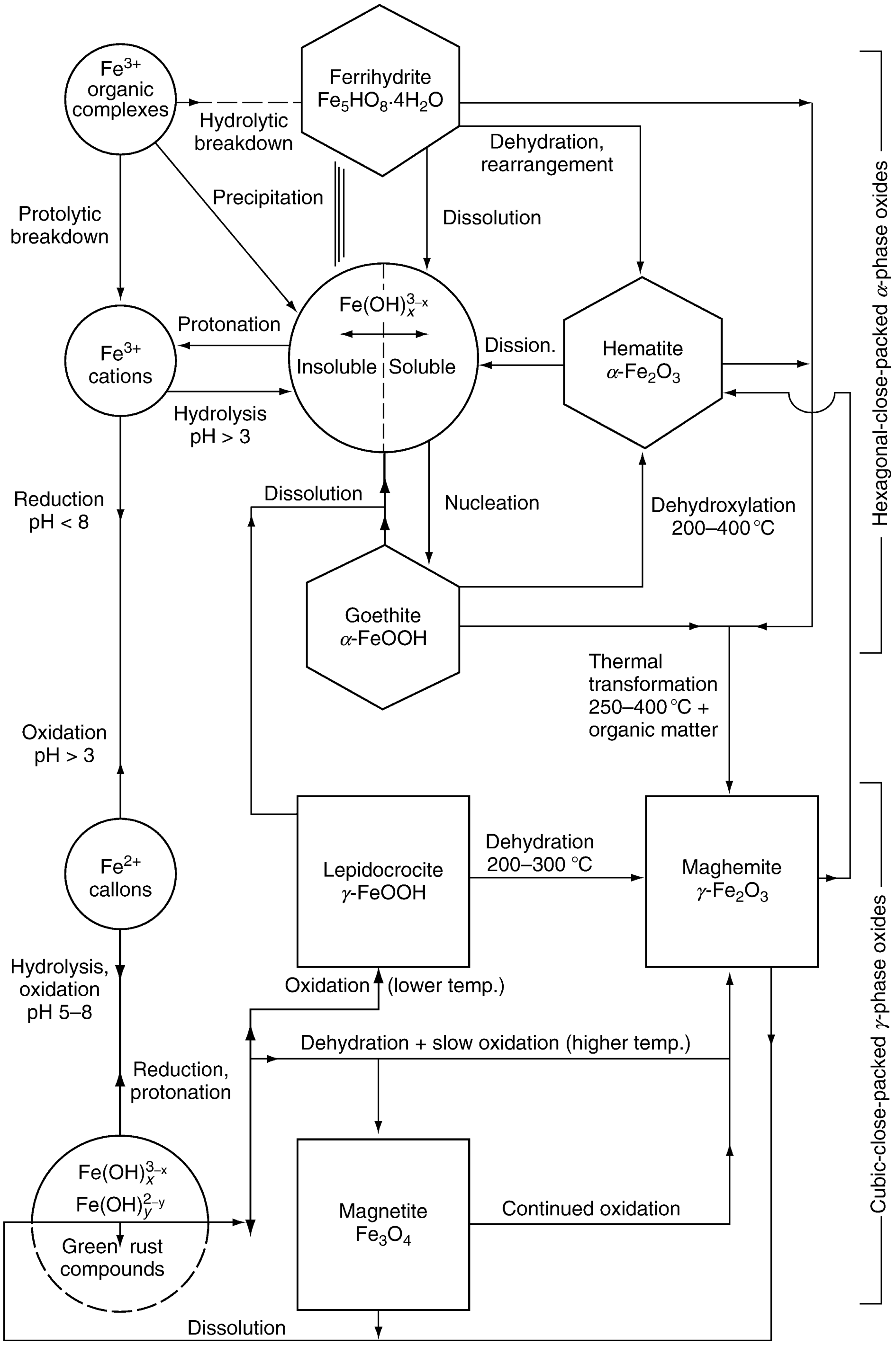


Figure I34 Common pathways of iron oxide formation and transformation.

hydrolyzed Fe^{III} ions (e.g., $Fe(OH)_2^+$) by nucleation and crystal growth, hematite crystals are believed to nucleate and grow within the nano-sized ferrihydrite aggregates.

Numerous factors direct these two competing processes in one or other direction, leading to widely varying ratios of the two oxides in soils. Among these factors are temperature (shown for the range of 4 to 30 °C), water activity, pH and Al-concentration. Hematite is favored over goethite in warmer and drier pedoclimates because these promote dehydration over dissolution of the ferrihydrite. Furthermore, conditions favoring ferrihydrite formation may also favor the formation of hematite. Among the former are fast Fe release from Fe minerals and rapid turnover of organic matter, thereby, avoiding Fe-organic matter complexes. In soils a direct transformation of goethite to hematite by solid-phase dehydration is unlikely because the temperature needed is usually too low. Nor has "rehydration" of hematite to goethite been observed. Admittedly, the coexistence of ferrihydrite and hematite in soils has not been found so far.

Besides the global distribution, regular variations in the goethite/hematite ratio in soil sequences (pedosequences) can also be observed on smaller scales. Usually, more hematite relative to goethite is formed as the regional climate becomes warmer and drier. Examples of such climosequences are found with an east-west orientation over several hundred km in southern Brazil and in southern Germany, and also as a function of altitude in Lebanon and Tasmania. Hematite-goethite ratios also vary along topo(hydro-)sequences over several hundred or thousand meters, where the soils in drier up-slope positions have more hematite than those in moister depressions. For a similar reason red soils (terra rossa) on hard limestone, rich in hematite, are closely associated in Mediterranean regions with rendzinas low in hematite on soft, marly limestone. At a profile scale, yellow topsoils are often found over red subsoils. The absence of hematite in these topsoils has been ascribed to the presence of labile organic matter, which has either inhibited hematite formation, or microbial oxidation (iron respiration) has caused the preferential reductive dissolution of originally formed hematite – turning red soils yellow (xanthization). At an even smaller scale, Fe oxide mottles or concretions can have goethitic rims and hematitic interiors.

Lepidocrocite forms in soils through the oxidation of dissolved Fe^{2+} directly or via a green rust intermediate (Figure I34). If, however, the concentration of carbonate ions (HCO_3^- over most of the pH range for soils) in solution is substantial, as in calcareous soils or around respiring roots, goethite rather than lepidocrocite will be the oxidation product. Lepidocrocite, therefore, frequently occurs in non-calcareous redoximorphic soils of various climates where Fe^{2+} is formed by biotic reduction (see above). It occurs as mottles, bands or pipe stems and can be recognized by its orange color (5–7.5YR). *Schwertmannite* forms only in so-called acid-sulfate soils, i.e., in the presence of high concentrations of sulfate and at very low pH.

Ferrihydrite occurs, commonly with goethite, in soils of temperate and cool climates, especially in concretions, oxidation horizons of gleyed soils (e.g., bog iron ores), Podzol B horizons and in drains and ditches of lowland soils. It usually forms when Fe^{2+}-containing soil water is aerated relatively quickly, or occurs in the presence of compounds with a high affinity for the Fe oxide surface, for example organic matter, phosphate and silicate, which inhibit the formation of the better crystalline FeOOH forms. Under these conditions proper structural order is not achieved. Furthermore, the above adsorbates will block or retard the transformation of ferrihydrite to the more stable goethite. On the other hand, ferrihydrite may be easily redissolved by reduction if, because of a rising water table, oxygen becomes deficient. In any case, given enough time, ferrihydrite can be expected to transform to a more stable Fe oxide and so is generally considered to be a relatively young Fe oxide.

Magnetite in soils is usually inherited from rocks. Recently, however, pedogenic magnetite has been reported. It is most likely of bacterial origin, similar to the magnetite of so-called magnetotactic bacteria. Bacterial magnetite in so-called magnetosomes probably results from the intracellular reaction of ferrihydrite with dissolved Fe^{2+} as simulated in synthesis experiments at ambient temperature and neutral pH. Magnetite can oxidize to *maghemite* or to hematite. The solid-state transformation to maghemite requires a migration of Fe within the structure and an addition of O atoms to change from Fe_3O_4 to Fe_2O_3. The widespread occurrence of maghemite in soils of the tropics and subtropics (from which it can be readily separated by hand magnet) is associated with heat caused by open fires. At 300–400 °C, a temperature easily reached during bush fires, goethite and other Fe-oxides are converted into maghemite, particularly under restricted O_2 supply. Essential in this process is the presence of organic matter as a reductant during the dehydration of the precursor oxide. The association of maghemite with corundum (Al_2O_3) in soils proves the participation of fire.

Significance of Fe-oxides in soil

Besides their pedological significance, Fe-oxides strongly affect a number of soil properties, which will only be briefly mentioned here. Among these are color (Table I2), surface adsorption of numerous ions and molecules, soil aggregation, and redox behavior.

Surface adsorption operates through Fe–OH groups at the surface of Fe-oxides and results from the completion of the ligand shell of surface Fe atoms. These groups attain negative or positive charge by dissociation ($\equiv FeOH \rightarrow \equiv FeO^- + H^+$) or association ($\equiv FeOH + H^+ \rightarrow \equiv FeOH_2^+$) of protons, depending on the pH of the surrounding solution. The pH at which the surface concentrations of $\equiv FeOH_2^+$ and $\equiv FeO^-$ groups are equal, the so-called point of zero charge, is generally around pH8 – 9 for all Fe-oxides. The magnitude of the pH dependent charge is proportional to (pH – pHpzc) and to the ionic strength of the equilibrium solution. The charge will be in the range of several µmol per m^2 of oxide surface.

The Fe–OH groups form surface complexes with a range of cations, especially heavy metal-hydroxy cations (MOH^+), and oxyanions such as phosphate, silicate, arsenate and chromate. The surface OH groups can have one, two or three Fe atoms as nearest neighbors. These singly, doubly and triply coordinated OH groups exhibit different reactivities (acid strength) with the singly coordinated group being by far the most reactive one. The association is by chemical bonds via O- or OH-bridges and is called specific adsorption, or an inner-sphere complex. Although pH-dependent, it takes place even if the net surface charge has the same sign as that of the adsorbate. Phosphate adsorption by Fe-oxides is of great ecological importance and has been widely studied. It reacts with two singly coordinated Fe–OH groups to form binuclear, bidentate $(Fe-O)_2-PO_2H$ complexes (Figure I35). With goethite, the (110) face is usually the main crystal face and carries one singly coordinated OH per unit cell surface area. This would amount to a binding capacity

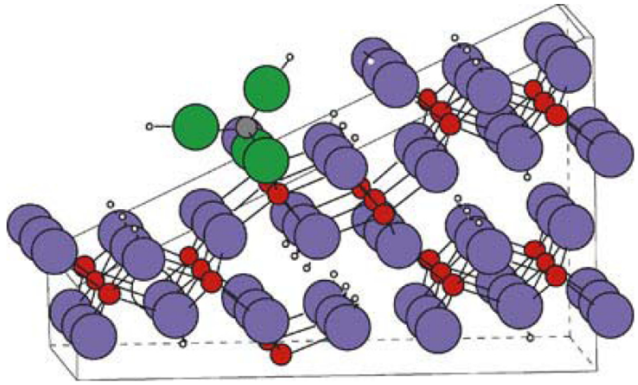


Figure I35 A phosphate molecule forming a bidentate, binuclear complex with two single coordinated surface Fe atoms on the (110) surface of a goethite crystal.

of about 2.5 μmol P m^{-2} of surface, a value which has been found for synthetic and natural goethites from soils and other surface environments. Among the toxic ions, arsenate and chromate have a high affinity for Fe-oxide surfaces, as have humic substances.

Aggregation and cementation. A contribution of Fe-oxides to soil aggregation and cementation is usually assumed but has not been accepted unequivocally. Aggregation into microaggregates (<1 mm) is particularly obvious in oxisols and ultisols rich in goethite and hematite. Cementation by Fe-oxides exists in concretions and ferricretes where Fe-oxides fill part of the pore space in which their crystals grew. Removal of Fe-oxides by dithionite often leads to complete dispersion. Addition of synthetic Fe-oxides, especially those with high surface area such as ferrihydrite, has aggregated soils or soil components. Microscopic and microprobe observations have demonstrated both intimate association with, as well as separation of, Fe-oxides from other soil materials, such as kaolinite. Complete or partial dispersion of microaggregates by organic anions (oxalate, citrate), however, was also achieved although only a small proportion of their Fe-oxides were extracted. These anions may have caused dispersion by modifying the surface charge of the Fe-oxides.

Redox behavior. All soils have the ability to buffer electrons produced preferentially during the metabolic oxidation of biomass by microorganisms. Fe^{3+} and Mn^{4+} bound in oxides, are important electron acceptors in anaerobic soils and can prevent methane formation under anoxic conditions. Electron titration of soils have shown buffer ranges corresponding to the thermodynamic stability of various Fe^{III} oxides according to the general reaction:

$$=Fe^{III}-OH^- + e^- + H^+ = Fe^{2+} + H_2O$$

which consumes protons.

The $(Fe^{2+})/(Fe^{3+})$ activity ratio in soils is controlled by the redox potential Eh, which may also be expressed as electron activity:

$$(e^-) = 10^{Eh/0.059} \text{ at } 25\,°C$$

or by its negative logarithm pe, which is analogous to pH.

According to the Nernst Equation:

$$Eh = E° + 0.059 \log a_{Fe^{3+}}/a_{Fe^{2+}}$$

where $E°$ = standard potential, and $a_{Fe^{3+}}$ and $a_{Fe^{2+}}$ are the ion-activities.

In the presence of Fe^{III} oxides, $a_{Fe^{3+}}$ is controlled by the solubility product of the specific Fe^{III} oxide and can be incorporated into $E°$, leading to

$$Eh = E° - 0.059 \log a_{Fe^{2+}} - 0.177pH$$

As seen from this equation, the Fe^{2+} activity increases as Eh and pH decrease. Using common thermodynamic data, $E°$ (in volts) may be taken as 0.73, 0.71, 0.86 and 1.06 for hematite, goethite, lepidocrocite, and ferrihydrite, respectively. With these values, the curves shown in Figure I37 were computed for Fe^{2+} activity of 10^{-4} mol l^{-1} (approximately 6 mg Fe^{2+} l^{-1}). The diagram shows that this Fe^{2+} activity will be reached at a pH and Eh which are higher the more soluble the Fe^{III} oxide, i.e., in the order ferrihydrite > lepidocrocite > hematite ≈ goethite. In other words, along this line the oxides become less reducible. For goethite and hematite the reducibility also decreases with increasing Al-for-Fe substitution. In soils, however, the Fe^{2+} concentration may be limited by the solubility of sparingly soluble Fe^{II} phases, such as magnetite Fe_3O_4, vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$, siderite $FeCO_3$ and Fe^{II} sulfides, if the solubility products of these phases are exceeded. Furthermore, Fe^{II}-humic complexes may form. In this way, the formation of soluble Fe^{II}-organic complexes may lead to an increase in total Fe^{2+} concentration, and thereby foster the reductive dissolution of Fe^{III} oxides.

A considerable variety of bacteria can reduce Fe^{3+} from Fe^{III} oxides to meet their Fe requirement (dissimilatory Fe^{III} reduction). The detailed mechanism of electron transfer is not yet fully understood. An immediate contact between the bacterial cell and the Fe^{III} oxide particle speeds up the reaction, indicating that the electron is located at the surface of the cell. In addition, humic acid may function as an electron shuttle between the electron donor (metabolized organics) and the electron accepting Fe^{III} oxide. The rate of bacterial reduction was found to increase in the order goethite, hematite < lepidocrocite < ferrihydrite. The difference in rates between the different oxides was, however, more a function of their surface area than of their solubilities.

Determination

The total amount of Fe^{III} oxides in soils is usually determined by an extraction with the strongly reducing Na-dithionite ($Na_2S_2O_4$) in a buffered solution (Fe_d). Other reducing agents of different strengths (e.g., ascorbic acid, hydroxylamine, $TiCl_3$) are also used. Acid oxalate (pH 3) extracts poorly crystalline Fe^{III} oxides (Fe_o), especially ferrihydrite, as well as organically-bound Fe and fine-grained magnetite. The ratio Fe_o/Fe_d is frequently used to characterize the degree to which Fe-oxides have transformed to goethite and hematite, because the latter two are barely soluble in oxalate solution. In acid soils rich in organic carbon, such as spodosols, pyrophosphate is used to extract organically-bound Fe, though some ferrihydrite is also extracted (by dispersion).

To identify and quantify various Fe oxide minerals, non-destructive methods must be used. This is often hampered by their low concentration of a few percent. Therefore, concentration procedures, such as particle size separation and preferential dissolution of kaolinite and gibbsite by boiling 5 M NaOH, facilitate the determination. X-ray diffraction is still the most widespread method for identification and quantification. In some cases, its potential is improved when used in a differential fashion. A Fe specific and very useful non-destructive method is Mössbauer spectroscopy (γ-ray absorption spectroscopy).

Also used are infrared and Raman spectroscopy, thermal analysis and magnetometry.

The help of Dr. S. Glasauer in revising the text is gratefully acknowledged.

U. Schwertmann

Bibliography

Cornell, R.M., and Schwertmann, U., 2003. *The Iron Oxides,* 2nd edn. Weinheim: Wiley-VCH, 664 pp.

Lovley, D.R., 1991. Dissimilatory Fe(lll) and Mn(IV) reduction. *Mircrobiol. Rev.*, **55**: 259–287.

Lovley, D.R., 1995. Microbial reduction of iron, manganese, and other metals. *Adv. Agron.*, **54**: 175–231.

Murad, E., and Johnston, J.J., 1987. Iron oxides and oxyhydroxides. In Long, G., ed., *Mossbauer Spectroscopy Applied to Inorganic Chemistry,* Vol. 2. New York: Plenum, pp. 507–582.

Schwertmann, U., 1985. The effect of pedogenic environments on iron oxide minerals. *Adv. Soil Sci.*, **1**: 172–200.

Schwertmann, U., 1991. Solubility and dissolution of iron oxides. *Plant Soil.*, **130**: 1–25.

Schwertmann, U., 1993. Relations between iron oxides, soil color, and soil formation. In Bigham, J.M., and Giolkosz, E.J., eds., *Soil Color.* SSSA Spec. Publ., **31**: 51–69.

Schwertmann, U., and Cornell, R.M., 2000. Iron oxides in the laboratory. 2nd Ed. Weinheim: Wiley-VCH, 188 pp.

Schwertmann, U., and Taylor, R.M., 1989. Iron oxides, Chapter 8. In Dixon, J.B., and Weed, S.B., eds., *Minerals in Soil Environments,* 2nd edn., Madison, WI: Soil Sci. Soc. America Book Ser. No. 1, pp. 379–438.

Skinner, K., and Fitzpatrick, R.W., eds., 1994. *Biomineralization Processes of Iron and Manganese.* Cremlingen-Destedt: Catena Verlag, 432 pp.

Stucki, J.W., Goodman, B.A., and Schwertmann, U. eds., 1988. *Iron in Soils and Clay Minerals.* NATO ASI Series. Dordrecht, Holland: D. Reidel, 893 pp.

Taylor, R.M., 1987. Non-silicate oxides and hydroxides. In Newman, A.C.D., ed., *Chemistry of Clays and Clay Minerals.* Harlow: Longman, pp. 129–201.

Waychunas, G.A., 1991. Crystal chemistry of oxides and oxyhydroxides. In Lindsley, D.H., ed., *Oxide Minerals Petrolic and Magnetic Significance.* Reviews in Mineralogy 25, Min. Soc. Amer., pp. 11–68.

Cross-references

Aggregate Stability to Drying and Wetting
Aggregation
Mineral Analysis (Geochemistry Volume)
Soil Color
Soil Mineralogy
Sorption Phenomena
Weathering Systems in Soil Science

IRON PAN

See *Pan*.

IRRIGATION

Objectives and constraints

The primary objective of irrigation is to supplement natural rainfall that may be insufficient in amount or temporal distribution in order to obtain high, stable yields in an intensive cropping system. Secondary objectives may include modification of microclimate for frost protection or crop cooling, facilitation of germination and emergence by moistening the surface soil, leaching of salts from the root zone, incorporation of fertilizers and other chemicals, and disposal of sewage effluent. Different irrigation methods vary in their ability to meet these objectives.

In order to maintain land productivity, assuring both high and stable yields, irrigation practice must meet certain constraints – a well-known problem recently included under the term “sustainability”. Problems commonly encountered are physical damage to fields by erosion, silting of reservoirs and water courses, pollutant transport to ground or surface waters, deterioration of soil structure due to inappropriate or untimely tillage operations or poor water quality, crusting due to raindrop or sprinkler drop impact, water logging and salinization of soil due to seepage from canals and over-irrigation. Once these problems make their appearance, the financial and social costs of the required land reclamation by far outweigh the cost of timely prevention.

Today water can be applied to a field on the one hand by techniques collectively known as *surface*, *gravity* or *flood irrigation*, and on the other hand by *pressurized delivery.* In the context of this entry these terms will refer to the actual method used to spread water on the land, and not necessarily for describing how water is conveyed to the field. Irrigation is almost as old as civilization itself, having started 5 000, and perhaps as early as 7 000 years ago in the ancient Near East (Gulhati and Smith, 1967; Marr, 1967). However, pressurized water application became possible only with the development of engine-powered pumps during the Industrial Revolution of the 19th century. Because of the limitation of human or animal power to pumping small discharges and low lifts (Molenaar, 1956), large scale irrigation first developed on flat, low lying valley lands adjacent to rivers, from which water could be diverted, conveyed and spread over the land by gravity. Valley soils are usually also the most fertile soils available. For most of its long history, irrigation has therefore been synonymous with gravity or surface irrigation. Along with the above advantages, valley soils have the disadvantage of intrinsic vulnerability to land degradation processes. Because of their location in the landscape, valley lands are often underlain by a fairly shallow water table, which may rise rapidly into the crop root zone due to over-irrigation, causing water-logging of the soil. Since most soils and watersources in arid and semi-arid regions contain some soluble salts, and water that evaporates from the soil surface or from crops is chemically pure water, the salts are left behind in the root zone and unless there is adequate rainfall and natural drainage, eventually reach concentrations harmful to crop growth. This accumulation can be prevented or corrected by leaching the salts downward out of the root zone by application of water in excess of evapotranspiration, which is tantamount to controlled over-irrigation. However, the leachate can only be removed by causing it to flow to a sink at a lower elevation, i.e., by drainage. Thus drainage water will invariably be more saline than the irrigation water. If artificial drainage is required, this is at best a costly operation. At worst, in the case of lowland valley soils the gradient may be insufficient to remove the drainage water, making drainage impossible without pumping.

There is evidence that some of the ancient civilizations in the Middle East underwent several cycles of prosperity and decline, accompanied by parallel fluctuations in the state of their irrigated agriculture. It is not known whether weakening of the political structure and foreign conquest were the causes of neglect and deterioration of the irrigation systems, or whether, conversely, mismanagement of the irrigation system weakened the society and thus made it vulnerable to breakdown of the governmental authority and foreign invasion. However, it is clear that there is an intimate connection between the sustained functioning of large, complex irrigation systems and the existence of a strong centralized authority able to organize water delivery and to enforce water law.

Principles

In order to achieve the goals of irrigation, the irrigator must strive to meet the requirements that (1) The actual amount of water applied (W_a) be as nearly equal as possible to the chosen amount of water, and (2) The required amount of water is applied as uniformly as possible over the land area to be wetted. In this entry we will define the single field as the land area of interest and will not deal with conveyance and storage losses upstream of the point of delivery to the field. Furthermore, it will be assumed that the amount of water to be replenished in the root zone (W_r) is known. The field water application efficiency (E_a) expressed as a percentage can then be defined as: $E_a = 100$ (W_r/W_a). The various irrigation methods available differ both in the physical principles employed to reach these specific goals and in the degree to which these ideals can be approached.

Surface or gravity irrigation

About 80% of the irrigated area in the U.S. is irrigated by surface irrigation, and probably more than 95% worldwide. The physical principles of surface irrigation are similar for border checks, basins and furrows. Thus a roughly square basin can be viewed as a relatively short and wide border check, and a furrow as the narrowest possible border check. Water is applied from a point- or line-source somewhere on the perimeter of the irrigated area bounded by low earth ridges or levees. The most important characteristic of gravity irrigation is that the actual distribution of water over the land takes place during overland flow on a properly prepared land surface. The manner in which water is spread over the land is not controlled by some mechanical device such as a sprinkler, but by the geometry and slope of the land, roughness of the surface, size of the input stream, and the infiltrability of the soil. The latter is a function of basic soil properties, mainly the pore size distribution, and changing conditions such as initial moisture content, the potential gradient and structural state of the soil. Surface soil structure commonly changes both during a single irrigation and over a season and affects both the surface roughness and the infiltrability of the soil. The geometry and slope of the land, input stream, and to a certain extent the infiltrability, are amenable to manipulation and control during design and land preparation, but once the land is prepared, only the input stream can be adjusted. The water flows from the point of entry down the slope of the hydraulic gradient, to the far end of the plot. This advance process can in principle be described by any one of several equations for open-channel flow, e.g., the Manning formula (Manning, 1890; Cuenca, 1989; Walker, 1993). Simultaneously, however, water infiltrates vertically into the soil wherever water is ponded on the surface. The combined effect of these two processes is analogous to the filling of a ditch with a leaky bottom. Thus the advancing stream gets smaller with distance from the delivery point due to abstraction of water by the infiltration process. Infiltration can be described by one of several Equations (Green-Ampt, 1911; Kostiakov, 1932; Norton, 1940; Philip, 1969). An important consequence of the advance process is that the time during which an elementary area of land has been covered by water (and thus presumably also the amount of water that could infiltrate into the soil) decreases as the distance from the delivery point increases. Also, the rate of advance of the water sheet across the land decreases with distance from the source. Thus, the amount of water infiltrated at various points along the flow path cannot be uniform at the moment the advancing stream reaches the end of the plot (Figure I36). Both infiltration and open-channel flow have been the subject of extensive research and, each taken by itself, is fairly well understood. However, the description of both processes acting simultaneously requires complex mathematical solutions (Hall, 1956; Hansen, 1960; Rawitz, 1973b; Hansen et al., 1980; Cuenca, 1989), and in spite of recent improvements of mathematical models reviewed by Walker (1993) and Walker and Skogerboe (1987), there is still not available a simple, direct, and accurate analytical solution applicable to practical design problems.

In addition to the mathematical and computational hurdles, some of the hydraulic and infiltration formulas present problems in that they contain empirical "constants" whose values are open to question and which may not be invariable with time (Rawitz et al., 1964), or variables which must either be determined empirically or more or less guessed at. Examples are the value of the friction coefficient in the Manning Equation, whose descriptions in published tables may not fit the situation at hand, or the "constants" used in some infiltration equations, e.g., Horton (1940). In order to make available data amenable to mathematical treatment, assumptions must sometimes be made which may not be justifiable, e.g., uniformity of soil conditions, constancy with time or depth of parameters such as soil wetness (Hillel, 1971), or depth of flow at various points in the field. Using values empirically determined in the field, the equations may *describe* the process fairly well by curve fitting, but fail when an attempt is made to *predict* performance under conditions different from those prevailing during evaluation of the constants (Bishop et al., 1967; Shull, 1960; Collis-George and Freebairn, 1979; Walker, 1993).

As was mentioned above, at the instant that the advance stream covers the entire plot, the water distribution cannot be uniform. The amount of water delivered during the time of advance is also approximately the smallest possible irrigation that can be applied. In practice, it is difficult to apply irrigations smaller than about 100 mm regardless of the uniformity

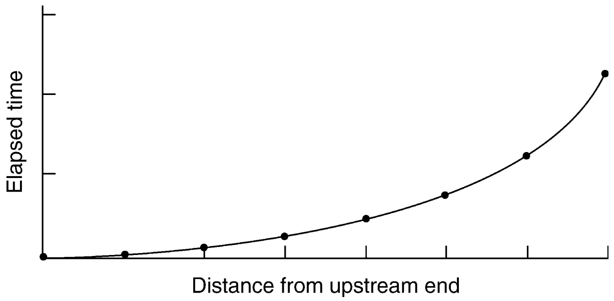


Figure I36 Typical advance curve, showing length of wetted surface in a furrow or border check as a function of irrigation time.

(Cuenca, 1989, Chapter 6). If the input stream is cut off at this time, and if the land has some slope (e.g., a graded border check), the water will continue to infiltrate and also flow downslope. If the lower edge of the plot is not blocked, some of the water may run off the plot as "tail water". If the lower end is blocked, whatever water does not infiltrate en route will pond in the lower section, will assume a horizontal surface, and infiltration will continue. In either case a "recession" process is observable, the soil surface becoming exposed progressively from the source to the lower end of the plot (Figure I37). The recession acts to compensate for the non-uniformity inherent in the advance process. If the land is horizontal, as in "dead-level" basins, then the recession will occur simultaneously over the entire land surface, and the graph of the recession curve will be a horizontal line. It is also common that recession in furrows is nearly instantaneous and difficult to observe. This is due to only partial wetting of the soil surface, the small amount of impoundment possible even in a blocked furrow, and the steeper slope required to move water through relatively rough, long channels.

Surface irrigation systems are generally designed so that the required W_a is larger than the amount delivered by the end of the advance process. Irrigation is then continued until the desired W_a is applied. In the case of border checks with small slope and blocked ends, the stream may remain unchanged, and water is impounded. If the end is not blocked, the delivery stream is "cut back", to balance the infiltration rate as closely as possible.

As infiltration slows, several cutbacks may be needed, and loss of some tail water may be unavoidable. Since infiltrability is lower at the upper end than at the advance front when impoundment begins, this stage also tends to compensate for the unequal distribution during the advance stage. Irrigation is terminated when the design amount of W_a has been applied, and the recession stage begins.

In the quest to achieve uniform wetting over the entire surface, it is the task of the designer to find the optimal combination of soil properties, land slope, plot dimensions, and size of irrigation stream (Criddle et al., 1956; Bishop et al., 1967; Rawitz, 1973b; USDA-SCS, 1974, 1983). At the simplest level, a crude rule of thumb was developed which states that the advance time should be no longer than 25% of the total irrigation time. This is simply an arbitrary decision to accept as tolerable the degree of non-uniformity associated with this practice. If an existing installation does not meet the above criterion, the only options to improve performance are to use a larger advance stream per unit width, or to shorten the length of run. The former may be limited by the capacity of the conveyance system, by the water source, or the maximum non-erosive stream, while the latter may require the construction of additional supply canals or ditches.

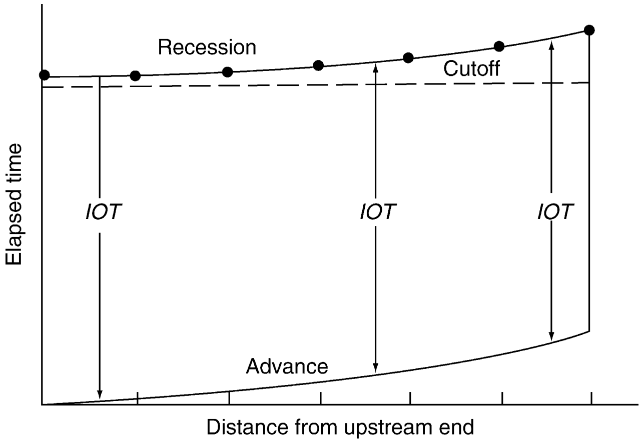


Figure I37 Example of a complete irrigation event in a border check with blocked lower boundary, showing the time functions of the advance, impoundment and recession stages. *IOT* is the Intake Opportunity Time.

If the distance to the advance and recession front is plotted as a function of time as in Figure I37, then the vertical distance between them represents the length of time that water was ponded on the surface during an irrigation, and is defined as the Intake Opportunity Time (IOT). Assuming uniform soil properties and pre-irrigation soil moisture, perfect uniformity of water distribution is achieved if the IOT is equal at all distances, i.e., if the advance and recession curves are parallel. If these functions can be predicted in the design stage by a model such as described by Walker (1993), uniformity can be achieved by determining the optimal combination of land slope, length of run, and input stream. If such prediction is not possible, field tests are required to observe the advance and recession functions, and the results are used to diagnose the performance and to modify the design to obtain the best possible uniformity. Unless such field tests are possible before the entire land area is prepared, changing the input stream may be the only post-construction remedy. Further details will be treated below, in the section on Practical Design Considerations and Guidelines.

Sprinkler irrigation

With this method water is spread over the land surface by static or rotating sprinklers, or static or oscillating nozzle lines. Water is delivered under pressure through some kind of nozzle, and in almost all cases the aim is to wet the irrigated area as uniformly as possible. However, the aim is not necessarily to wet the entire land area: In some orchards strips of land may be deliberately left dry along the centerline between rows of trees.

Nozzle lines are designed to wet a rectangular area with a uniform depth of water both along the lateral and perpendicular to it. Nozzle lines have a number of drawbacks limiting their usefulness, and today serve but a very minor portion of irrigated land. They have been described in greater detail by Rawitz (1973a) and by Benami and Ofen (1993), and will not be given any further consideration here.

Unlike nozzle lines, sprinklers almost invariably wet a circular area or some sector of a circle (part-circle sprinklers). A few attempts have been made to produce sprinklers wetting a square or rectangular area, but these have resulted in elaborate, clumsy, and expensive devices with poor uniformity, and they are not in practical use except in some landscape installations. Sprinkler heads are mounted at constant intervals on a lateral, and laterals are laid parallel to each other in the field. The sprinklers are thus located at the nodes of a square, rectangular, or triangular grid. This is in apparent conflict with the circular wetted area. The problem is overcome by choosing the distance between the sprinklers so that the patterns of adjacent sprinklers overlap sufficiently to cover the entire area. Distance between laterals is usually 60–75% of the wetted diameter, and about 40% of the wetted diameter along the lateral, depending on the mounting pattern, expected wind velocity, and individual sprinkler design. In order to avoid excess water in the zone of overlap, most sprinklers are designed to deposit less water as distance from the sprinkler increases, i.e., they have a roughly triangular cross-section of application (Christiansen, 1942; Cuenca, 1989). With the exception of some microsprinklers, most agricultural sprinklers are of the rotating type. Static sprinklers have a shorter radius of throw than rotating sprinklers, and tend to have a lower uniformity of distribution. The energy required to rotate the sprinkler is derived from the water flowing through the sprinkler. Some sprinklers are turned by an internal gear drive, but most models (oscillating impact sprinklers) are turned by the water jet impinging on a spring-loaded deflector arm as it leaves the nozzle. As the arm is returned by the spring, it strikes an anvil on the side of the sprinkler, thus turning it through a small angle. Various other devices acting as reaction motors may be found on a variety of microsprinklers. There is a vast choice of sprinklers on the market to suit a wide variety of conditions. A sprinkler may have one to four nozzles, with discharge per sprinkler ranging from 20 l h^{-1} to about 8 000 l h^{-1}. Throw diameter ranges from about 1 m, to over 100 m.

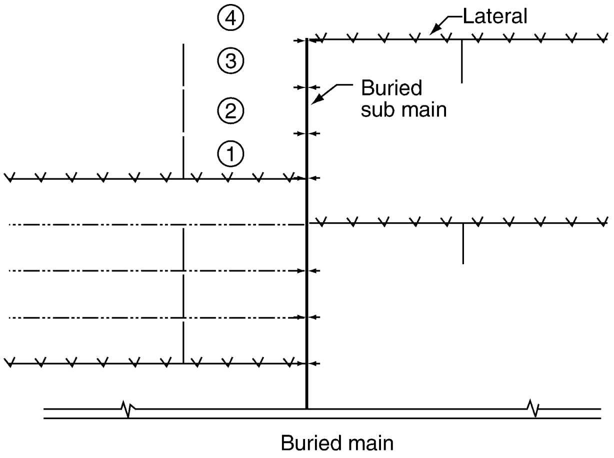


Figure I38 Schematic layout of semi-portable hand-move or side-roll sprinkler system with four laterals each irrigating four sets. *Circled numbers* indicate sequence of sets.

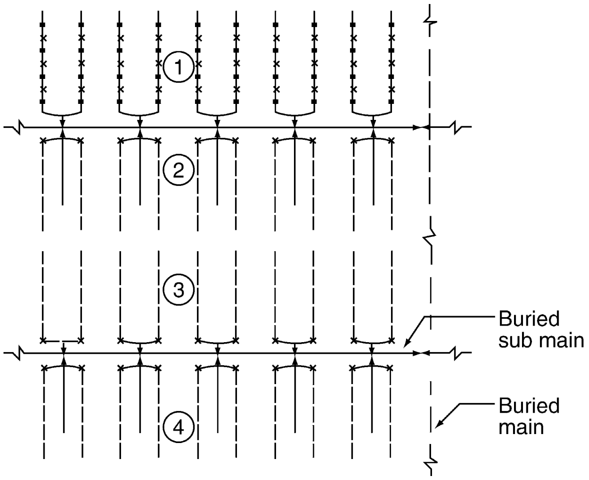


Figure I39 Schematic layout of semi-portable tractor tow-move sprinkler system with ten laterals per set. *Circled numbers* indicate sequence of sets.

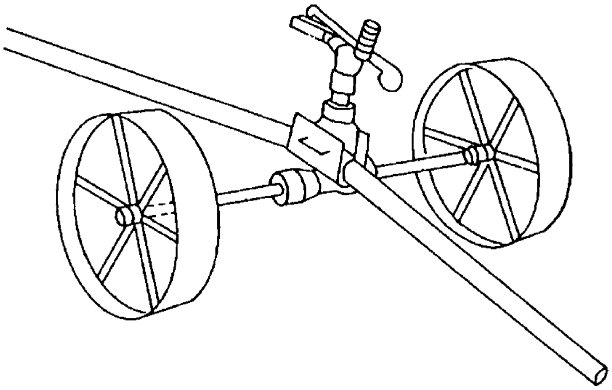


Figure I40 Carriage with plastic wheels on tow-move lateral.

Various components of a sprinkler system may be fixed in place or portable. The source itself may be portable, as in the case of a trailer-mounted pump and motor taking water at various points along a ditch. The conveyance network may consist of fixed, underground pipes of steel, concrete, asbestos-cement or PVC, or of more or less temporary aluminum pipes laid on the surface. Water is taken from the mains system by risers and valves mounted on the mains at regular intervals. Permanently installed sprinkler laterals are generally used for the irrigation of orchards and similar perennial crops, where moving the laterals would be very laborious. Sprinkler laterals are often left in place for an entire season with field crops requiring frequent irrigations, such as potatoes, but are dismantled and removed at the end of the season. The latter two systems are called "solid-set". For most low-growing annual field crops the common practice is to use portable laterals fed from permanent underground mains. Laterals may be moved in several ways: (1) *Hand Move:* The lateral is disassembled at the quick couplers, and individual pipes, usually 6 m long, are carried by hand to the next position, in a direction perpendicular to the axis of the lateral, and reconnected (Figure I38). This method is laborious, subject's equipment to hard wear and tear, and has a high incidence of leaks and nozzle clogging due to dirt entering the pipes during moving. (2) *Roll Move:* In the side-roll method light metal wheels up to 2 m in diameter are mounted on the lateral at every other coupler so that the pipe acts as the axle, and the entire lateral is rolled in a direction perpendicular to the lateral, as in hand move. Power for rolling the lateral may be manual, using a ratchet lever, or a small internal combustion engine mounted at the mid-point of the lateral. A length of flexible pipe connects the lateral to a riser. This method is limited to crops lower than the wheel radius, and is popular in some regions of the western U.S. for irrigating hay and forage crops and vegetables. (3) *Tow Move:* The entire lateral is moved by towing it by tractor along the axis of the lateral, for a distance equal to the length of the lateral (Figure I39). Small wheels or skids are mounted on the laterals (usually every 12 m) to facilitate towing and to keep the risers in an upright position (Figure I40). This is a very efficient method for most field crops, and is the popular method of choice in many large sprinkler installations. (4) *Linear Move:* Frontal-advance or linear-move sprinkler machines resemble the side-roll system in that a special lateral advances across a field perpendicular to

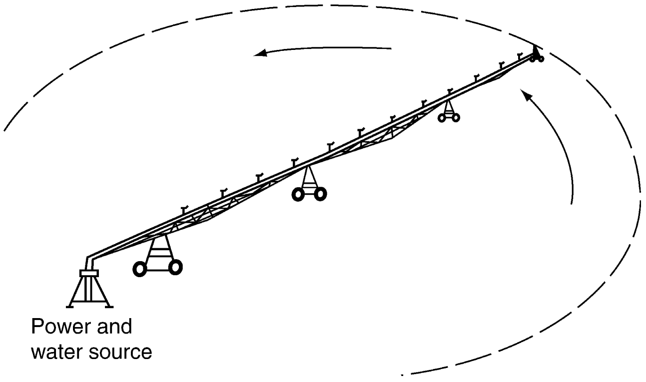


Figure I41 Center pivot system. The same type of lateral is used in frontal-advance systems with water pumped from a canal or supplied from a pipeline by a flexible hose.

the lateral axis. The lateral consists of a number of sections, each on a truss about 30–50 m long, supported at the junction of two sections by an A-frame tower on wheels (Figure I41). The lateral pipe is mounted on the truss at a height of 3–4 m, and water is delivered either by regular oscillating impact sprinklers or by special spray nozzles at the lower end of drop tubes operating just above the crop canopy. Unlike side-roll systems, the frontal-advance lateral moves forward continuously. An electronic control unit in the main tower switches electric power to the drive wheels of each tower in turn, so that only one tower moves at any one time – thus the power requirement for moving the lateral is low. Water may be supplied from a pipeline through a flexible hose, or may be pumped out of a ditch by a pump mounted at the mid-point of the lateral. Special position sensors assure that the lateral stays in alignment. Laterals up to about 400 m long are in use (Figure I45). Machines using spray nozzles on drop tubes have a very high instantaneous application rate and cause runoff problems on soils with low intake rates. (5) *"Big Gun" Sprinklers:* Large sprinklers may be mounted either on tripods in a solid set, mounted on skids or a trailer and moved to the next hydrant at the termination of each set, or may be fed by a flexible hose which is continuously reeled in on a water-motor driven drum, and may be moved laterally when the traveling sprinkler reaches the reel, or returned to its original position. Various other methods of "moving the set" exist, but are of only minor importance. (6) *Center pivot* irrigation machines are a hybrid between solid set and portable systems. Similar in construction to the frontal advance machines, the lateral turns around a pivot at one end, which is usually permanently positioned (Figure I41). In some cases the entire system may be towed to an adjacent field once the irrigation at the first position is finished. Since the angular velocity of the lateral is constant but the linear velocity increases with distance from the pivot, the discharge rate per unit length of lateral must increase along the lateral (Cuenca, 1989).

Drip or trickle irrigation

This method is based on small-diameter (typically 10–20 mm) plastic tubing from which water is discharged in a small stream (typically 1–10 $\mathrm{l\ h^{-1}\ m^{-1}}$ of lateral) either continuously along a porous lateral or from a series of emitters or drippers mounted at intervals along the lateral. The porous tubing version has not gained wide acceptance, and will not be discussed here. Drippers may be mounted integrally in the lateral tube (in-line drippers), or externally mounted on the lateral by a barbed connector (on-line drippers). The latter may have multiple outlets which may be placed at various points around a tree, or irrigate a number of containers in greenhouse culture and nurseries. This makes it possible to deliver very small discharges through each outlet. For the irrigation of many field and orchard crops parallel laterals are placed along the plant rows, either on the surface or underground, with drippers mounted on the lateral at uniform intervals (30–150 cm). In orchards, one or more laterals per tree row are used, and the distances between laterals and drippers may not be uniform. In row crops, a group about 60 laterals comprising a set are connected to a common manifold and control head on the boundary of a plot (Figure I42). The control head includes some or all of the following: manual main valve, a remotely-controlled metering valve, a no-return check valve, vacuum breaker, fertilizer injector, filter, manometer, and pressure or discharge regulator (Figure I43).

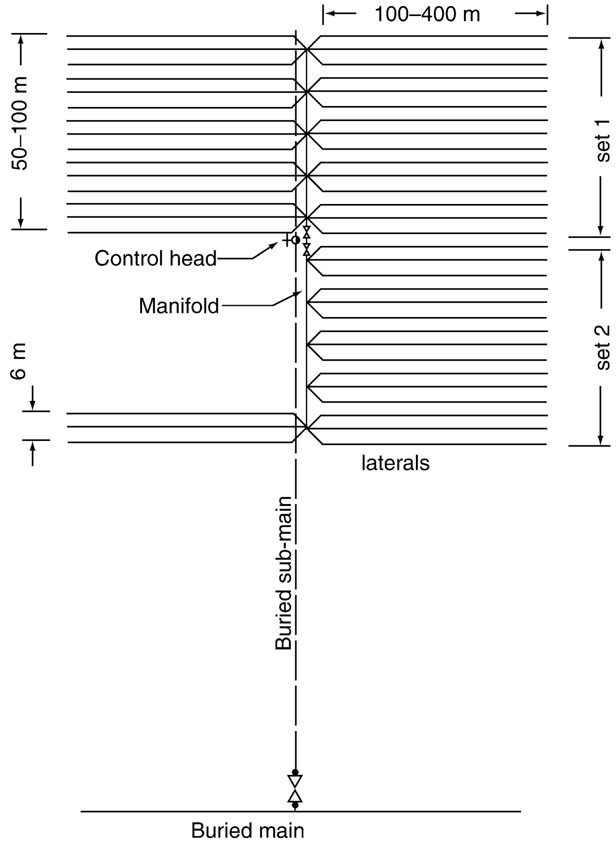
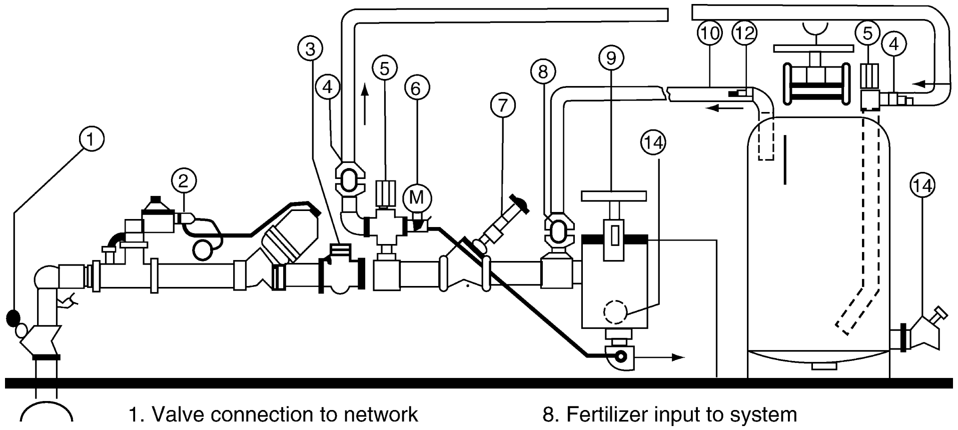


Figure I42 Schematic layout of a portion of a typical drip-irrigated field.

Drip irrigation as it has evolved over the past several decades has a number of unique features, which distinguish it from other methods, and which present both challenges and opportunities:

1. The relatively high cost per unit area argues for the use of small diameter laterals, which can however carry only a small discharge. This makes it difficult to apply large irrigations, which in turn necessitates giving small, frequent irrigations. This is the foundation of high-frequency irrigation



1. Valve connection to network
2. Volumetric valve with counter
3. One way valve
4. Water supply to fertilizer
5. Vacuum valve
6. Differential manometer
7. Main pressure control valve
8. Fertilizer input to system
9. Main filter
10. Water line
10. Water line
12. Fertilizer exit
13. Fertilizer container
14. Flushing valve

Figure I43 Example of a complete drip-irrigation control head (Goldberg, 1976).

regimes, which have revolutionized our view of soil water availability to plants (Ehlig and Gardner, 1964; Gardner and Nieman, 1964; Gardner, 1965; Goldberg et al., 1976; Rawitz, 1969). A common consequence of the small applications is that the depth to which the soil is wetted is often shallower than under flood or sprinkler irrigation, although this is not an intrinsic property of the system.

2. For similar reasons of economy, early users tried to save on equipment by wetting only a part of the total land area under the crop, e.g., leaving dry strips between tree rows or irrigating only every other row in row crops, and found that this did not adversely affect yields of many crops.
3. The drip system is very well suited for the injection of fertilizers into the irrigation stream and delivery to the root zone together with the water. The system is also very adaptable to automated control of water and nutrient application.
4. During irrigation the soil in the immediate vicinity of a dripper becomes saturated, and some surface ponding occurs. To avoid runoff, the application rate must be adjusted to the soil infiltration properties. Water moves radially away from the dripper along a potential gradient, wetting a soil volume that is roughly hemispherical or spherical in the early stage of infiltration from surface and subsurface emitters, respectively. The radial flow leaches accumulating salts to the wetting front at the outer boundary of the wetted volume, and thus the concentration of the soil solution in the root zone can be kept very nearly equal to that of the irrigation water (Goldberg et al., 1976; Dasberg and Bresler, 1985; Heller and Bresler, 1973). As irrigation continues, the matric potential gradient decreases and the gravity gradient becomes more important, producing vertical elongation of the wetted volume. The ratio between horizontal and vertical wetting is a function of application rate and soil properties, with vertical penetration being relatively greater with sandy soils and lesser with fine-textured soils. The wetted volumes of adjacent drippers often coalesce, so that the lateral becomes practically a line source rather than a series of point sources.

The combined effects of the above properties are that water and fertilizer can be delivered accurately where and when needed by the crop, whose root system has been restricted by the wetting pattern. This restriction transfers control over the fate of the crop from the soil water reservoir, which has been largely eliminated, to the irrigation system. On the one hand this makes the crop vulnerable to system failures, but on the other hand maintains a soil moisture regime, which fluctuates within narrow limits around an optimal, high average osmotic and matric water potential, while eliminating losses by runoff and deep percolation. Other consequences are decreased water loss through evaporation and weeds, the possibility of implement traffic on the dry portion of the surface even during irrigation, and avoidance of wetting the plant canopy.

Practical design considerations and guidelines

Surface irrigation

For many years modern surface irrigation installations have been designed on the basis of accumulated practical experience, which was summarized in the form of empirical data bases (Marr, 1964; Benami and Ofen, 1993). Cuenca (1989) quotes a number of tables from Booher (1974) with recommended furrow, border and basin dimensions, slopes, and discharges for various soil types. He points out that design procedures based on empirical data require less extensive data than more complex hydraulic analyses, and that because of the limited and general data required, these procedures yield only approximate solutions to design problems. However, this is to be expected in any case, due to uncertainty regarding the proper values of various parameters required for more rigorous mathematical solutions. Consider the example of crops like alfalfa or small grains irrigated in border checks. The roughness coefficient will depend on soil surface roughness and on crop characteristics, including height of plants, and also on discharge through its effect on depth of flow. In addition to an expected change in roughness with the age of the crop, one can envision that increased discharge at any time may cause the plants to be bent, which can result in a sudden and appreciable decrease in the roughness. Such detailed data are generally not available to the planner.

The initial step in practical system design is choosing the method to be used: Graded border checks, "dead level" basins, contour checks, or furrows. Choice will depend on crop characteristics, topography, soil properties and available discharge. In modern irrigation, some land grading is commonly acceptable either to bring a field or individual check to the average slope of the land, or to actually change the slope to a desired value. The introduction of laser-guided earth moving machinery has greatly increased the precision with which the desired grade can be achieved. Although there are cases where the depth of the removed layer (depth of cut) is as large as one meter, cuts should be kept to a minimum so as to avoid removal of the top soil, as well as for economic reasons.

Graded border checks are typically 5–30 m wide, 50–300 m long, and may have a slope between about 0.2% and 2.0%. The required input stream per meter of width ranges between about 3 m^3 h^{-1} and 50 m^3 h^{-1}. In general, permissible length increases with increasing slope and discharge, and with decreasing roughness and soil infiltrability. In order to achieve reasonable uniformity of wetting, it is extremely important that the surface be smooth, and that there be no cross-slope at all within the border check. Laser-guided leveling has very much facilitated achievement of these goals as well. The permissible width of border checks is a function of the natural cross-slope of the land. The cross-section through a field with graded border checks shows a series of horizontal steps, separated by earth levees. In order to maintain their stability and to prevent overtopping, the absolute difference in elevation between neighboring checks should be less than about 6 cm, and thus the permissible width of a border check is a function of the land slope perpendicular to the check axis. Border check irrigation is adaptable to a wide variety of orchard and field crops. The difficulty of applying irrigations of less than about 100 mm favors crops with a deep root system and crops that tolerate relatively long intervals between irrigations.

Level basins, sometimes called "dead level basins" are similar in construction to border checks, except that they are completely level. Their dimensions are more nearly square or circular than the elongated border checks. They are adapted to as many different crops as are border checks, and are particularly popular in modern systems for orchard irrigation, where square basins may contain 1, 4, 9, 16 or 25 trees. In traditional irrigation, especially in Southeast Asia, level basins or terraces on the contour are the only method used for rice culture, and are also used for grain, forage and vegetable crops. Since the soil surface is level, water recession after infiltration will be instantaneous, i.e., the land surface becomes exposed at the same time at all points. In order to achieve uniform water distribution, the entire volume of the irrigation should ideally be applied instantaneously as well. In order to approach this ideal as closely as possible, very large input streams and small basins should be used. Thus, from the general guidelines given by Booher (1974), a basin of 0.1 ha area on a loam soil would need an input stream of about 100 m^3 h^{-1}. The permissible width of a basin is limited by the same criteria as with border checks, and is therefore a function of the natural land slope.

Furrows are generally about 20–40 cm deep from their bottom to the top of the ridge. Spacing between furrows is a function of soil properties and crop characteristics, but the minimum spacing is technically limited to about 60 cm. Furrows are used to irrigate a variety of row crops and orchards, and can be constructed within graded border checks. Furrows are more vulnerable to erosion than the other methods, and the maximum non-erosive stream should be determined. Depending on slope, furrow shape and soil type, this may range between about 1 and 15 m^3 h^{-1}. The same parameters determine maximum furrow length that can be irrigated with reasonable uniformity, and it ranges between about 60 and 400 m. Since recession is generally very rapid, a rapid advance is desirable, within the limitations of maximum non-erosive stream and avoidance of overtopping of the ridges. Furrow slopes range between 0.1 and 2%, and cross-slope may be as high as 10% (Figure I44). Both furrows and border checks can be laid out at a constant slope on a "falling contour", which requires much less major earth moving, but generally does not allow straight plant rows.

When approaching the design of a surface-irrigated area, one may refer to the general recommendations quoted above, and resort to some of the more detailed design procedures (Cuenca, 1989). At this stage it is most desirable to either obtain more site-specific data by field testing, or to carry out observations in existing installations on a similar soil type. A good criterion for choosing such a field would be a comparison

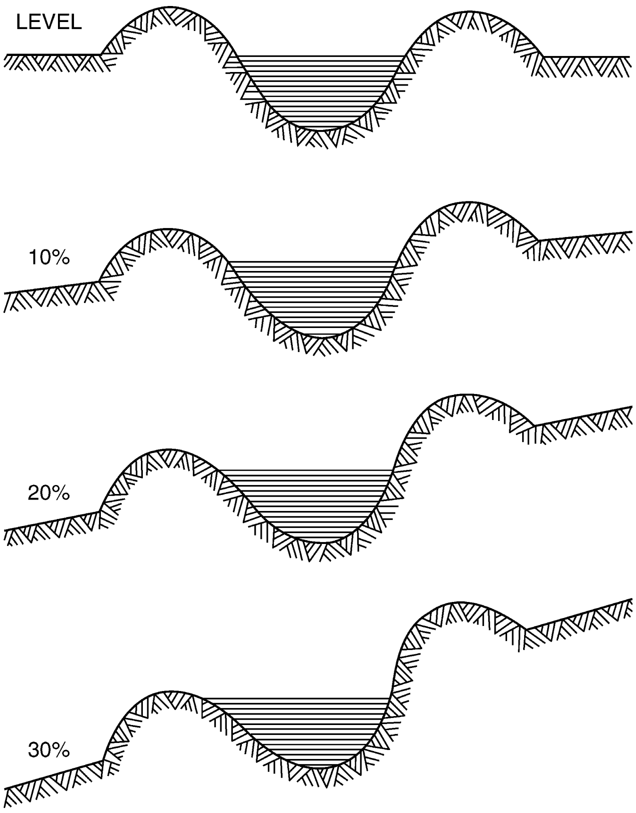


Figure I44 Effect of cross-slope on freeboard and danger of overtopping in irrigated furrows.

Figure I45 Center pivot irrigation in La Mancha, Spain. The image is 14 km square. Photo: ESA.

of the infiltration functions of the existing and planned fields. The problem is that tests on a field that is not yet developed are often difficult to carry out due to absence of leveling and availability of a water supply. For this reason it is often simpler to do field tests with furrows than with border checks, since furrows require a much smaller discharge. For a field test several groups of furrows or border checks are constructed on a sloping field along "falling contours" so that the various test plots have different slopes between zero and the estimated maximum permissible slope, and each furrow or border within a group is irrigated with a different input stream. Marker stakes are placed at constant distance intervals along the plots, and the time of advance and recession occurrence is recorded for each. At the end of the advance, the input may be "cut back" to the "infiltration stream" until the design amount of water has been applied. These data can then be analyzed to determine the optimal combination of input discharge and slope. This solution, as any other, will only be approximate, since infiltrability is likely to change during an irrigation season. More detailed treatment of this procedure has been given by Criddle et al. (1956), Rawitz (1973b); Cuenca, chapter 6, (1989); Benami and Ofen (1993).

Sprinkler irrigation

Since it is not customary to level sprinkled land, the first requirement of sprinkler system design is to ascertain that no runoff will occur, i.e., the water application rate will not exceed soil infiltrability during the time required to apply the design amount of water. This time may be shorter than the time to reach the final infiltration rate, and the application rate may be larger than the final infiltration rate. In this case again the expectable change in infiltrability during a season must be taken into account. Sprinkler application rates may range from as low as 2 mm h^{-1} delivered by microsprinklers to instantaneous (not average) rates of over 100 mm h^{-1} characteristic of center pivot and linear advance machines. Once the maximum application rate has been established, the type of sprinkler to be used can be determined, taking into account whether the sprinklers will be mounted above or below the crop canopy, anticipated wind conditions, topography, and available discharge and pressure. Manufacturers' catalogs are then consulted to find available nozzle sizes, pressure-discharge relations, recommended sprinkler spacing and range of operating conditions. A single sprinkler model is generally available with a range of nozzle sizes and discharges, and will operate satisfactorily over a range of pressures. When a sprinkler model has been chosen, the permissible number of sprinklers for a given diameter of lateral is determined. Guidelines for the hydraulic design of sprinkler laterals are generally included in the sprinkler manufacturers' specification sheets. Various specialized slide rules and nomograms are also available. Moderately priced pocket calculators can be programmed to solve the Hazen-Williams or other formula (Brater et al., 1996) for pressure loss in pipes, taking into account discharge from multiple outlets according to Christiansen (1942). Detailed procedures of sprinkler system design and worked out examples are given by Christiansen (1942), Rawitz (1973a), Cuenca (1989), and Benami and Ofen (1993) among others. Using this information, lateral diameter and length suitable to the desired field dimensions are determined. The next step is to choose the method of "changing the set" i.e., the portability of various system components. This will range from solid-set systems at one extreme, where the set is changed by simply turning the supply on or off to some of the laterals in the field set by means of valves, through semi-portable systems where the conveyance lines are permanent and the laterals are moved, to completely portable systems where all pipes, and possibly the pump, are moved from one set to another. Depending on the degree of portability, there is usually an inverse relationship between equipment costs and operational costs including labor. The size and number of sets needed for a given area with a given application rate depends on the maximum irrigation frequency required, including provision for some "down-time".

The ideal of sprinkler system design and operation is to deliver exactly the same depth of water to all points in the sprinkler pattern. However, this is never achieved even under standardized and ideal conditions (no wind, standard height of risers, all risers vertical, accurate and constant pressure). This portion of the variability is intrinsic to each sprinkler. Any departure from the above listed ideal conditions during field operation will further impair uniformity of distribution. Several procedures have been developed to characterize sprinkler uniformity; all based on empirical determination of the depth of water collected by catch cans placed on a grid within the sprinkler pattern. The earliest and still most commonly used index was proposed by Christiansen (1942), where the Coefficient of Uniformity,

$$C_u = 100(1.0 - E|x|/m\ n)$$

where $|x|$ is the absolute deviation of individual observations from the mean value, m, n is the number of observations, and C_u is expressed in percent. Before the introduction of computers this index had the great advantage of not requiring the calculation of squares and square roots needed for more rigorous statistical methods of analysis. While a number of other computation procedures has been developed since (Benami and Ofen, 1993), the Christiansen index has remained the industry standard. A coefficient of 84% under standard conditions has been agreed upon as the lower limit of acceptability. Values of >90% are attainable, sometimes even under field conditions. Manufacturers do not generally publish information on the C_u of their products, and it is up to the planner or user to conduct his own field tests. A source of systematic variation is the energy loss due to friction along a lateral. A more or less arbitrary decision has been made to accept a maximum discharge differential of 10% between the extreme sprinklers of a single set, which is equivalent to a 20% difference in pressure. In some cases this energy loss can be eliminated if the laterals can be placed along a slope that produces an energy gain due to elevation of equal magnitude and opposite direction. Alternatively, the use of pressure-regulated sprinklers eliminates the pressure differential, but at the cost of additional pressure and of equipment.

Similarly to the case of surface irrigation, – the existence of non-uniform distribution raises the question of the consequences in terms of water application efficiency and crop response. The irrigator must be aware of this, and choose where the depth of penetration should be located with respect to the lower root-zone boundary. If all spots in a field are to receive at least enough water to replace the average deficit to the full root-zone depth, then any water penetrating beyond this depth will by definition be a deep percolation loss. Conversely, if only spots receiving maximal penetration will be wetted to the full design depth, then all other areas will receive less than the design amount of water. A good practical compromise is to permit deep percolation and inadequate depth of wetting over approximately half the area, respectively. More detailed reviews of sprinkler uniformity are given by Christiansen (1942), Rawitz (1973a), Cuenca (1989) and Benami and Ofen (1993).

Drip irrigation

The hydraulics of drip irrigation is essentially identical to that of sprinkler systems, except that small diameter tubing is used and that emitter spacing is much closer than with sprinklers, typically 30 to 150 cm. This affects the structure of the system. In sprinkler systems, 1–3 laterals may be fed by a common riser and valve on a sub-main. In drip irrigation of row crops, laterals may be laid in every row or in every other row. Three to 6 laterals converge at a multi-outlet connector, often also incorporating a pressure regulator, mounted on a 50–75 mm diameter manifold at 6 m intervals. The manifold is laid parallel to the submain, which is usually underground. A set is defined by length of manifold (commonly between 70 and 90 m) connected to the control head (Figure I42).

The hydraulic calculations for drip design are not as simple to carry out as for sprinkler systems with standard formulas or calculation aids, because drip laterals of the same nominal diameter may not have the same friction coefficient. This is due to the fact that various emitter models differ in the shape of the protrusion into the flow path (e.g., in-line drippers vs. on-line barbed connections) and thus have a different effect on friction losses in the lateral. Drip equipment manufacturers do supply specifications giving the maximum recommended lateral lengths for given emitter spacings, nominal discharge, operating pressure and land slope. In drip design, a stricter criterion of discharge loss within the set is often applied: 5% or 7.5% instead of 10%. In recent years pressure-regulated drip emitters have come on the market, thus solving the problem of pressure drop along a lateral due to friction or topography, provided a specified minimum inlet pressure is maintained. This has made it possible to design laterals up to about 900 m long on level ground.

The narrow passages in drip emitters make them vulnerable to clogging, and therefore effective and reliable filtration is essential. Other accessories include fertilizer injectors, vacuum breakers, no-return check valves, manometers, metering valves and telemetry equipment for communicating data and execution commands to and from a remote control center (irrigation computer). Some or all of these accessories are generally grouped in a control station at the head of a set or a field.

Automation

All permanent systems, and to a more limited extent also semi-portable systems are well suited for automatic control of irrigation. The key component of automated systems is the hydraulic valve which receives commands by a pressure pulse and is turned on or off by differential water pressure, thus not requiring electric power. At the simplest level, the hydraulic valve of a metering valve based on an integrating water meter is turned on manually by dialing the desired delivery amount. A propeller-driven gear train registers volume delivered, and when the desired amount is reached the hydraulic valve is tripped again and sends a pressure pulse to close the metering valve. Small diameter plastic tubing can interconnect such valves so that when one lateral is shut off, the next one in line, preset for the desired volume, begins irrigating. This process cascades sequentially across any number of laterals. At the next higher level of complexity, a battery-powered electronic controller produces the pressure pulse to both initiate and terminate irrigation by activating a solenoid valve. The controller can be programmed to open the valve after any given time delay, and thus the irrigator does not have to be in attendance for initiating irrigation. Neither of the above two options can make any decisions, nor are the events recorded. At the next level, a small dedicated irrigation computer in the field can control up to 16 independent valves to deliver desired volumes of water and fertilizer solution to separate consumers, and activate filter back-flush cleaning when a chosen threshold pressure differential is reached. It stores information in a temporary memory, and presents the information on an LCD display when manually called for. Such local field units can also be linked as slave units to a central computer. The highest level of automation currently used consists of a centrally located microcomputer that can be programmed for a wide range of requirements. It is connected by wire to any number of field stations consisting of banks of solenoid valves activated by the computer to initiate or terminate irrigation of numerous independent valves. In addition, the output of various field sensors can be sent to the computer, which can be programmed to over-ride the prepared standard irrigation schedule in case of need. For example, irrigation can be initiated or terminated according to cumulative pan evaporation, soil moisture sensors, water pressure fluctuations beyond a specified range, excessive wind speed, or threshold values of ambient temperature. The computer program thus includes some decision-making subroutines, including irrigation of alternative consumers in case of shutdown of a given set or field. The central irrigation computer continuously displays the status of all control points, and produces a hard copy of all events. This is an extremely useful management tool not only for control in real time, but also for reviewing and analyzing water management during a whole season and for planning and modifying the irrigation program for the coming season.

Comparative evaluation

No single irrigation method can be expected to be universally the best, particularly as the criteria applied may not be the same. For example, under a given set of conditions one method may be the most profitable, but also wasteful of water, especially where the price of water does not reflect its true value. Surface irrigation is best suited to naturally smooth and nearly level land, medium- to moderately heavy-textured soils, and deep-rooted crops that do well with relatively large, infrequent irrigations. Under favorable conditions, both initial investment and operating costs are low. On the negative side, removal of topsoil during leveling may impair soil productivity for years; large but intermittent discharges are required, and the conveyance network is utilized for only a small fraction of the time; surface irrigation is not well suited for night-time operation; even small flaws in design or operation can have drastic results, and may be difficult or impossible to correct; open conveyance systems take up about 5% of the land area, interfere with movement of machinery and require maintenance; much of the success of a system depends on the skill of the irrigator.

Sprinkler irrigation does not require prior land leveling, is fairly adaptable to steep and irregular topography, and application rate can be selected to suit soils with low infiltrability. Shallow and stony soils and those with very high infiltrability, where surface irrigation would be disqualified, are irrigable by sprinkling. Sprinkler systems can utilize a small, continuous supply of water more efficiently than surface irrigation, but require water under pressure, generally at least about 3 bars. Irrigation amount can be easily controlled so as to minimize surface runoff and deep percolation losses. In sprinkler systems there is generally a trade-off between initial costs and operating costs: greater portability and smaller pipe diameter have higher labor and energy costs and higher depreciation rate, while larger pipe diameter and fewer portable system components have higher initial cost but lower energy, labor and depreciation costs. Sprinklers should not be operated under windy conditions, which affect irrigation efficiency both by loss through wind drift and impairment of distribution uniformity. Some crops are damaged by wetting of the foliage due to salt accumulation and leaf burn, or by providing conditions favorable to bacterial and fungal diseases.

Drip irrigation is relatively the most successful under marginal conditions of soil, topography, water quality and climate, on land which would otherwise not be irrigable, and where the cost of water is high. Much of the success is due to the positive response of many crops to the high-frequency irrigation regime typical of drip, and the ability to apply water and fertilizer accurately where and when needed. Water savings may be achieved by decreased evaporation losses, less water use by weeds, and the better control of deep percolation. Similar to the case of permanent solid-set sprinkler systems, drip systems have a high initial cost per unit of land area. This must be compensated for by lower cost per unit of water (higher yields, water savings) and low labor costs. To fully realize the potential benefits of drip irrigation and to make it economically justifiable, it is therefore necessary to assure a high overall level of management (nutrient supply, pest and disease control, proper planning and control of irrigation regime, timely maintenance), and to grow high-return crops. These are all characteristics of intensive agriculture. Drip irrigation is the best suited among all the methods for computer-aided monitoring and control of the irrigation schedule, and can derive the greatest benefit from such automation.

There has been some discussion about the relative merits of the various irrigation methods regarding water application efficiency. Tests have shown that it is theoretically possible to achieve efficiencies of 90% or better with any of the methods. However, this is much harder to achieve with surface irrigation than with sprinkling, and easiest with drip. In actual practice, application efficiencies of surface systems range between about 30 and 60% with the latter figure being found in modern, well designed and managed systems; sprinkler systems generally achieve efficiencies in the range of 60–85%, and drip systems commonly operate at 85–95% efficiency.

Ernest Rawitz

Bibliography

Brater, E.F., King, H.W., Lindell, J.E., and Wei, C.Y., 1996. *Handbook of Hydraulics for the Solution of Hydraulic Engineering Problems,* 7th edn. New York: McGraw-Hill, various pagings.

Benami, A., and Ofen, A., 1993. *Irrigation Engineering.* Haifa, Israel: Agripro, p. 257.

Bishop, A., Jensen, M.E., and Hall, W.A., 1967. Surface irrigation systems. In Hagan, R.M., Haise, H.R., and Edmister, T.W., eds., *Irrigation of Agricultural Lands.* Madison, WI: American Society Agronomy, pp. 865–884.

Booher, L.J., 1974. *Surface Irrigation.* Rome: FAO Agric. Dev. Paper No. 95.

Christiansen, J.E., 1942. *Irrigation by sprinkling.* Bull. 670, Berkeley, CA: California Agric. Experiment Station, 124 pp.

Collis-George, N., and Freebairn, D.M., 1979. A laboratory and field study of border check irrigation. *Aust. J. Soil Res.*, **17**: 75–87.

Criddle, W.D., Davis, S., Pair, C.S., and Shockley, D.G., 1956. Methods for evaluating irrigation systems. In *Agriculture Handbook 82.* Washington, DC: USDA-SCS, 24 pp.

Cuenca, R.H., 1989. *Irrigation System Design.* Englewood Cliffs, NJ: Prentice-Hall, p. 552.

Dasberg, S., and Bresler, E., 1985. *Drip Irrigation Manual.* Pub. No. 9, Bet Dagan, Israel: International Irrigation Information Center (IIIC), 95 pp.

Ehlig, C.F., and Gardner, W.R., 1964. Relationship between transpiration and the internal water relations of plants. *Agron. J.*, **56**: 127–130.

Gardner, W.R., 1965. Dynamic aspects of soil–water availability to plants. *Ann. Rev. Plant Physiol.*, **16**: 323–342.

Gardner, W.R., and Nleman, R.H., 1964. Lower limit of water avilability to plants. *Science*, **143**: 1460–1462.

Goldberg, D., Gornat, B., and Rimon, D., 1976. *Drip Irrigation, Principles, Design and Agricultural Practices.* Kfar Shmaryahu, Israel: Drip Irrigation Scientific Publications, p. 296.

Green, W.H., and Ampt, G.A., 1911. Studies on soil physics: I. Flow of air and water through soils. *J. Agric. Sci.*, **4**: 1–24.

Hall, W.A., 1956. Estimating irrigation border flow. *Agric. Eng.*, **37**: 262–265.

Hansen, V.E., 1960. Mathematical relationships expressing the hydraulics of surface irrigation. In *ARS 41–43,* Proc. Workshop on Hydraulics of Surface Irrigation (Denver). Washington, DC: USDA, pp. 29–35.

Hansen, V.E., Israelsen, O.W., and Stringham, G.E., 1980. *Irrigation Principles and Practices.* New York: John Wiley & Sons. p. 416.

Heller, J., and Bresler, E., 1973. Trickle irrigation. In Yaron, B., Danfors, E., and Vaadia, Y., eds., *Arid Zone Irrigation, Ecological Studies 5.* Berlin, Heidelberg, New York: Springer-Verlag, pp. 339–351.

Horton, R.E., 1940. An approach toward a physical interpretation of infiltration capacity. *Soil Sci. Soc. Am. Proc.*, **5**: 399–417.

Kostiakov, A.M., 1932. On the dynamics of the coefficient of water percolation in soils and on the necessity of studying it from a dynamic point of view for purposes of amelioration. *Trans. Comm. Int, Soil Sci. Soc., Moscow, Part A*, **6**: 17–21.

Manning, R., 1890. Flow of water in open channels and pipes. *Trans. Inst. Civil Eng. Ireland*, Vol. 20.

Marr, J.C., 1964. *The Border Method of Irrigation.* Circular 408, Berkeley, CA: California Agricultural Experiment Station Extension Service, p. 24.

Molenaar, A., 1956. *Mater Lifting Devices for Irrigation.* FAO Agricultural Development Paper No. 60. Rome: Food and Agriculture Organization of the United Nations, p. 76.

Nakayama, F.S., and Bucks, D.A., eds., 1986. *Trickle Irrigation for Crop Production.* Developments in Agricultural Engineering 9. Amsterdam: Elsevier, p. 383.

Philip, J.R., 1969. Theory of infiltration. *Adv. Hvdrosci.*, **5**: 216–296.

Rawitz, E., 1969. The dependence of growth rate and transpiration rate on plant and soil physical parameters under controlled conditions. *Soil Sci.*, **110**: 172–182.

Rawitz, E., 1973a. Sprinkler irrigation. In Yaron, *et al., Arid Zone Irrigation, Ecological Studies 5.* Berlin, Heidelberg, New York: Springer-Verlag, pp. 303–321.

Rawitz, E., 1973b. Gravity irrigation. In Yaron, *et al., Arid Zone Irrigation. Ecological Studies 5.* Berlin, Heidelberg, New York: Springer-Verlag, pp. 323–337.

Rawitz, E., Dasberg, S., Hadas, A., and Hillel, D., 1964. The effects of irrigation method and cropping system on some structural properties of a loessial sierozem in the northern Negev. *Isr. J. Agric. Res.*, **14**: 197–202.

Shull, H., 1960. Furrow hydraulics study at the Southwestern Irrigation Field Station. In *ARS 41–43,* Proc. Workshop on Hydraulics of Surface Irrigation (Denver, Colorado). Washington, DC: USDA, pp. 55–62.

U.S. Department of Agriculture, Soil Conservation Service, 1974. Border Irrigation. In Sect. 15, Ch. 4, *National Engineering Handbook*, Washington, DC.

U.S. Department of Agriculture, Soil Conservation Service, 1983. Furrow Irrigation. In Sect. 15, Ch. 5, *National Engineering Handbook*, Washington, DC.

Walker, W.R., 1993. Two decades of surface irrigation research: four significant results and their practical consequences. In Proc. 6th Int. Conference on Irrigation, Tel Aviv, Israel, pp. 137–158.

Walker, W.R., and Skogerboe, G.V., 1987. *Surface Irrigation: Theory and Practice.* Englewood Cliffs, NJ: Prentice-Hall, p. 386.

J

JOURNALS

Scientific and technical journals are a primary means of disseminating information to the soil science community. Without communication among groups of like-minded scientists and technicians and with researchers in ancillary fields, it would be impossible for the science to advance. The overall field of soil science, including all of the subfields of interest, is well represented by numerous mainline journals. Most journals today are available in different formats, in paper print form or online in electronic format. A sample of some primary journals that cover aspects of the soil science discipline are listed in Table J1. This table is not meant to be comprehensive, but rather to give an indication of the kinds of journals that are available. Included in abbreviated form is the content, scope, or society affiliation of the journal. Also given is the publisher, which may or may not be the same as the professional society because some societies contract printing services to commercial publishers. The ISSN is given, when available, for both print and online versions of the same journal. It was not always possible to easily discern the date of first issue of a journal and so the current volume number is indicated instead. In some cases, when the year of first issue is readily available in online searches, it is provided with the current volume number in the format year of first issue/current volume number, e.g., 1910/97 for the *Agronomy Journal*; 1963/43 for the *Australian Journal of Soil Research* (AJSR), and 1967/134 for *Geoderma*. Some ancillary notes are also provided in the table as background information relating to interesting comments or facts about the journal. In the case of the *Australian Journal of Soil Research*, as one example, the notes indicate that the AJSR "... has been the premier soil science journal of the Asia-Pacific region since 1963. It attracts an enthusiastic international authorship due to its breadth of scope and recognition of emerging issues in land care and environmental science. The journal includes an interesting, high quality selection of papers to appeal to researchers and practitioners in all areas of soil science." (Table J1).

The journals in Table J1 cover a range of subdisciplines that come under the general aegis of soil science viz. agronomy, soil ecology, arid soil research and rehabilitation, biology and fertility (biochemistry and soil nutrients) of soils, biotechnology, soils geomorphology, land degradation, plant-soil relationships, soil and sediment contamination, tillage research, among numerous other topics. Most mainline journals cover a wide range of topics and it is impossible to list them all here. The general or overarching subject areas are made clear enough from the journal titles and researchers can work from there. One of the older soil science journals was originally published in 1899 under the title *Pochvovedenie* but the English version of the journal of the Russian Academy of Sciences *Agrokhimiya* is now published in the journal *Eurasian Soil Science*.

As an applied science, the study of soils has developed many tentacles that now reach into myriad nooks and crannies that heretofore would have been unsuspected or unanticipated. Because soils are basic to life and especially for humans as supporting crop production, aspects of soil science seem to find never-ending applications. Table J2 lists major and minor journals from the world over in an effort to indicate the breadth and depth of investigations of soil properties and their widespread application or use. This table was compiled form online searches using key words related to soil or soil or soil science. In some cases, the application or use or relationship to soils is not immediately apparent but further inspection may indicate why the journal was accessed in online searches. If nothing else, Table J2 indicates or indeed emphasizes the crucial role of soils in sustainable development, as habitat, as a basis for food production, land care and conservation, pollution abatement, and even as an engineering material. Titles are listed in alphabetical order followed by the ISSN, publisher, and country of publication. In this way, it is anticipated that the contained information will serve some useful purpose for researchers who may not be aware of all journals that are related to their field of interest. With such a vast literature, it is perhaps somewhat difficult to imagine that any researcher would be fully conversant with all sources of information. Further, important details or data do not make it into the mainstream journals for a variety of

Table J1 Sample list of some mainline journals dealing with aspects of soil science

Journal title	Content, scope, or society affiliation	Publisher, society	ISSN	First issue or current volume	Frequency-cost	Description and notes
Agronomy Journal	American Society of Agronomy	American Society of Agronomy	1435-0645 (OL) 0002-1962(P)	1910, 97	$50	Articles relating to original research in soil-plant relationships; crop science; soil science; biometry; crop, soil, pasture, and range management; crop, forage, and pasture production and utilization; turfgrass; agroclimatology; agronomic modeling; statistics; production agriculture; and computer software are published in *Agronomy Journal* subsequent to review and approval by the editorial board.
Applied Soil Ecology	International, commercial	Elsevier	0929-1393	1994	3/$1246	Applied Soil Ecology addresses the role of soil organisms and their interactions in relation to: agricultural productivity, nutrient cycling and other soil processes, the maintenance of soil structure and fertility, the impact of human activities and xenobiotics on soil ecosystems and bio(techno)logical control of soil-inhabiting pests, diseases and weeds.
Archives of Agronomy and Soil Science	International, commercial	Taylor & Francis	0365-0340(P) 1476-3567(OL)	51	6, + online $1740 (I) $253 (P)	An established journal, in publication for over thirty years, Archives of Agronomy and Soil Science publishes papers over the entire range of agronomy and soil science.
Arid Land Research And Management	International, commercial Formerly Arid Soil Research and Rehabilitation	Taylor & Francis	1532-4982 (P) 1532-4990 (OL)	19	4 + online $437 (I) $173 (P)	Arid Land Research and Management is a common outlet and a valuable source of information for fundamental and applied research on soils affected by aridity. This journal covers land ecology, including flora and fauna, as well as soil chemistry, biology, physics, and other edaphic aspects.
Australian Journal of Soil Research	Supported by ASSSI and NZSSS and cooperating journal of the IUSS	CSIRO Publishing	0004-9573	1963, 43	8, $925 online + print	Has been the premier soil science journal of the Asia-Pacific region since 1963. It attracts an enthusiastic international authorship due to its breadth of scope and recognition of emerging issues in land care and environmental science. The journal includes an interesting, high quality selection of papers to appeal to researchers and practitioners in all areas of soil science.
Biology and Fertility of Soils	Cooperating Journal of International Society of Soil Science	Springer-Verlag	0178-2762 (P) 1432-0789 (OL)	41	4	Publishes original papers, reviews and short communications (in English) on all fundamental and applied aspects of biology (microflora and microfauna) and fertility (productivity) of soils.
Biotechnology, Agronomy, Society and Environment	University of Gembloux (FUSAGx) and of the Agricultural Research Centre, Gembloux of the Ministry of the Middle Classes and Agriculture (CRA)	les Presses agronomiques de Gembloux	1370-6233	9	4, E80	Publishes original papers, research notes, review articles, summaries of books and theses as well as reviews of workshops and conferences in the fields of crop and animal productions and sciences, forest sciences, soil and earth sciences, rural engineering, environment, bioindustries, food technologies, economy and sociology.

Canadian Journal of Soil Science	International journal - Agricultural Institute of Canada	Canadian Society of Soil Science and the Canadian Society of Agrometeorology	0008-4271	85	4	Research is published in a number of topic sections: agrometeorology, ecology, biological processes and plant interactions, composition and chemical processes, physical processes and interfaces, genesis, landscape processes and relationships contamination and environmental stewardship, management for agricultural, forestry and urban uses open (a section title suggested by an author or the Editor)
CATENA	International, commercial Interdisciplinary Journal of Soil Science - Hydrology - Geomorphology focusing on Geoecology and Landscape Evolution	Elsevier	0341-8162	1993	12, $1428	CATENA publishes original contributions in the fields of: GEOECOLOGY, the geoscientific-hydro-climatological subset of process-oriented studies of the present ecosystem, the total environment of landscapes and sites, the flux of energy and matter (water, solutes, suspended matter, bed load) with special regard to space-time variability, the changes in the present ecosystem, including the earth's surface and landscape evolution, the genesis of the present ecosystem, in particular the genesis of its structure concerning soils, sediment, relief, their spatial organization and analysis in terms of paleoprocesses; soils: surface, relief and fossil soils, their spatial organization pertaining to relief development, sediment with relevance to landscape evolution, the paleohydrologic environment with respect to surface runoff, competence, and capacity for transport of bed material and suspended matter, infiltration, groundwater and channel flow, the earth's surface, relief elements and their spatial-hierarchical organization in relation to soils and sediment, the paleoclimatological properties of the sequence of paleoenvironments.
Clays and Clay Minerals	International journal	Clay Minerals Society	0009-8604	1963	Institutional $250 Personal $70	To stimulate research and to disseminate information relating to all aspects of clay science and technology.
Eurasian Soil Science *(Pochvovedenie)*	English version of the journal of the Russian Academy of Sciences *Agrokhimiya*, is no longer being published as a separate title, but has been merged into the journal *Eurasian Soil Science*.	Nauka/Interperiodica – International Academic Publishing Company	1064-2293	1899	$3266	Publishes original papers on global and regional theoretical and experimental studies on the problems of genesis, geography, physics, chemistry, biology, fertility, management, conservation, and remediation of soils.
European Journal of Soil Science	National Societies of Soil Science in Europe)	Blackwell	Print + online	56	$519.12	Publishing the latest significant findings of research, the description of new techniques, and up-to-date authoritative and critical reviews over the whole field of soil science and its applications.
Geoderma	International Journal of Soil Science	Elsevier	0016-7061	1967, 134	4, $2562	The different fields of soil science by bringing together papers from the entire field of soil research rather than emphasizing any one sub-discipline. The Journal welcomes interdisciplinary work preferably focussing on occurrence and dynamic characterization in space and time of soils in the field.

(Continued)

Table J1 (Continued)

Journal title	Content, scope, or society affiliation	Publisher, society	ISSN	First issue or current volume	Frequency-cost	Description and notes
Journal of Environmental Quality	International journal	ASA, CSSA, and SSSA	1085-3278 (P) 1099-145X (OL)	1972, 16	6, $915 (I) $685 (P)	Contributions under the headings of (i) Technical Reports, (ii) Reviews and Analyses, (iii) Environmental Issues, (iv) Short Communications, (v) Letters to the Editor, and (vi) Book Reviews. Papers in JEQ cover various aspects of anthropogenic impacts on the environment, including terrestrial, atmospheric, and aquatic systems. Emphasis is given to the understanding of underlying processes rather than to monitoring.
Journal of Plant Nutrition and Soil Science	International journal, Zeitschrift für Pflanzenernährung und Bodenkunde	Wiley Interscience - A Cooperation Journal of the International Union of Soil Sciences	1436-8730 (P) 1522-2624 (OL)	168	6, E878	Publishes reviews, high-standard original papers, and short communications covering the entire spectrum of plant nutrition and soil science.
Journal of Soils & Sediments	International journal	Springer, Associated Journal of SedNet (Demand-driven, European Sediment Research Network) Cooperating Journal of IUSS (International Union of Soil Sciences)	1439-0108	5	4, print + online, E122	The first journal entirely devoted to soils and sediments, hereby dealing not only with contaminated, but also with intact and disturbed soils and sediments. JSS elucidates the common aspects as well as the differences between these two environmental compartments. JSS is an interdisciplinary journal intended to be of benefit to the scientist as well as to the practitioner.
Land Degradation & Development	International journal	Wiley Interscience	1099-145X (OL) 1085-3278 (P)	16	$685	Seeks to promote rational study of the recognition, monitoring, control and rehabilitation of degradation in terrestrial environments. The journal focuses on: what land degradation is; what causes land degradation; the impacts of land degradation the scale of land degradation; the history, current status or future trends of land degradation; avoidance, mitigation and control of land degradation; remedial actions to rehabilitate or restore degraded land; sustainable land management.
Plant and Soil	International Journal on Plant-Soil Relationships	Springer-Verlag	0032-079X (P) 1573-5036 (OL)	274		Publishes original papers and solicited review articles that deal with the interface of plant biology and soil sciences, are of general interest, and provide a clear mechanistic component. This area includes both fundamental and applied aspects of mineral nutrition, plant-water relations, symbiotic and pathogenic plant-microbe interactions, root anatomy and morphology, soil biology, ecology, agrochemistry and agrophysics. Articles including a major molecular or mathematical component also fall within the scope of the journal.

Soil and Sediment Contamination	Formerly Journal of Soil Contamination	Taylor & Francis, Association for the Environmental Health of Soils (AEHS)	1532-0383 (P) 1549-7887 (OL)	14	6, \$862 (I) \$129 (P)	All types of soil contamination. Sludges and petroleum contamination and their chemical constituents are recent concerns; however, the journal will also discuss petrochemical, chlorinated hydrocarbon, pesticide and heavy metal (especially lead) contamination.
Soil & Tillage Research	International journal	Elsevier; International Soil Tillage Research Organization (ISTRO)	0167-1987	1981, 89	\$2076	Research and development in soil tillage and field traffic, and their relationship with land use, crop production and the environment. This journal is concerned with the changes in the physical, chemical and biological parameters of the soil environment brought about by soil tillage and field traffic, their effects on both below and above ground environmental quality, crop establishment, root development and plant growth, and the interactions between these various effects.
Soil Biology & Biochemistry	International journal	Elsevier	0038-0717	1969, 38	15, \$2509 (I) \$327 (P)	A forum for research on soil organisms, their biochemical activities and their influence on the soil environment and plant growth. It publishes original work on quantitative, analytical and experimental aspects of such research.
Soil Science	International journal; An Interdisciplinary Approach to Soil Research	Lippincott Williams and Wilkins	0038-075X	170	12	Every area of soil and plant science-soil chemistry, physics, fertility, morphology, microbiology, and environmental soil science.
Soil Science Society of America Journal	International journal	Soil Science Society of America		69	6, \$50.00 (P)	Original research, reviews of research, and comments and letters to the editor
Soil Use and Management	International forum	Blackwell, CABI Publishing, British Society of Soil Science	0266-0032 (P) 1475-2743 (OL)	21	4	Topics covered include: Environmental protection, soil-crop interactions, soil erosion and conservation, pollution control, restoration and reclamation of land, evaluation of soil surveys, development of methodology.
Water, Air, and Soil Pollution	International journal of Environmental Pollution	Springer-Verlag	0049-6979 (P) 1573-2932 (OL)	166	6, \$3708 (I)	Interdisciplinary journal on all aspects of pollution and solutions to pollution in the biosphere. This includes chemical, physical and biological processes affecting flora, fauna, water, air and soil in relation to environmental pollution.

Notes: *P* = print version; *OL* = online version; *I* = institutional subscript price; *P* = personal or individual rate.

Table J2 Worldwide list of soil science related journals, arranged alphabetically and based on an online search of the Internet

Title	ISSN	Publisher	Publisher country
ABARE Current Issues	1329-0355	Australian Bureau of Agricultural and Resource Economics	Australia
ABARE EReport	1447-817X	Australian Bureau of Agricultural and Resource Economics	Australia
Abhandlungen der Zoologisch-Botanischen Gesellschaft in Osterreich	0084-5639	Zoologisch-Botanische Gesellschaft in Osterreich	Austria
Abhandlungen und Berichte des Naturkundemuseums Gorlitz	0373-7586	Staatliches Museum fur Naturkunde Gorlitz	Germany
Accreditation and Quality Assurance	0949-1775	Springer-Verlag GmbH	Germany
ACIAR Technical Reports Series		Australian Centre for International Agricultural Research (ACIAR)	Australia
Acta Agraria et Silvestria. Series Silvestris	0065-0927	Polska Akademia Nauk, Oddzial w Krakowie	Poland
Acta Agriculturae Boreali-Sinica	1000-7091	Acta Agriculturae Boreali-Sinica	China
Acta Agriculturae Scandinavica. Section B - Soil and Plant Science	0906-4710	Taylor & Francis	UK
Acta Agriculturae Shanghai	1000-3924	Shanghai Academy of Agricultural Sciences	China
Acta Agriculturae Universitatis Jiangxiensis	1000-2286	Jiangxi Agricultural University	China
Acta Agriculturae Zhejiangensis	1004-1524	Zhejiang Academy of Agricultural Sciences	China
Acta Agrobotanica	0065-0951	Polskie Towarzystwo Botaniczyne (Polish Botanical Society)	Poland
Acta Agronomica Hungarica	0238-0161	Akademiai Kiado	Hungary
Acta Agronomica Ovariensis	1416-647X	University of West Hungary, Faculty of Agricultural Sciences	Hungary
Acta Agronomica Sinica	0496-3490	Science Press	China
Acta Alimentaria (Budapest)	0139-3006	Akademiai Kiado	Hungary
Acta Amazonica	0044-5967	Instituto Nacional de Pesquisas da Amazonia (INPA)	Brazil
Acta Biologica Universitatis Daugavpiliensis	1407-8953	University of Daugavpils, Department of Biology	Latvia
Acta Biologica Venezuelica	0001-5326	Institute de Zoologia Tropical, Universidade Central de Venezuela	Venezuela
Acta Biotechnologica	0138-4988	Wiley-VCH	Verlag
Acta Botanica Barcinonensia	0210-7597	Departament de Biologia Vegetal, Universitat de Barcelona	Spain
Acta Botanica Boreali-Occidentalia Sinica	1000-4025	Science Press	China
Acta Botanica Brasilica	0102-3306	Sociedade Botanica do Brasil	Brazil
Acta Botanica Croatica	0365-0588	Division of Biology, Faculty of Science	Croatia
Acta Botanica Gallica	1253-8078	Societe Botanique de France	France
Acta Botanica Hungarica	0236-6495	Akademiai Kiado	Hungary
Acta Botanica Malacitana	0210-9506	Departamento de Biologia Vegetal, Facultad de Ciencias	Spain
Acta Botanica Sinica	0577-7496	Science Press	China
Acta Fytotechnica et Zootechnica	1335-258X	Slovenska Polnohospodarska Univerzita v Nitre	Slovakia
Acta Horticulturae	0567-7572	International Society for Horticultural Science (ISHS)	Belgium
Acta Horticulturae et Regiotecturae	1335-2563	Vydavatel'ske a edicne stredisko SPU v Nitre	Slovakia
Acta Horticulturae Sinica	0513-353X	Chinese Society for Horticultural Science	China
Acta Hydrobiologica Sinica	1000-3207	Institute of Hydrobiology	Academia Sinica
Acta Hydrochimica et Hydrobiologica	0323-4320	WILEY-VCH Verlag GMBH & Co. KGaA	Germany
Acta Microbiologica et Immunologica Hungarica	1217-8950	Akademiai Kiado	Hungary
Acta Oecologica	1146-609X	Elsevier SAS	France
Acta Oeconomica et Informatica	1335-2571	Slovenska Polnohospodarska Univerzita v Nitre	Slovakia
Acta Pedologica Sinica	0564-3929	Science Press	China
Acta Physiologiae Plantarum	0137-5881	Franciszek Gorski Institute of Plant Physiology, Polish Academy of Sciences	Poland
Acta Phytoecologica Sinica	1005-264X	Science Press	China
Acta Phytophylacica Sinica	0577-7518	China Society of Plant Protection	China
Acta Prataculturae Sinica	1004-5759	Editorial Committee of Acta Prataculturae Sinica	China
Acta Protozoologica	0065-1583	Nencki Institute of Experimental Biology, Polish Academy of Sciences	Poland
Acta Scientiarum - Agronomy	1679-9275	Universidade Estadual de Maringa	Brazil
Acta Scientiarum Polonorum - Agricultura	1644-0625	Wydawnictwa Uczelniane Akademii Techniczno-Rolniczej w Bydgoszczy	Poland
Acta Scientiarum Polonorum - Biologia	1644-0641	Dzial Wydawnictw Akademii Podlaskiej w Siedlcach	Poland
Acta Scientiarum Polonorum - Formatio Circumiectus	1644-0765	Wydawnictwo Akademii Rolniczej w Krakowie	Poland
Acta Scientiarum Polonorum - Piscaria	1644-0706	Wydawnictwo Akademii Rolniczej, Szczecin	Poland
Acta Sericologica Sinica	0257-4799	Editorial Board of Acta Sericolgica Sinica	China
Acta Societatis Botanicorum Poloniae	0001-6977	Botanical Society of Poland	Poland

Acta Technologica Agriculturae	1335-2555	Slovenska Polnohospodarska Univerzita v Nitre	Slovakia
Acta Universitatis Agriculturae et Silviculturae Mendelianae Brunensis	1211-8516	Ustredni knihovna MZLU v Brne	Czech Republic
Acta Zoologica Academiae Scientiarum Hungaricae	1217-8837	Hungarian Natural History Museum	Hungary
Acta Zoologica Lituanica	1392-1657	Lithuanian Academy of Sciences, Institute of Ecology	Lithuania
Advances in Agricultural Research in India	0971-6394	International Book Distributors	India
Advances in Agronomy	0065-2113	Elsevier Inc.	USA
Advances in Atmospheric Sciences	0256-1530	Science Press	China
Advances in Botanical Research	0065-2296	Elsevier Ltd	UK
Advances in Forestry Research in India	0971-2704	International Book Distributors	India
Advances in Geoecology	0722-0723	Catena Verlag	Germany
Advances in Horticultural Science	0394-6169	Department of Horticulture, University of Florence	Italy
Advances in Horticulture and Forestry		Scientific Publishers (India)	India
Advances in Plant Sciences	0970-3586	Academy of Plant Sciences	India
Advances in Vegetation Science	0168-8022	Kluwer Academic Publishers	Netherlands
Advantage - Forest Engineering Research Institute of Canada (FERIC)	1493-3381	Forest Engineering Research Institute of Canada	Canada
AERU Discussion Paper	1170-7607	Agribusiness & Economics Research Unit, Lincoln University	New Zealand
Africa Insight	0256-2804	Africa Institute of South Africa	South Africa
African Crop Science Journal	1021-9730	African Crop Science Society	Uganda
African Farming and Food Processing	0266-8017	Alain Charles Publishing Ltd	UK
African Journal of Agricultural Teacher Education	0794-7739	VoTeX Publishers	Nigeria
African Journal of Biotechnology	1684-5615	Academic Journals	Kenya
African Journal of Ecology	0141-6707	Blackwell Publishing	UK
African Journal of Environmental Assessment and Management	1438-7890	African Journal of Environmental Assessment and Management	Ghana
African Journal of Health Sciences	1022-9272	Kenya Medical Research Institute	Kenya
African Journal of Mycology and Biotechnology	1110-5879	Regional Center for Mycology and Biotechnology	Egypt
African Journal of Range & Forage Science	1022-0119	NISC Pty Ltd	South Africa
Agnote - Northern Territory of Australia	0157-8243	Northern Territory Government	Australia
Agnote - NSW Agriculture	1034-6848	NSW Agriculture	Australia
Agraarteadus	1024-0845	Akadeemiline Pollumajanduse Selts	Estonia
Agrar- und Umweltrecht	0340-840X	Landwirtschaftsverlag GmbH	Germany
Agrarforschung	1022-663X	Bundesamt fur Landwirtschaft	Switzerland
Agrarokologie		Verlag Agrarokologie	Switzerland
Agrartechnische Forschung	0948-7298	Institut fur Agrartechnik Bornim e.V.	Germany
Agrarwirtschaft	0002-1121	Deutscher Fachverlag GmbH	Germany
Agricoltura Mediterranea	0394-0438	Edizioni Plus	Italy
Agricultura - Revista de stiinta si practica agricola	1221-5317	Universitatea de Stiinte Agricole si Medicina Veterinara Cluj-Napoca	Romania
Agricultura Tecnica	0365-2807	Instituto de Investigaciones Agropecuarias	Chile
Agricultura Tecnica en Mexico	0568-2517	Instituto Nacional de Investigaciones Forestales, Agricolas y Pecuarias (INIFAP)	Mexico
Agricultura Tropica et Subtropica	0231-5742	Institute of Tropical and Subtropical Agriculture, Czech University of Agriculture	Czechoslovakia
Agriculturae Conspectus Scientificus (Poljoprivredna Znanstvena Smotra)	1331-7768	Agronomski Fakultet, Sveucilista u Zagrebu	Croatia
Agricultural and Food Science	1459-6067	Agrifood Research Finland	Finland
Agricultural and Food Science in Finland	1239-0992	Agrifood Research Finland	Finland
Agricultural and Forest Meteorology	0168-1923	Elsevier	Netherlands
Agricultural and Resource Economics Review	1068-2805	Northeastern Agricultural and Resource Economics Association	USA
Agricultural Economics	0169-5150	Blackwell Publishing	USA
Agricultural Economics and Management	0205-3845	National Centre for Agrarian Sciences in Bulgaria	Bulgaria
Agricultural Engineering International	1682-1130	International Commission of Agricultural Engineering (CIGR)	Switzerland
Agricultural Information Research	0916-9482	Japanese Society of Agricultural Informatics, Institut fur Landtechnik	Japan
Agricultural Reviews	0253-1496	Agricultural Research Communication Centre	India
Agricultural Science	1030-4614	Australian Institute of Agricultural Science & Technology	Australia
Agricultural Science & Technology - Hunan	1009-4229	Hunan Academy of Agricultural Sciences	China
Agricultural Science (Tabriz)	1680-242X	College of Agriculture, Tabriz University	Iran

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Agricultural Science Digest	0253-150X	Agricultural Research Communication Centre	India
Agricultural Sciences and Technology	1029-4791	College of Agriculture, Ferdowsi University of Mashhad	Iran
Agricultural Sciences in China	1671-2927	Editorial Department of Agricultural Sciences in China	China
Agricultural Systems	0308-521X	Elsevier	UK
Agricultural Water Management	0378-3774	Elsevier	Netherlands
Agriculture Scientific and Professional Review	1330-7142	Sveuciliste Josipa Jurja Strossmayera u Osijeku	Croatia
Agriculture - Ecosystems & Environment	0167-8809	Elsevier	Netherlands
AgriScientia	0327-6244	Facultad de Ciencias Agropecuarias de la Universidad Nacional de Cordoba	Argentina
AgriTopia	1015-9762	Ethiopian Agricultural Research Organization	Ethiopia
Agro-Ciencia	0716-1689	Ediciones Universidad de Concepcion	Chile
Agro-Science - Journal of Tropical Agriculture, Food, Environment and Extension	1119-7455	Faculty of Agriculture of the University of Nigeria	Nigeria
Agroanalysis	0100-4298	Instituto Brasileiro de Economia, Fundacao Getulio Vargas	Brazil
Agrochimica	0002-1857	Universita degli Studi di Pisa	Italy
Agrociencia (Montecillo)	1405-3195	Colegio de Postgraduados	Mexico
Agrociencia (Montevideo)	1510-0839	Facultad de Agronomia, Universidad de la Republica Oriental del Uruguay	Uruguay
Agroforestry Forum	0966-8616	School of Agricultural and Forest Sciences, University of Wales	UK
Agroforestry Systems	0167-4366	Springer Science + Business Media	Netherlands
Agrokemia es Talajtan	0002-1873	Akademiai Kiado	Hungary
Agrokhimiya	0002-1881	MAIK Nauka/Interperiodica Publishing	Russia
Agronomia	0365-2718	Universidade Federal Rural do Rio de Janeiro (UFRRJ)	Brazil
Agronomia Colombiana	0120-9965	Facultad de Agronomia, Universidad Nacional de Colombia	Colombia
Agronomia Costarricense	0377-9424	Editorial de la Universidad de Costa Rica	Costa Rica
Agronomia Lusitana	0002-1911	Estacao Agronomica Nacional	Portugal
Agronomia Mesoamericana	1021-7444	Estacion Experimental Fabio Baudrit Moreno	Costa Rica
Agronomia Tropical (Maracay)	0002-192X	Fondo Nacional de Investigaciones Agropecuarias (FONAIAP)	Venezuela
Agronomico	0365-2726	Instituto Agronomico	Brazil
Agronomski Glasnik	0002-1954	Hrvatsko Agronomsko Drustvo	Croatia
Agronomy for Sustainable Development	0249-5627	EDP Sciences	France
Agronomy Journal	0002-1962	American Society of Agronomy	USA
Agronomy New Zealand	0110-6589	Agronomy Society of New Zealand	New Zealand
Agronomy Research	1406-894X	Faculty of Agronomy, Estonian Agricultural University	Estonia
Agropecuaria Clima Temperado	1415-6822	Centro de Pesquisa Agropecuaria de Clima Temperado, EMBRAPA	Brazil
Agropedology	0971-1570	Indian Society of Soil Survey & Land Use Planning	India
Agrosearch	1117-9996	Agro Publishers	Nigeria
Agrotropica	0103-3816	Centro de Pesquisas do Cacau (CEPEC)	Brazil
Akadeemilise Metsaseltsi Toimetised	1406-9946	Eesti Pollumajandusulikool, Metsanduslik Uurimisinstituut	Estonia
Aktuelt fra Skogforskningen	0803-284X	Norsk Institutt for Skogforskning (Norwegian Forest Research Institute)	Norway
Al Awamia	0572-2721	Institut National de la Recherche Agronomique	Morocco
Alberi e Territorio	1724-4021	Gruppo Calderini Edagricole Srl	Italy
Alexandria Journal of Agricultural Research	0044-7250	Faculty of Agriculture, University of Alexandria	Egypt
Alimentaria	0300-5755	EYPASA (Ediciones y Publicaciones Alimentarias SA)	Spain
Allelopathy Journal	0971-4693	International Allelopathy Foundation	India
Allgemeine Forst- und Jagdzeitung	0002-5852	J.D. Sauerlander's Verlag	Germany
Aloe	0002-6301	Succulent Society of South Africa	South Africa
Alon Hanotea	0333-8886	Israel Fruit Growers Association	Israel
Ambio	0044-7447	Royal Swedish Academy of Sciences	Sweden
American Journal of Enology and Viticulture	0002-9254	American Society for Enology and Viticulture	USA
American Journal of Potato Research	1099-209x	Potato Association of America	USA
American Journal of Public Health	0090-0036	American Public Health Association	USA
American Midland Naturalist	0003-0031	University of Notre Dame Press	USA
American Naturalist	0003-0147	University of Chicago Press	USA
AMK Mededelingen	0771-9884	Antwerpse Mycologische Kring (AMK)	Belgium

Anadolu	1300-0225	Ege Tarimsal Arastirma Enstitusu Mudurlugu, Aegean Agricultural Research Institute Directorate	Greece
Anais da Academia Brasileira de Ciencias	0001-3765	Academia Brasileira de Ciencias	Brazil
Anale Institutul de Cercetari si Amenajari Silvice	1583-2023	Institutul de Cercetari si Amenajari Silvice Bucuresti	Romania
Anales de Botanica Agricola	1315-6284	Instituto de Botanica Agricola, Facultad de Agronomia	Argentina
Anales del Jardin Botanico de Madrid	0211-1322	Instituto Botanico, Real Jardin de Botanico CSIC	Spain
Analytica Chimica Acta	0003-2670	Elsevier	Netherlands
Analytical and Bioanalytical Chemistry	1618-2642	Springer-Verlag GmbH	Germany
Analytical Chemistry (Washington)	0003-2700	American Chemical Society	USA
Analytical Letters	0003-2719	Taylor & Francis	USA
Annales Botanici Fennici	0003-3847	Finnish Zoological and Botanical Publishing Board	Finland
Annales Universitatis Mariae Curie-Sklodowska. Sectio E	0365-1118	Wydawnictwo Uniwersytetu Marii Curie-Sklodowskiej	Poland
Annales Universitatis Mariae Curie-Sklodowska. Sectio EEE	1233-2127	Wydawnictwo Uniwersytetu Marii Curie-Sklodowskiej	Poland
Annali - Accademia Italiana di Scienze Forestali	0515-2178	Accademia Italiana di Scienze Forestali	Italy
Annali dell'Istituto Sperimentale Agronomico	0304-0615	Istituto Sperimentale Agronomico	Italy
Annali dell'Istituto Sperimentale per la Selvicoltura	0390-0010	Istituto Sperimentale per la Selvicoltura	Italy
Annali della Facolta di Agraria	0347-4981	Universita degli Studi di Perugia	Italy
Annals of Agri Bio Research	0971-9660	Agri Bio Research Publishers	India
Annals of Agricultural Research	0970-3179	Indian Society of Agricultural Science	India
Annals of Agricultural Science (Cairo)	0570-1783	Faculty of Agriculture, Ain Shams University	Egypt
Annals of Applied Biology	0003-4746	Blackwell Publishing	UK
Annals of Bangladesh Agriculture	1025-482X	Bangabandhu Sheikh Mujibur Rahman Agricultural University	Bangladesh
Annals of Forest Science	1286-4560	EDP Sciences	France
Annals of Forestry	0971-4022	Jyoti Publishers & Distributors	India
Annals of Microbiology	1590-4261	University of Milan, Department of Food Science and Microbiology	Italy
Annals of Plant Physiology	0970-9924	Forum for Plant Physiologists	India
Annals of Plant Protection Sciences	0971-3573	Society of Plant Protection Sciences	India
Annual Review of Agricultural Engineering	1429-303X	Agricultural Engineering Committee, Polish Academy of Sciences	Poland
Annual Review of Ecology and Systematics	0066-4162	Annual Reviews Inc	USA
Annual Review of Energy and the Environment	1056-3466	Annual Reviews Inc	USA
Annual Review of Environment and Resources	1543-5938	Annual Reviews Inc	USA
Applied and Environmental Microbiology	0099-2240	American Society for Microbiology (ASM)	USA
Applied Biochemistry and Biotechnology	0273-2289	Humana Press	USA
Applied Biological Research	0972-0979	Centre for Advancement of Applied Sciences	India
Applied Ecology and Environmental Research	1589-1623	Landscape Architecture and Decision Support System	Hungary
Applied Economics	0003-6846	Routledge	UK
Applied Engineering in Agriculture	0883-8542	American Society of Agricultural Engineers	USA
Applied Microbiology and Biotechnology	0175-7598	Springer-Verlag GmbH	Germany
Applied Soil Ecology	0929-1393	Elsevier	Netherlands
Applied Turfgrass Science	1552-5821	Plant Management Network	USA
Applied Vegetation Science	1402-2001	Opulus Press	Sweden
Appropriate Technology	0305-0920	Research Information Ltd	UK
Aquacultural Engineering	0144-8609	Elsevier	Netherlands
Aquaculture	0044-8486	Elsevier	Netherlands
Aquaculture Economics & Management	1365-7305	International Association of Aquaculture Economics and Management	Australia
Aquaculture International	0967-6120	Kluwer Academic Publishers	Netherlands
Aquaculture Research	1355-557X	Blackwell Publishing	UK
Aquatic Botany	0304-3770	Elsevier	Netherlands
Arab Universities Journal of Agricultural Sciences	1110-2675	Faculty of Agriculture, Ain Shams University	UAE
Arboricultural Journal	0307-1375	AB Academic Publishers	UK
Arboriculture Fruitiere	0003-794X	ATC	France
Archiv fur Hydrobiologie	0003-9136	E. Schweizerbart'sche Verlagsbuchhandlung	Germany
Archives of Environmental Contamination and Toxicology	0090-4341	Springer Science + Business Media	Netherlands

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Archives of Microbiology	0302-8933	Springer-Verlag GmbH	Germany
Archives of Phytopathology and Plant Protection	0323-5408	Taylor & Francis	UK
Arid Land Research and Management	1532-4982	Taylor & Francis	UK
Arid Soil Research and Rehabilitation	0890-3069	Taylor & Francis	UK
Aspects of Applied Biology	0265-1491	Association of Applied Biologists	UK
ASSET - Series A: Agriculture & Environment	1595-9694	University of Agriculture	Nigeria
Assiut Journal of Agricultural Sciences	1110-0486	Faculty of Agriculture, Assiut University	Egypt
Austral Ecology	1442-9985	Blackwell Publishing	Australia
Australasian Parks and Leisure	1446-5604	Parks and Leisure Australia	Australia
Australasian Plant Pathology	0815-3191	CSIRO Publishing	Australia
Australian & New Zealand Wine Industry Journal	0819-2421	Winetitles	Australia
Australian Forestry	0004-9158	Institute of Foresters of Australia	Australia
Australian Journal of Agricultural and Resource Economics	1364-985X	Blackwell Publishing	Australia
Australian Journal of Agricultural Research	0004-9409	CSIRO Publishing	Australia
Australian Journal of Botany	0067-1924	CSIRO Publishing	Australia
Australian Journal of Environmental Management	1322-1698	Environment Institute of Australia and New Zealand	Australia
Australian Journal of Experimental Agriculture	0816-1089	CSIRO Publishing	Australia
Australian Journal of Grape and Wine Research	1322-7130	Australian Society of Viticulture and Oenology	Australia
Australian Journal of Soil Research	0004-9573	CSIRO Publishing	Australia
Australian Landcare	1440-4397	Agricultural Publishers Pty Ltd	Australia
Australian Parks and Leisure	1441-6263	Parks and Leisure Australia	Australia
Avance Agroindustrial	0326-1131	Estacion Experimental Agroindustrial ‘Obispo Colombres’	Argentina
Baltic Forestry	1392-1355	Lithuanian Forest Research Institute (Lietuvos Misku Institutas)	Lithuania
Bangladesh Journal of Agricultural Economics	0237-3539	Bureau of Socioeconomic Research and Training, Bangladesh Agricultural University of Agricultural Economics	Bangladesh
Bangladesh Journal of Botany	0253-5416	Bangladesh Botanical Society	Bangladesh
Bangladesh Journal of Forest Science	1021-3279	Bangladesh Forest Research Institute	Bangladesh
Bangladesh Journal of Plant Pathology	1012-9279	Bangladesh Phytopathological Society	Bangladesh
Bangladesh Journal of Scientific and Industrial Research	0304-9809	Bangladesh Council of Scientific and Industrial Research	Bangladesh
Basic and Applied Ecology	1439-1791	Elsevier GmbH	Germany
BC Journal of Ecosystems and Management	1488-4666	FORREX - Forest Research Extension Partnership	Canada
Beijing Agricultural Sciences	1001-8344	Beijing Academy of Agricultural and Forestry Sciences	China
Beitrage zur Tabakforschung International	0173-783X	Verband der Cigarettenindustrie	Germany
Belgian Journal of Botany	0037-9557	Societe Royale de Botanique de Belgique (Koninklijke Belgische Botanische Vereniging)	Belgium
Berichte der Naturforschenden Gesellschaft der Oberlausitz	0941-0627	Naturforschende Gesellschaft der Oberlausitz e.V.	Germany
Berichte uber Landwirtschaft	0005-9080	Landwirtschaftsverlag GmbH	Germany
Berita - Pusat Penelitian Perkebunan Gula Indonesia	0852-0321	Balai Penelitian Perusahaan Gula Perkebunan (Indonesian Sugar Research Institute)	Indonesia
Better Crops International		Potash and Phosphate Institute (PPI)	USA
Better Crops with Plant Food	0006-0089	Potash and Phosphate Institute (PPI)	USA
BFW Berichte	1013-0713	Bundesamt und Forschungszentrum fur Wald (BFW), Institut fur Forstschutz	Germany
Bhartiya Krishi Anusandhan Patrika	0303-3821	Agricultural Research Communication Centre	India
BIABAN	1026-1346	Iran Desert Research Center, University of Tehran	Iran
Bibliotheca Lichenologica	1436-1698	Gebruder Borntraeger Verlagsbuchhandlung	Germany
Bio-research	1596-7409	Faculty of Biological Sciences	Nigeria
Bioagro	1316-3361	Decanato de Agronomia, Universidad Centroccidental ‘Lisandro Alvarado’	Venezuela
Biochemical Systematics and Ecology	0305-1978	Elsevier	UK
Biochemistry (Washington)	0006-2960	American Chemical Society	USA
Biociencias	0104-3455	Pontificia Universidade Catolica do Rio Grande do Sul, Faculdade de iociencias	Brazil
BioControl	1386-6141	Springer Science + Business Media	Netherlands
BioCycle	0276-5055	JG Press Inc.	USA
Biodegradation	0923-9820	Springer Science + Business Media	Netherlands

Biodiversity	1488-8386	Tropical Conservancy	Canada
Biodiversity and Conservation	0960-3115	Springer Science + Business Media	Netherlands
Biodiversity Science	1005-0094	Science Press	China
BioFactors	0951-6433	IOS Press	Netherlands
Biogeochemistry	0168-2563	Springer Science + Business Media	Netherlands
Biogeosciences	1726-4170	Copernicus GmbH	Germany
Biogeosciences Discussions	1810-6277	Copernicus GmbH	Germany
Biologia (Bratislava)	0006-3088	SAP - Slovak Academic Press Ltd	Slovakia
Biologia Plantarum	0006-3134	Institute of Experimental Botany, Academy of Sciences of the Czech Republic	Czech Republic
Biological Agriculture & Horticulture	0144-8765	AB Academic Publishers	UK
Biological Bulletin	0006-3185	Marine Biological Laboratory	USA
Biological Conservation	0006-3207	Elsevier	UK
Biological Control	1049-9644	Elsevier	Netherlands
Biological Trace Element Research	0163-4984	Humana Press	USA
Biology and Fertility of Soils	0178-2762	Springer-Verlag GmbH	Germany
Biology Bulletin of the Russian Academy of Sciences	1062-3590	MAIK Nauka/Interperiodica Publishing	Russia
Biomass and Bioenergy	0961-9534	Elsevier	UK
Bionotes	0972-1800	A Biologists Confrerie	India
Bioresource Technology	0960-8524	Elsevier	UK
Bioscience	0916-8451	Japan Society for Bioscience	Japan
BioScience	0006-3568	American Institute of Biological Sciences	USA
Bioscience Journal	1516-3725	Universidade Federal de Uberlandia	Brazil
Biosensors & Bioelectronics	0956-5663	Elsevier	UK
Biosphere Science	1348-1371	Graduate School of Biosphere Science, Hiroshima University	Japan
Biosystems Engineering	1537-5110	Elsevier Ltd	UK
Biotechnology Advances	0734-9750	Elsevier	USA
Biotechnology and Bioengineering	0006-3592	John Wiley and Sons	Inc
Biotechnology in Animal Husbandry	1450-9156	Institute for Animal Husbandry	Serbia and Montenegro
Biotechnology Letters	0141-5492	Springer Science + Business Media	Netherlands
Biotronics	0289-0011	Biotron Institute	Japan
Biuletyn Naukowy	1640-1395	Wydawnictwo UWM	Poland
BMC Microbiology	1471-2180	BioMed Central Ltd	UK
Bodenkultur	0006-5471	WUV-Universita~umlaut~tsverlag	Austria
Bois et Forets des Tropiques	0006-579X	CIRAD-Foret	France
Boletim de Pesquisa - Embrapa Meio Ambiente	1516-4675	Embrapa Meio Ambiente	Brazil
Boletim de Pesquisa - Embrapa Solos	1517-5219	Embrapa Solos	Brazil
Boletim de Pesquisa e Desenvolvimento - Embrapa Cerrados	1676-918X	Embrapa Cerrados	Brazil
Boletim de Pesquisa e Desenvolvimento - Embrapa Semi-Arido	1516-1641	Embrapa Semi-Arido	Brazil
Boletim do Herbario Ezechias Paulo Heringer	0104-5334	Herbario Ezechias Paulo Heringer, Jardim Botanico de Brasilia	Brazil
Boletim do Museu Paraense Emilio Goeldi. Serie Botanica	0077-2216	Museu Paraense Emilio Goeldi	Brazil
Boletim Fepagro	0104-9089	Fundacao Estadual de Pesquisa Agropecuaria (FEPAGRO)	Brazil
Boletim Informativo da Sociedade Brasileira de Ciencia do Solo	1806-9657	Sociedade Brasileira de Ciencia do Solo	Brazil
Boletim Tecnico - Instituto Agronomico do Parana	0100-3054	Instituto Agronomico do Parana	Brazil
Boletin PROMECAFE	1010-1527	Instituto Interamericano de Cooperacion para la Agricultura (IICA)	Guatemala
Bolleti de la Societat d'Historia Natural de les Balears	0212-260X	Societat d'Historia Natural de les Balears (SHNB)	Spain
Bosque	0304-8799	Facultad de Ciencias Forestales, Universidad Australe de Chile	Chile
Brazilian Archives of Biology and Technology	1516-8913	Instituto De Tecnologia Do Parana (TECPAR)	Brazil
Brazilian Journal of Biology	1519-6984	Instituto Internacional de Ecologia	Brazil
Brazilian Journal of Microbiology	1517-8382	Sociedade Brasileira de Microbiologia	Brazil
Brazilian Journal of Plant Physiology	1677-0420	Universidade Estadual de Campinas (UNICAMP)	Brazil

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
British Sugar Beet Review	0007-1854	British Sugar plc	UK
Bryologist	0007-2745	American Bryological and Lichenological Society	USA
Buletinul Universitatii de Stiinte Agricole si Medicina Veterinara Cluj-Napoca. Seria Agricultura	1454-2382	University of Agricultural Sciences, Central Library (Exchanges)	Italy
Buletinul Universitatii de Stiinte Agricole si Medicina Veterinara Cluj-Napoca. Seria Agricultura si Horticultura	1454-2382	University of Agricultural Sciences, Central Library (Exchanges)	Italy
Buletinul Universitatii de Stiinte Agricole si Medicina Veterinara Cluj-Napoca. Seria Horticultura	1454-2382	University of Agricultural Sciences, Central Library (Exchanges)	Italy
Bulgarian Journal of Agricultural Science	1310-0351	National Centre for Agrarian Sciences in Bulgaria	Bulgaria
Bulletin - Society of Wetland Scientists	0732-9393	Society of Wetland Scientists	USA
Bulletin of Environmental Contamination and Toxicology	0007-4861	Springer-Verlag	USA
Bulletin of Faculty of Agriculture	0526-8613	Cairo University	Egypt
Bulletin of Hokkaido Prefectural Agricultural Experiment Stations	0441-0807	Hokkaido Central Agricultural Experiment Station	Japan
Bulletin of Indian Academy of Sericulture	0972-1657	Indian Academy of Sericulture	India
Bulletin of the Chugoku National Agricultural Experiment Station	0913-4239	Chugoku National Agricultural Experiment Station	Japan
Bulletin of the Geobotanical Institute ETH	1420-6803	Geobotanisches Institut ETH	Switzerland
Bulletin of the Gunma Agricultural Experiment Station	1341-2019	Gunma Agricultural Research Center	Japan
Bulletin of the Hiroshima Prefectural Agriculture Research Center	0918-4848	Hiroshima Prefectural Agricultural Research Center	Japan
Bulletin of the Hokuriku National Agricultural Experiment Station	0439-3600	Hokuriku National Agricultural Experiment Station	Japan
Bulletin of the Institute of Tropical Agriculture	0915-499X	Institute of Tropical Agriculture	Japan
Bulletin of the Nara Prefectural Agricultural Experiment Station	1345-6393	Nara Prefectural Agricultural Experiment Station	Japan
Bulletin of the National Agricultural Research Center	1347-3441	National Agricultural Research Organization	Japan
Bulletin of the National Agricultural Research Center for Tohoku Region	1347-3379	National Agricultural Research Center for Tohoku Region	Japan
Bulletin of the National Institute of Vegetable and Tea Science	1346-6984	National Institute of Vegetable and Tea Science (NIVTS)	Japan
Bulletin of the National Research Centre (Cairo)	1110-0591	National Information and Documentation Centre (NIDOC)	Egypt
Bulletin of the Rubber Research Institute of Sri Lanka	1391-0051	Rubber Research Institute of Sri Lanka	Sri Lanka
Bulletin of the Shikoku National Agricultural Experiment Station	0037-3702	Shikoku National Agricultural Experiment Station, Ministry of Agriculture	Japan
Bulletin of the Tokyo University Forests	0371-6007	Tokyo University Forests	Japan
Bulletin of the Utsunomiya University Forests	0286-8733	Utsunomiya University	Japan
Caatinga	0100-316X	Escola Superior de Agricultura de Mossoro, Ministerio da Educacao	Brazil
Cactus and Succulent Journal	0007-9367	Cactus & Succulent Society of America Inc	USA
Cahiers Agricultures	1166-7699	John Libbey Eurotext	France
Cahiers d’Economie et Sociologie Rurales	0755-9208	INRA Economie et Sociologie Rurales	France
Cahiers d’Etudes et de Recherches Francophones/Sante	1157-5999	John Libbey Eurotext	France
Cahiers Espaces	0992-3950	Editions Touristiques Europeennes	France
Cahiers Options Mediterraneennes	1022-1379	Centre International de Hautes Etudes Agronomiques Mediterraneennes	France
California Agriculture	0008-0845	Agriculture and Natural Resources, University of California	USA
Cana de Azucar	0798-2224	Fondo Nacional de Investigaciones Agropecuarias (FONAIAP)	Venezuela
Canadian Agricultural Engineering	0045-432X	Canadian Society for Engineering in Agriculture	Canada
Canadian Biosystems Engineering	1492-9058	Canadian Society for Engineering in Agriculture	Canada
Canadian Field-Naturalist	0008-3550	Ottawa Field-Naturalists’ Club	Canada
Canadian Geotechnical Journal	0008-3674	National Research Council of Canada	Canada
Canadian Journal of Agricultural Economics	0008-3976	Blackwell Publishing	USA
Canadian Journal of Botany	0008-4026	National Research Council of Canada	Canada

Canadian Journal of Development Studies	0225-5189	University of Ottawa	Canada
Canadian Journal of Fisheries and Aquatic Sciences	0706-652X	National Research Council of Canada	Canada
Canadian Journal of Forest Research	0045-5067	National Research Council of Canada	Canada
Canadian Journal of Microbiology	0008-4166	National Research Council of Canada	Canada
Canadian Journal of Plant Science	0008-4220	Agricultural Institute of Canada	Canada
Canadian Journal of Soil Science	0008-4271	Agricultural Institute of Canada	Canada
Canadian Water Resources Journal	0701-1784	Canadian Water Resources Association	Canada
Caryologia	0008-7114	Department of Plant Biology, University of Florence	Italy
Castanea	0008-7475	Southern Appalachian Botanical Society	USA
Catena	0341-8162	Elsevier	Netherlands
Central European Journal of Chemistry	1644-3624	Central European Science Journals	Poland
Centralblatt fur das Gesamte Forstwesen	0379-5292	Osterreichischer Agrarverlag, Druck- und Verlagsgesellschaft	Austria
Centro Agricola	0253-5785	Universidad Central ‘Marta Abreu’ de Las Villas	Cuba
Centro Azucar	0253-5757	Universidad Central ‘Marta Abreu’ de Las Villas	Cuba
Cercetari Agronomice in Moldova	0379-5837	Statiunile de Cercetari Agricole din Moldova	Romania
Cereal Research Communications	0133-3720	Cereal Research Non-Profit Company	Hungary
Champignon	0009-1308	Bund Deutscher Champignonzuchter e.V.	Germany
Chemical Speciation & Bioavailability	0954-2299	Science and Technology Letters	UK
Chemistry & Biodiversity	1612-1872	Verlag Helvetica Chimica Acta AG	Switzerland
Chemistry of Natural Compounds	0009-3130	Consultants Bureau	USA
Chemosphere	0045-6535	Elsevier	UK
Chile Forestal	0716-1190	Corporacion Nacional Forestal (CONAF)	Chile
China Cotton	1000-632x	Chinese Academy of Agricultural Sciences (CAAS), Scientech Documentation and Information Centre	China
China Environmental Science	1000-6923	China Environmental Science	China
China Fruits	1000-8047	Research Institute of Pomology	China
China Rice	1006-8082	China National Rice Research Institute (CNRRI)	China
China Tropical Medicine	1009-9727	Editorial Department of China Tropical Medicine	China
China Vegetables	1000-6346	Institute of Vegetables and Flowers	China
China’s Fibre Crops	1000-6338	Zhongguo Nongye Kexueyuan Malei Yanjiusuo	China
Chinese Forestry Science and Technology	1671-492X	Chinese Academy of Forestry, Institute of Scientific and Technological Information	China
Chinese Journal of Agrometeorology	1022-9779	Chinese Society of Agrometeorology	Taiwan
Chinese Journal of Applied and Environmental Biology	1006-687X	Science Press	China
Chinese Journal of Applied Ecology	1001-9332	Chinese Journal of Applied Ecology	China
Chinese Journal of Endemiology	1000-4955	Center for Endemic Disease Control, Chinese Center for Disease Control and Prevention	China
Chinese Journal of Information on Traditional Chinese Medicine	1005-5304	Chinese Journal of Information on Traditional Chinese Medicine	China
Chinese Journal of Oil Crop Sciences	1007-9084	Editorial Department of Chinese Journal of Oil Crop Sciences	China
Chinese Journal of Rice Science	1001-7216	China National Rice Research Institute (CNRRI)	China
Chinese Rural Economy	1002-8870	Institute of Rural Development, Chinese Academy of Social Sciences	China
Chromatographia	0009-5893	Friedr. Vieweg & Sohn Verlagsgesellschaft mbH	Germany
Ciencia Agricola	0103-8699	Universidade Federal de Alagoas, Centro de Ciencias Agrarias	Brazil
Ciencia del Suelo	0326-3169	Asociacion Argentina de la Ciencia del Suelo	Argentina
Ciencia e Agrotecnologia	1413-7054	Universidade Federal de Lavras	Brazil
Ciencia e Investigacion Agraria	0304-5609	Facultad de Agronomia e Ingenieria Forestal, Pontificia Universidad Catolica de Chile	Chile
Ciencia e Tecnica Vitivinicola	0254-0223	Estacao Vitivinicola Nacional	Portugal
Ciencia Florestal	0103-9954	IPA, Instituto Porto Alegre da Igreja Metodista	Portugal
Ciencia Forestal en Mexico	1405-3586	Instituto Nacional de Investigaciones Forestales, Agricolas y Pecuarias (INIFAP)	Mexico
Circular - Instituto Agronomico do Parana	0100-3356	Instituto Agronomico do Parana	Brazil
Circular Tecnica - Centro Nacional de Pesquisa de Algodao	0100-6460	Embrapa Algodao	Brazil
Circular Tecnica - Embrapa Agropecuaria Oeste	1517-4557	Embrapa Agropecuaria Oeste	Brazil
Circular Tecnica - Embrapa Cerrados	1517-0187	Embrapa Cerrados	Brazil
Circular Tecnica - Embrapa Meio-Norte	0104-7633	Embrapa Meio-Norte	Brazil
Circular Tecnica - Embrapa Milho e Sorgo	1518-4269	Embrapa Milho e Sorgo	Brazil

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Circular Tecnica da Embrapa Semi-Arido	1516-1617	Embrapa Semi-Arido	Brazil
Circular Tenica - Embrapa Mandioca e Fruticultura	1516-5612	Embrapa Mandioca e Fruticultura	Brazil
Clays and Clay Minerals	0009-8604	Clay Minerals Society	USA
Climate Research	0936-577x	Inter-Research	Germany
Climatic Change	0165-0009	Springer Science + Business Media	Netherlands
Colture Protette	0390-0444	Gruppo Calderini Edagricole Srl	Italy
Communications in Agricultural and Applied Biological Sciences	1379-1176	Faculteit Landbouwkundige en Toegepaste Biologische Wetenschappen	Belgium
Communications in Soil Science and Plant Analysis	0010-3624	Taylor & Francis	USA
Compost Science & Utilization	1065-657X	J G Press Inc	USA
Comptes Rendus Biologies	1631-0691	Elsevier SAS	France
Comptes Rendus de l'Academie d'Agriculture de France	0989-6988	Academie d'Agriculture de France	France
Computers & Geosciences	0098-3004	Elsevier	UK
Computers and Electronics in Agriculture	0168-1699	Elsevier	Netherlands
Comunicado Tecnico - EMBRAPA Agropecuaria Oeste	1516-8441	Embrapa Agropecuaria Oeste	Brazil
Comunicado Tecnico da Embrapa Semi-Arido	1516-1609	Embrapa Semi-Arido	Brazil
Conservation Biology	0888-8892	Blackwell Publishing	USA
Conservation Ecology	1195-5449	Resilience Alliance	Canada
Conservation in Practice	1539-6827	Society for Conservation Biology	USA
Conservation Science Western Australia	1447-3682	Department of Conservation and Land Management, Western Australia	Australia
Contemporary Economic Policy	0735-0007	Oxford University Press	UK
Continental Shelf Research	0278-4343	Pergamon Press	UK
CORBANA	1409-0031	Corporacion Bananera Nacional (CORBANA)	Costa Rica
Cotton Science	1002-7807	Chinese Academy of Agricultural Sciences (CAAS), Scientech Documentation and Information Centre	China
Critical Reviews in Environmental Science and Technology	1064-3389	Taylor & Francis	USA
Critical Reviews in Plant Sciences	0735-2689	Taylor & Francis	UK
Croatian Medical Journal	0353-9504	Pabst Science Publishers	Germany
Crop Management	1543-7833	Plant Management Network	USA
Crop Protection	0261-2194	Elsevier	UK
Crop Research (Hisar)	0970-4884	Agricultural Research Information Centre	India
Crop Science	0011-183X	Crop Science Society of America	USA
Cruciferae Newsletter	0263-9459	UMR Amelioration des plantes et biotechnologies vegetales - INRA-ENSAR	France
Crustaceana	0011-216X	Brill Academic Publishers	Netherlands
CTBA Info	0296-8541	Centre Technique du Bois et de l'Ameublement (CTBA)	France
Cuban Journal of Agricultural Science	0864-0408	Instituto de Ciencia Animal of the Universidad Agraria de la Habana	Cuba
Cultura Agronomica	0104-1010	Faculdade de Engenharia, UNESP	Brazil
Current Agriculture	0254-1092	Indian Society of Salinity Research Scientists	India
Current Microbiology	0343-8651	Springer-Verlag	USA
Current Nematology	0971-0116	Bioved Research Society	India
Current Opinion in Biotechnology	0958-1669	Current Biology Ltd	UK
Current Opinion in Microbiology	1369-5274	Elsevier	UK
Current Research - University of Agricultural Sciences (Bangalore)	0253-7133	Communications Centre	India
Current Science	0011-3891	Indian Academy of Sciences	India
Currents (Uppsala)	1403-6304	Swedish University of Agricultural Sciences, Research Information Centre	Sweden
Cytobios	0011-4529	Faculty Press	UK
Cytologia	0011-4545	International Society of Cytology	Japan
Debate Agrario (Lima)	1017-9011	Centro Peruano de Estudios Sociales (CEPES)	Peru
Deciduous Fruit Grower	0302-7074	Deciduous Fruit Producers Trust	South Africa
Dendrochronologia	1125-7865	Elsevier GmbH	Germany
Dendronatura		Associazione Forestale del Trentino	Italy

Derevoobrabatyvayushchaya Promyshlennost’	0011-9008	Derevoobrabatyvayushchaya Promyshlennost’	Russia
Diversity and Distributions	1366-9516	Blackwell Publishing	UK
Documentos - Embrapa Cerrados	1517-5111	Embrapa Cerrados	Brazil
Documentos - Embrapa Meio-Norte	0104-866X	Embrapa Meio-Norte	Brazil
Documentos - Embrapa Soja	1516-781X	Embrapa Centro Nacional de Pesquisa de Soja	Brazil
Documentos - Embrapa Solos	1517-2627	Embrapa Solos	Brazil
Documentos - Emprapa Informatica Agropecuaria	1518-3602	Centro Nacional de Pesquisa Tecnologica em Informatica para a Agricultura	Brazil
Documentos da Embrapa Semi-Arido	1516-1633	Embrapa Semi-Arido	Brazil
Drewno	1644-3985	Instytut Technologii Drewna	Poland
DST - Dansk Skovbrugs Tidsskrift	0905-295X	Dansk Skovforening Sekretariat	Denmark
Earth Surface Processes and Landforms	0197-9337	John Wiley & Sons	UK
Ecletica Quimica	0100-4670	Universidade Estadual Paulista	Brazil
Ecography	0906-7590	Blackwell Publishing	Denmark
Ecologia (Madrid)	0214-0896	O. A. Parques Nacionales	Spain
Ecologia Austral	0327-5477	Asociacion Argentina de Ecologia	Argentina
Ecologia en Bolivia	1605-2528	Instituto de Ecologia, Universidad Mayor de San Andres	Bolivia
Ecological Applications	1051-0761	Ecological Society of America	USA
Ecological Economics	0921-8009	Elsevier	UK
Ecological Engineering	0925-8574	Elsevier	UK
Ecological Management & Restoration	1442-7001	Blackwell Publishing	Australia
Ecological Modelling	0304-3800	Elsevier	Netherlands
Ecological Monographs	0012-9615	Ecological Society of America	USA
Ecological Research	0912-3814	Springer-Verlag Tokyo	Japan
Ecologie	1259-5314	Societe Francaise d’Ecologie	France
Ecology	0012-9658	Ecological Society of America	USA
Ecology and Future - Bulgarian Journal of Ecological Science	1312-076x	Association Ecological Alliance	Bulgaria
Ecology and Future - Journal of Agricultural Science and Forest Science	1312-0751	Association Ecological Alliance	Bulgaria
Ecology Letters	1461-023X	Blackwell Publishing	UK
Ecology of Freshwater Fish	0906-6691	Blackwell Publishing	Denmark
Ecoscience	0028-0798	Universite Laval	Canada
Ecossistema	0100-4107	Curso de Engenharia Agronomica Manoel Carlos Goncalves	Brazil
Ecosystem Health	1076-2825	Blackwell Publishing	USA
Ecosystems	1432-9840	Springer-Verlag	USA
Ecotoxicology	0963-9292	Springer Science + Business Media	Netherlands
Ecotoxicology and Environmental Safety	0147-6513	Elsevier Inc.	USA
Ecotropica	0949-3026	Society for Tropical Ecology	Germany
Edafologia	1135-6863	Sociedad Española de la Ciencia del Suelo	Spain
Ege Universitesi Ziraat Fakultesi Dergisi	1018-8851	Ege Universitesi Ziraat Fakultesi Dekanligi	Turkey
Egyptian Journal of Agricultural Research	1110-6336	Agricultural Research Centre, Ministry of Agriculture and Land Reclamation	Egypt
Egyptian Journal of Agronomy	0379-3575	National Information and Documentation Centre (NIDOC)	Egypt
Egyptian Journal of Biology	1110-6859	Egyptian British Biological Society	Egypt
Egyptian Journal of Biophysics and Biomedical Engineering	1110-8525	National Information and Documentation Centre (NIDOC)	Egypt
Egyptian Journal of Botany	0375-9237	National Information and Documentation Centre (NIDOC)	Egypt
Egyptian Journal of Chemistry	0449-2285	National Information and Documentation Centre (NIDOC)	Egypt
Egyptian Journal of Horticulture	1110-0206	National Information and Documentation Centre (NIDOC)	Egypt
Egyptian Journal of Microbiology	0022-2704	National Information and Documentation Centre (NIDOC)	Egypt
Egyptian Journal of Soil Science	0302-6701	National Information and Documentation Centre (NIDOC)	Egypt
Ekologia (Bratislava)	1335-342X	SAP - Slovak Academic Press Ltd	Slovakia
Ekoloji	1300 -1361	Cevre Koruma ve Arastirma Vakfi	Turkey
Electronic Journal of Polish Agricultural Universities	1505-0297	Wydawnictwo Akademii Rolniczej we Wroclawiu	Poland
Electrophoresis	0173-0835	WILEY-VCH Verlag GMBH & Co. KGaA	Germany
Emerging Infectious Diseases	1080-6040	National Center for Infectious Diseases, Centers for Disease Control and Prevention	Egypt

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Emirates Journal of Agricultural Sciences	1021-1357	College of Food Systems, UAE University	UAE
Encarte Tenico - Informacoes Agronomicas	1000-3711	Associacao Brasileira para Pesquisa da Potassa e do Fosfato (POTAFOS)	Brazil
Energia na Agricultura	0102-9169	Faculdade de Ciencias, Agrono-circumflex-micas, Universidade Estadual Paulista (UNESP)	Brazil
Energy (Oxford)	0360-5442	Elsevier	UK
Energy Conversion and Management	0196-8904	Elsevier	UK
Engenharia Agricola	1808-4389	Sociedade Brasileira de Engenharia Agricola (SBEA)	Brazil
Entomologia Generalis	0171-8177	E. Schweizerbart'sche Verlagsbuchhandlung	Germany
Entomologia y Vectores	0328-0381	Editora Gama Filho	Brazil
Entomological News	0013-872X	American Entomological Society at the Academy of Natural Sciences	USA
Entwicklung + Landlicher Raum	0343-6462	DLG-Verlag	Germany
Environment (Washington)	0013-9157	Heldref Publications	USA
Environment and Ecology	0970-0420	MKK Publication	India
Environment and History	0967-3407	White Horse Press	UK
Environment Control in Biology	0582-4087	Japanese Society of Environment Control in Biology	Japan
Environment International	0160-4120	Elsevier	UK
Environment Development and Sustainability	1387-585X	Springer Science + Business Media	Netherlands
Environmental & Waste Management	1460-5147	EPP Publications	UK
Environmental and Experimental Botany	0098-8472	Elsevier	Netherlands
Environmental and Resource Economics	0924-6460	Springer Science + Business Media	Netherlands
Environmental Conservation	0376-8929	Cambridge University Press	UK
Environmental Economics and Policy Studies	1432-847X	Springer-Verlag Tokyo	Japan
Environmental Engineering Science	1092-8758	Mary Ann Liebert	USA
Environmental Entomology	0046-225X	Entomological Society of America	USA
Environmental Forensics	1527-5922	Taylor & Francis	USA
Environmental Geochemistry and Health	0269-4042	Kluwer Academic Publishers	Netherlands
Environmental Geology	0943-0105	Springer-Verlag GmbH	Germany
Environmental Hazards	1464-2867	Elsevier Ltd	Netherlands
Environmental Health Perspectives	0091-6765	Public Health Service, U.S. Department of Health and Human Services	USA
Environmental Management	0364-152X	Springer-Verlag	USA
Environmental Management and Health	0956-6163	MCB University Press Ltd	UK
Environmental Microbiology	1462-2912	Blackwell Publishing	UK
Environmental Modeling & Assessment	1420-2026	Kluwer Academic Publishers	Netherlands
Environmental Monitoring and Assessment	0167-6369	Springer Science + Business Media	Netherlands
Environmental Pollution	0269-7491	Elsevier	UK
Environmental Research	0013-9351	Academic Press	USA
Environmental Reviews	1181-8700	National Research Council of Canada	Canada
Environmental Science & Technology	0013-936X	American Chemical Society	USA
Environmental Science and Pollution Research	0944-1344	Ecomed Publishers	Germany
Environmental Technology	0959-3330	Selper Ltd	UK
Environmental Toxicology	1520-4081	John Wiley and Sons	USA
Environmental Toxicology and Chemistry	0730-7268	Society of Environmental Toxicology and Chemistry (SETAC)	USA
Environmentalist	0251-1088	Springer Science + Business Media	Netherlands
Environmetrics	1180-4009	John Wiley & Sons	UK
Enzyme and Microbial Technology	0141-0229	Elsevier	USA
Episodes	0705-3797	International Union of Geological Sciences (IUGS)	Austria
ERD Working Paper Series - Economics and Research Department	1655-5252	Asian Development Bank	Philippines
Eurasian Journal of Forest Research	1345-8221	Hokkaido University Forests	Japan
European Environment	0961-0405	John Wiley & Sons	UK
European Journal of Agronomy	1161-0301	Elsevier	Netherlands
European Journal of Forest Research	1612-4669	Springer-Verlag GmbH	Germany
European Journal of Horticultural Science	1611-4434	Verlag Eugen Ulmer GmbH	Germany

European Journal of Phycology	0967-0262	Taylor & Francis	UK
European Journal of Protistology	0932-4739	Elsevier GmbH	Germany
European Journal of Soil Biology	1164-5563	Elsevier SAS	France
European Journal of Soil Science	1351-0754	Blackwell Publishing	UK
European Review of Agricultural Economics	0165-1587	Oxford University Press	UK
Evolutionary Ecology Research	1522-0613	Evolutionary Ecology Ltd	USA
Experimental Agriculture	0014-4797	Cambridge University Press	UK
Experimental and Applied Acarology	0168-8162	Springer Science + Business Media	Netherlands
Fagopyrum	0352-3032	Plant Germ-plasm Institute, Graduate School of Agriculture	Italy
FAO Agricultural Policy and Economic Development Series	1020-6531	Food and Agriculture Organization of the United Nations (FAO)	Italy
FAO Irrigation and Drainage Paper	0254-5284	Food and Agriculture Organization of the United Nations (FAO)	Italy
FAO Land and Water Bulletin	1024-6703	Food and Agriculture Organization of the United Nations (FAO)	Italy
FAO Plant Production and Protection Paper	0259-2517	Food and Agriculture Organization of the United Nations (FAO)	Italy
FAO Soils Bulletin	0253-2050	Food and Agriculture Organization of the United Nations (FAO)	Italy
Feedstuffs	0014-9624	Miller Publishing Co	USA
FEMS Microbiology Ecology	0168-6496	Elsevier	Netherlands
FEMS Microbiology Letters	0378-1097	Elsevier	Netherlands
FEMS Microbiology Reviews	0168-6445	Elsevier	Netherlands
Fennia	0015-0010	Geographical Society of Finland	Finland
Fertiliser Marketing News	0257-8034	Fertiliser Association of India	India
Fertiliser News	0015-0266	Fertiliser Association of India	India
Field Crops Research	0378-4290	Elsevier	Netherlands
Flora (Jena)	0367-2530	Elsevier GmbH	Germany
Flora and Fauna (Jhansi)	0971-6920	Flora and Fauna	India
Floresta	0015-3826	Fundacao de Pesquisas Florestais do Parana (FUPEF)	Brazil
Floresta e Ambiente	1415-0980	Instituto de Florestas, Universidade Federal Rural do Rio de Janeiro	Brazil
Folia Forestalia Polonica. Seria A	0071-6677	Instytut Badawczy Lesnictwa (Forest Research Institute)	Poland
Folia Geobotanica	1211-9520	Institute of Botany, Academy of Sciences of the Czech Republic	Czechoslovakia
Folia Horticulturae	0867-1761	Polskie Towarzystwo Nauk Ogrodniczych (Polish Society for Horticultural Science)	Poland
Folia Microbiologica	0015-5632	Institute of Microbiology, Academy of Sciences of the Czech Republic	Czechoslovakia
Folia Universitatis Agriculturae Stetinensis	1506-1973	Wydawnictwo Akademii Rolniczej	Poland
Folia Universitatis Agriculturae Stetinensis	1506-1965	Wydawnictwo Akademii Rolniczej	Poland
Forest & Landscape Research - Forskningscentret for Skov & Landskab	1601-6734	Danish Centre for Forest, Landscape and Planning	Denmark
Forest Ecology and Management	0378-1127	Elsevier	Netherlands
Forest Policy and Economics	1389-9341	Elsevier	Netherlands
Forest Research Information Paper - Ontario Forest Research Institute	0319-9118	Ontario Forest Research Institute	Canada
Forest Research Report - Ontario Forest Research Institute	0381-3924	Ontario Forest Research Institute	Canada
Forest Research	1001-1498	Chinese Academy of Forestry	China
Forest Research	1344-4174	Kyoto University Forests	Japan
Forest Science	0015-749X	Society of American Foresters	USA
Forest Snow and Landscape Research	1424-5108	Paul Haupt Verlag	Switzerland
Forestry & British Timber	0308-7638	United Business Media	UK
Forestry (Oxford)	0015-752X	Oxford University Press	UK
Forestry Chronicle	0015-7546	Canadian Institute of Forestry	Canada
Forestry Commission Bulletin	0950-6470	Forestry Commission	UK
Forestry Studies in China	1008-1321	Beijing Forestry University	China
Forests	1472-8028	AB Academic Publishers	UK
Foret Privee	0153-0216	La Foret Privee	France
Foret-Entreprise	0752-5974	Institut pour le Developpement Forestier	France
Forschungsberichte - Hessen-Forst Forsteinrichtung	1436-2910	Versuchswesen	Germany
Forst und Holz	0932-9315	Verlag M. & H. Schaper	Germany
Forstarchiv	0300-4112	Verlag M. & H. Schaper	Germany

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Forstliche Forschungsberichte Munchen	0174-1810	Wissenschaftszentrum Weihenstephan fur Ernahrung, Landnutzung und Umwelt der Technischen Universitat Munchen und Bayerische Landesanstalt fur Wald und Forstwirtschaft	Germany
Forstwissenschaftliches Centralblatt	0015-8003	Springer-Verlag GmbH	Germany
Fourrages	0429-2766	Association Francaise pour la Production Fourragere, I.N.R.A.	France
Fragmenta Faunistica	0015-9301	Muzeum i Instytut Zoologii Polskiej Akademii Nauk	Poland
Fresenius Environmental Bulletin	1018-4619	Lehrstuhl fur Chemisch-Technische Analyse, Technische Universitat Munchen	Germany
Fresenius' Journal of Analytical Chemistry	0937-0633	Springer-Verlag GmbH	Germany
Freshwater Biology	0046-5070	Blackwell Publishing	UK
Fujian Journal of Agricultural Sciences	1000-0384	Fujian Academy of Agricultural Science	China
Functional Ecology	0269-8463	Blackwell Publishing	UK
Functional Plant Biology	1445-4408	CSIRO Publishing	Australia
Futuribles	0337-307x	Association Internationale Futuribles	France
GAIA	0940-5550	Okom Verlag	Germany
Gartenbauwissenschaft	0016-478X	Verlag Eugen Ulmer GmbH	Germany
Gatekeeper Series - Sustainable Agriculture and Rural Livelihoods Programme	1357-9258	International Institute for Environment and Development (IIED)	UK
Gayana Botanica	0016-5301	Ediciones Universidad de Concepcion	Chile
Gemuse (Munchen)	0016-6286	BLV Verlagsgesellschaft mbH	Germany
General and Comparative Endocrinology	0016-6480	Elsevier Inc.	USA
Geochemical Journal	0016-7002	The Geochemical Society of Japan	Japan
Geoderma	0016-7061	Elsevier	Netherlands
Geoforum	0016-7185	Elsevier	UK
Geographie Physique et Quaternaire	0705-7199	Presses de l'Universite de Montreal	Canada
GeoJournal	0343-2521	Springer Science + Business Media	Netherlands
Geomicrobiology Journal	0149-0451	Taylor & Francis	USA
Georgica	1132-810X	Escuela Universitaria Politecnica de Huesca, Universidad de Zaragoza	Spain
Georgofili	0367-4134	Accademia dei Georgofili	Italy
Geothermics	0375-6505	Elsevier	UK
Gesunde Pflanzen	0367-4223	Springer-Verlag GmbH	Germany
Gewasbescherming	0166-6495	Koninklijke Nederlandse Planteziektenkundige Vereniging	Netherlands
Ghana Journal of Agricultural Science	0855-0042	Council for Scientific and Industrial Research	Ghana
Glasnik za Sumske Pokuse	0352-3861	Sveucilista u Zagrebu, Sumarski Fakultet (Faculty of Forestry	Croatia
Global and Planetary Change	0921-8181	Elsevier	Netherlands
Global Biogeochemical Cycles	0886-6236	American Geophysical Union	USA
Global Change Biology	1354-1013	Blackwell Publishing	UK
Global Change Biology	1460-7212	Blackwell Publishing	UK
Global Ecology and Biogeography	1466-822X	Blackwell Publishing	UK
Global Environmental Change	0959-3780	Elsevier	UK
Global Journal of Environmental Sciences	1596-6194	Bachudo Science Co. Ltd.	Nigeria
Global Journal of Pure and Applied Sciences	1118-0579	Bachudo Science Co. Ltd.	Nigeria
Gortania	0391-5859	Museo Friulano di Storia Naturale	Italy
Gorteria	0017-2294	Nationaal Herbarium Nederland	Netherlands
Gozdarski Vestnik	0017-2723	Zveza Gozdarskih Drustev Slovenije	Slovenia
Grana	0017-3134	Taylor & Francis	Norway
Grass and Forage Science	0142-5242	Blackwell Publishing	UK
Grassland of China	1011-6311	Editorial Department of Grassland of China	China
Grassland Science	0447-5933	Blackwell Publishing	Australia
Green Chemistry	1463-9262	Royal Society of Chemistry	UK
Gron Viden	1397-985x	Danmarks JordbrugsForskning	Denmark
Ground Water	0017-467X	Blackwell Publishing	USA
Ground Water Monitoring and Remediation	1069-3629	Blackwell Publishing	USA
Grundwasser	1430-483X	Springer-Verlag GmbH	Germany

Gujarat Agricultural University Research Journal	0250-5193	Gujarat Agricultural University	India
Hacettepe Journal of Biology and Chemistry	1303-5002	Elsevier	Turkey
Hacquetia	1581-4661	Institute of Biology, Scientific Research Center of the Slovenian Academy of Sciences and Arts	Slovania
Hamdard Medicus	0250-7188	Bait al-Hikmah	Pakistan
Harmful Algae	1568-9883	Elsevier	Netherlands
Haryana Agricultural University Journal of Research	0379-4008	CCS Haryana Agricultural University	India
Haryana Journal of Agronomy	0970-5414	Haryana Agronomists Association	India
Haryana Journal of Horticultural Sciences	0970-2876	Horticultural Society of Haryana	India
Helia	1018-1806	Institute of Field and Vegetable Crops, Oil Crops Department	Hungary
Hemijska Industrija	0367-598X	Savez Hemicara i Tehnologa Jugoslavije (SHTJ)	Serbia
Herba Polonica	0018-0599	Instytut Roslin i Przetworow Zielarskich	Poland
Herbologia	1512-6714	Weed Science Society of Bosnia and Herzegovina	Bosnia-Hercegovina
Hercynia	0018-0637	Martin-Luther-Universitat Halle Wittenberg	Germany
Higiene Alimentar	0101-9171	Faculdade de Medicina Veterinaria e Zootecnia, Universidade de Sao Paulo	Brazil
Himachal Journal of Agricultural Research	0970-0595	Himachal Pradesh Krishi Vishvavidyalaya (HPKV)	India
Historia Agraria	1139-1472	Seminario de Historia Agraria (SEHA)	Spain
Hmeljarski Bilten	0350-0756	Institut za Hmeljarstvo in Pivovarstvo	Slovenia
Holocene	0959-6836	Arnold	UK
Holzforschung	0018-3830	Walter de Gruyter	Germany
Holzzucht	0437-7158	Forschungsinstitut fur schnellwachsende Baumarten	Germany
Horticultura Argentina	0327-3431	Asociacion Argentina de Horticultura	Argentina
Horticultura Brasileira	0102-0536	Sociedade de Olericultura do Brasil, UNESP - FCA	Brazil
Horticultural Journal	0972-8538	Society for Advancement of Horticulture	India
Horticultural Research (Japan)	1347-2658	Yokendo Ltd.	Publishers
Horticultural Reviews	0163-7851	John Wiley and Sons	Inc
HortScience	0018-5345	American Society for Horticultural Science	USA
HortTechnology	1063-0198	American Society for Horticultural Science	USA
Hrvatske Vode	1330-1144	Hrvatske Vode	Croatia
Hrvatski Geografski Glasnik	1331-5854	Hrvatsko Geografsko Drustvo (Croatian Geographical Society)	Croatia
Hydro International	1385-4569	GITC bv	Netherlands
Hydrobiologia	0018-8158	Springer Science + Business Media	Netherlands
Hydrological Processes	0885-6087	John Wiley & Sons	UK
Hydrological Sciences Journal	0262-6667	IAHS Press	UK
IAWA Journal	0928-1541	International Association of Wood Anatomists (IAWA)	Netherlands
Ibis (London)	0019-1019	Blackwell Publishing	UK
ICARDA Caravan	1025-0972	International Center for Agricultural Research in the Dry Areas (ICARDA)	Syria
ICES Journal of Marine Science	1054-3139	Elsevier Ltd	UK
IDESIA	0073-4675	Facultad de Agronomia, Universidad de Tarapaca	Chile
IDS Bulletin	0265-5012	Institute of Development Studies, University of Sussex	UK
IGER Innovations	1368-5503	IGER, Institute of Grassland and Environmental Research	UK
Igiene Moderna	0019-1655	E.J.E. Publisher s.r.l.	Italy
Iheringia - Serie Botanica	0073-4705	Museu de Ciencias Naturais	Brazil
IK Notes		World Bank	USA
Impact Assessment and Project Appraisal	1461-5517	Beech Tree Publishing	UK
Indian Agriculturist	0019-4336	Agricultural Society of India	India
Indian Coconut Journal	0970-0579	Coconut Development Board	India
Indian Coffee	0019-4549	Coffee Board	India
Indian Dairyman	0019-4603	Indian Dairy Association	India
Indian Forester	0019-4816	Indian Forester	India
Indian Journal of Agricultural Biochemistry	0970-6399	Indian Society of Agricultural Biochemists	India
Indian Journal of Agricultural Economics	0019-5014	Indian Society of Agricultural Economics	India
Indian Journal of Agricultural Research	0367-8245	Agricultural Research Communication Centre	India
Indian Journal of Agricultural Sciences	0019-5022	Indian Council of Agricultural Research	India
Indian Journal of Agroforestry	0972-0715	Indian Society of Agroforestry, National Research Centre for Agroforestry	India
Indian Journal of Agronomy	0537-197X	Indian Society of Agronomy	India

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Indian Journal of Animal Sciences	0367-8318	Indian Council of Agricultural Research	India
Indian Journal of Arecanut - Spices and Medicinal Plants	0972-2483	Directorate of Arecanut & Spices Development	India
Indian Journal of Dryland Agricultural Research and Development	0971-2062	Central Research Institute for Dryland Agriculture	India
Indian Journal of Ecology	0304-5250	Indian Ecological Society, College of Agriculture	India
Indian Journal of Environment and Toxicology	0971-2127	Jai Research Foundation	India
Indian Journal of Forestry	0971-9431	M/S Bishen Singh Mahendra Pal Singh	India
Indian Journal of Hill Farming	0970-6429	Indian Association of Hill Farming	India
Indian Journal of Horticulture	0019-5251	Horticultural Society of India	India
Indian Journal of Microbiology	0046-8991	Association of Microbiologists of India	India
Indian Journal of Nematology	0303-6960	Nematological Society of India	India
Indian Journal of Plant Physiology	0019-5502	Indian Society for Plant Physiology	India
Indian Journal of Pulses Research	0970-6380	Indian Society of Pulses Research and Development	India
Indian Journal of Regional Science	0046-9017	Regional Science Association India	India
Indian Journal of Sericulture	0445-7722	Central Sericultural Research and Training Institute, Central Silk Board	India
Indian Journal of Soil Conservation	0970-3349	Indian Association of Soil & Water Conservationists	India
Indian Journal of Sugarcane Technology	0970-3233	Association of Sugarcane Technologists of India	India
Indian Journal of Weed Science	0253-8040	Indian Society of Weed Science	India
Indian Sugar	0019-6428	Indian Sugar Mills Association	India
Indonesian Journal of Agricultural Science	1411-982X	Agency for Agricultural Research and Development	Indonesia
Indonesian Journal of Crop Science	0216-8170	Agency for Agricultural Research and Development	Indonesia
Indus Journal of Biological Sciences	1811-1505	Indus Scientific Publications	Pakistan
Indus Journal of Plant Sciences	1682-0371	Indus Scientific Publications	Pakistan
Industria Saccarifera Italiana	0019-7734	Associazione Nazionale fra i Tecnici dello Zucchero e dell'Alcole	Italy
Industrial Crops and Products	0926-6690	Elsevier	UK
Industry and Environment	0378-9993	United Nations Environment Programme	France
Informationsblatt Forschungsbereich Wald	1424-5701	Eidgenossische Forschungsanstalt fur Wald, Schnee und Landschaft	Switzerland
Informatore Agrario	0020-0689	Edizioni l'Informatore Agrario Srl	Italy
Informatore Agrario Supplemento	0020-0689	Edizioni l'Informatore Agrario Srl	Italy
Informatore Fitopatologico	0020-0735	Gruppo Calderini Edagricole Srl	Italy
Informe Agropecuario	0100-3364	Empresa de Pesquisa Agropecuaria de Minas Gerais	Brazil
Infos-Ctifl	0758-5373	Centre Technique Interprofessionnel des Fruits et Legumes	France
Ingenieria Hidraulica en Mexico	0186-4076	Ingenieria Hidraulica en Mexico	Mexico
Interciencia	0378-1844	Asociacion Interciencia	Venezuela
International Agricultural Engineering Journal	0858-2114	Asian Association for Agricultural Engineering	Thailand
International Agrophysics	0236-8722	Institute of Agrophysics, Polish Academy of Sciences	Poland
International Arachis Newsletter	1010-5824	International Crops Research Institute for the Semi-Arid Tropics (ICRISAT)	India
International Biodeterioration & Biodegradation	0964-8305	Elsevier	UK
International Chickpea and Pigeonpea Newsletter	1023-4861	International Crops Research Institute for the Semi-Arid Tropics (ICRISAT)	India
International Forestry Review	1465-5489	Commonwealth Forestry Association	UK
International Journal of Agricultural Resources - Governance and Ecology	1462-4605	Inderscience Enterprises Ltd	Switzerland
International Journal of Agriculture and Biology	1560-8530	Friends Science Publishers	Pakistan
International Journal of Agriculture and Rural Development	1595-9716	School of Agriculture and Agricultural Technology, Federal University of Technology	Nigeria
International Journal of Applied Earth Observation and Geoinformation	0303-2434	Elsevier	Netherlands
International Journal of Biology and Biotechnology	1810-2719	Z-A Scientific Publisher	Pakistan
International Journal of Biometeorology	0020-7128	Springer-Verlag GmbH	Germany
International Journal of Chemical Sciences	0972-768X	Sadguru Publications	India
International Journal of Climatology	0899-8418	John Wiley & Sons	UK
International Journal of Ecohydrology & Hydrobiology	1642-3593	International Centre of Ecology, Polish Academy of Sciences	Poland
International Journal of Environment and Pollution	0957-4352	Inderscience Enterprises Ltd	Switzerland

International Journal of Environmental Analytical Chemistry	0306-7319	Taylor & Francis	UK
International Journal of Environmental Health Research	0960-3123	Taylor & Francis	UK
International Journal of Environmental Technology and Management	1466-2132	Inderscience Enterprises Ltd	Switzerland
International Journal of Food Microbiology	0168-1605	Elsevier	Netherlands
International Journal of Forest Engineering	0843-5243	Faculty of Forestry & Environmental Management, University of New Brunswick	USA
International Journal of Forest Usufructs Management	0972-3927	Centre of Minor Forest Products (COMFORPTS)	India
International Journal of Geomechanics	1532-3641	American Society of Civil Engineers	USA
International Journal of Global Energy Issues	0954-7118	Inderscience Enterprises Ltd	Switzerland
International Journal of Global Environmental Issues	1466-6650	Inderscience Enterprises Ltd	Switzerland
International Journal of Horticultural Science	1585-0404	AGROINFORM Publishing House	Hungary
International Journal of Nematology	1368-8774	Afro-Asian Society of Nematologists	UK
International Journal of Phytoremediation	1522-6514	Taylor & Francis	USA
International Journal of Plant Sciences	1058-5893	University of Chicago Press	USA
International Journal of Remote Sensing	0143-1161	Taylor & Francis	UK
International Journal of Sustainable Development	0960-1406	Inderscience Enterprises Ltd	Switzerland
International Journal of Sustainable Development and World Ecology	1350-4509	Sapiens Publishing	UK
International Journal of Technology Management & Sustainable Development	1474-2748	Intellect Books	UK
International Journal of Tropical Agriculture	0254-8755	Vidya International Publishers	India
International Journal of Water	1465-6620	Inderscience Enterprises Ltd	Switzerland
International Journal of Water Resources Development	0790-0627	Routledge	UK
International Journal of Wilderness	1086-5519	WILD Foundation	USA
International Journal of Wildland Fire	1049-8001	CSIRO Publishing	Australia
International Review for Environmental Strategies	1345-7594	Institute for Global Environmental Strategies	Japan
International Review of Hydrobiology	1434-2944	Wiley-VCH Verlag	USA
International Rice Commission Newsletter	0538-9550	Food and Agriculture Organization of the United Nations (FAO)	Italy
International Rice Research Notes	0117-4185	International Rice Research Institute (IRRI)	Philippines
International Sorghum and Millets Newsletter	1023-487X	Sorghum Improvement Conference of North America	USA
International Sugar Journal	0020-8841	Agra Europe (London) Ltd	UK
International Turfgrass Bulletin	1362-9255	Sports Turf Research Institute	UK
International Water & Irrigation	0334-5807	International Water and Irrigation	Israel
Investigacion Agraria - Produccion y Proteccion Vegetales	0213-5000	Instituto Nacional de Investigacion y Tecnologia Agraria y Alimentaria (INIA)	Spain
Investigacion Agraria - Sistemas y Recursos Forestales	1131-7965	Instituto Nacional de Investigacion y Tecnologia Agraria y Alimentaria (INIA)	Spain
InVet - Investigacion Veterinaria	1514-6634	Ciencia Veterinaria Editora S.R.L	Argentina
Inzynieria Rolnicza	1429-7264	Neilson Publishing Ltd.	New Zealand
IPI-Research Topics		International Potash Institute (IPI)	Switzerland
Iranian Journal of Agricultural Sciences	1017-5652	Faculty of Agriculture, University of Tehran	Iran
Iranian Journal of Forest and Poplar Research	1735-0883	Research Institute of Forests and Rangelands	Iran
Iranian Journal of Natural Resources	1025-1316	Faculty of Natural Resources, University of Tehran	Iran
Iranian Journal of Range and Desert Research	1735-0875	Research Institute of Forests and Rangelands	Iran
Iranian Journal of Soil and Water Sciences	1735-1979	Soil & Water Research Institute	Iran
Irish Forestry	0021-1192	Society of Irish Foresters	Irish Republic
Irish Grassland Association Journal	0322-0588	Irish Grassland Association	Irish Republic
IRRIGA	1413-7895	Faculdade de Ciencias Agronomicas, Universidade Estadual Paulista	Poland
Irrigation and Drainage	1531-0353	John Wiley & Sons Ltd	UK
Irrigation and Drainage Systems	0168-6291	Springer Science + Business Media	Netherlands
Irrigation Science	0342-7188	Springer-Verlag GmbH	Germany
Irrigazione e Drenaggio	0394-9338	Gruppo Calderini Edagricole Srl	Italy
Isotopes in Environmental and Health Studies	1025-6016	Harwood Academic Publishers	UK
Israel Journal of Chemistry	0021-2148	Science From Israel	Israel
Israel Journal of Earth Sciences	0021-2164	Laser Pages Publishing	Israel
Israel Journal of Plant Sciences	0792-9978	Laser Pages Publishing	Israel

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Israel Journal of Zoology	0021-2210	Laser Pages Publishing	Israel
Issues in Environmental Science and Technology	1350-7583	Royal Society of Chemistry	UK
Istanbul Universitesi Orman Fakultesi Dergisi. Seri A	0535-8418	Istanbul Universitesi Orman Fakultesi (Forestry Faculty, Istanbul University)	Turkey
Italia Forestale e Montana	0021-2776	Accademia Italiana di Scienze Forestali	Italy
Italian Journal of Agronomy	1125-4718	Forum Societa Editrice Universitaria Udinese srl	Italy
Italus Hortus	1127-3496	Societa Orticola Italiana	Italy
ITEA	1130-6009	Asociacion Interprofesional para el Desarrollo Agrario	Spain
ITEA Produccion Vegetal	1130-6017	Asociacion Interprofesional para el Desarrollo Agrario	Spain
Izvestiya Akademii Nauk. Seriya Biologicheskaya	0002-3329	MAIK Nauka/Interperiodica Publishing	Russia
Izvestiya Timiryazevskoi Sel'skokhozyaistvennoi Akademii	0021-342X	Moskovskaya Sel'skokhozyaistvennaya Akademiya	Russia
Japanese Journal of Crop Science	0011-1848	Crop Science Society of Japan	Japan
Japanese Journal of Ecology	0021-5007	Ecological Society of Japan	Japan
Japanese Journal of Soil Science and Plant Nutrition	0029-0610	Japanese Society of Soil Science and Plant Nutrition	Japan
Japanese Journal of Tropical Agriculture	0021-5260	Japanese Society for Tropical Agriculture	Japan
JAPS - Journal of Animal and Plant Sciences	1018-7081	Pakistan Agricultural Scientists Forum	Pakistan
JARQ - Japan Agricultural Research Quarterly	0021-3551	Japan International Research Center for Agricultural Sciences, Japan International Research Center for Agricultural Sciences	Japan
Jiangsu Journal of Agricultural Sciences	1000-4440	Jiangsu Academy of Agricultural Sciences	China
JIRCAS Journal	1340-7686	Japan International Research Center for Agricultural Sciences	Japan
JIRCAS Working Report	1341-710X	Japan International Research Center for Agricultural Sciences	Japan
JNKVV Research Journal	0021-3721	Jawaharlal Nehru Krishi Vishwa Vidyalaya (JNKVV)	India
Jordan Journal of Applied Science (Natural Sciences)	1605-2587	Deanship of Scientific Research, Applied Science University	Jordan
Journal for Nature Conservation	1617-1381	Elsevier GmbH	Germany
Journal International des Sciences de la Vigne et du Vin	1151-0285	Vigne et Vin Publications Internationales	France
Journal of African Earth Sciences	0899-5362	Pergamon Press	UK
Journal of African Economies	0963-8024	Oxford University Press	UK
Journal of Agrarian Change	1471-0358	Blackwell Publishing	UK
Journal of Agricultural and Food Chemistry	0021-8561	American Chemical Society	USA
Journal of Agricultural and Resource Economics	0162-1912	Western Agricultural Economics Research Association	USA
Journal of Agricultural Economics	0021-857X	Agricultural Economics Society	UK
Journal of Agricultural Economics & Development	0856-6070	Department of Agricultural Economics & Agribusiness, Sokoine University of Agriculture	Tanzania
Journal of Agricultural Economics (Nongye Jingyi)	0546-9600	Research Institute of Agricultural Economics, National Chung Hsing University	China
Journal of Agricultural Education and Extension	1389-224X	Stichting Cereales Publishers	Netherlands
Journal of Agricultural Engineering Research	0021-8634	Academic Press	UK
Journal of Agricultural Research of China	0376-477X	Taiwan Agricultural Research Institute, Council of Agriculture	Taiwan
Journal of Agricultural Science	0021-8596	Cambridge University Press	UK
Journal of Agricultural Science and Technology	1680-7073	National Research Center of Medial Sciences	Iran
Journal of Agricultural Sciences - Islamic Azad University	1562-5559	Islamic Azad University, Scientific Publication Center	India
Journal of Agricultural and Environmental Statistics	1085-7117	American Statistical Association and the International Biometric Society	USA
Journal of Agriculture and Environment for International Development	1590-7198	Istituto Agronomico per l'Oltremare	Italy
Journal of Agriculture and Forestry	0550-3744	College of Agriculture and Natural Resources, National Chung Hsing University	China
Journal of Agriculture and Rural Development in the Tropics and Subtropics	0041-3186	Verband der Tropenlandwirte Witzenhausen	Germany
Journal of Agriculture in the Tropics and Subtropics	0041-3186	Verband der Tropenlandwirte Witzenhausen	Germany
Journal of Agriculture of the University of Puerto Rico	0041-994X	University of Puerto Rico, Agricultural Experiment Station	USA
Journal of Agriculture Technology & Education	0189-0506	Enugu State University of Science & Technology	Nigeria
Journal of Agriculture Science and Technology	1561-7645	Jomo Kenyatta University of Agriculture and Technology (JKUAT)	Kenya
Journal of Agrometeorology	0972-1665	Association of Agrometeorologists	India
Journal of Agronomy	1680-8207	ANSInet, Asian Network for Scientific Information	Pakistan

Journal of Agronomy and Crop Science	0931-2250	Blackwell Publishing	Germany
Journal of Allergy and Clinical Immunology	0091-6749	Elsevier Inc.	USA
Journal of Anhui Agricultural University	1672-352X	Anhui Agricultural University	China
Journal of Animal and Veterinary Advances	1680-5593	Grace Publications Network	Pakistan
Journal of Animal Science and Technology	1598-9429	Korean Society of Animal Sciences and Technology, Korea Science & Technology Center	Korea
Journal of AOAC International	1060-3271	AOAC International	USA
Journal of Applied Aquaculture	1045-4438	Food Products Press	USA
Journal of Applied Biology	0971-4324	Indian Society of Applied Biology	India
Journal of Applied Botany	0949-5460	Blackwell Publishing	Germany
Journal of Applied Botany and Food Quality	1613-9216	Blackwell Publishing	Germany
Journal of Applied Ecology	0021-8901	Blackwell Publishing	UK
Journal of Applied Genetics	1234-1983	Institute of Plant Genetics, Polish Academy of Sciences	Poland
Journal of Applied Horticulture (Lucknow)	0972-1045	Society for the Advancement of Horticulture	India
Journal of Applied Meteorology	0894-8763	American Meteorological Society	USA
Journal of Applied Microbiology	1364-5072	Blackwell Publishing	UK
Journal of Applied Phycology	0921-8971	Springer Science + Business Media	Netherlands
Journal of Applied Poultry Research	1056-6171	Poultry Science Association	USA
Journal of Applied Science & Environmental Management	1119-8362	NCRP, Faculty of Science	USA
Journal of Applied Zoological Researches	0970-9304	Applied Zoologists Research Association	India
Journal of Aquatic Ecosystem Stress and Recovery	1386-1980	Kluwer Academic Publishers	Netherlands
Journal of Aquatic Plant Management	0146-6623	Aquatic Plant Management Society Inc.	USA
Journal of Aquatic Sciences	0189-8779	Nigerian Association for Aquatic Sciences	Nigeria
Journal of Arboriculture	0278-5226	International Society of Arboriculture	USA
Journal of Arid Environments	0140-1963	Elsevier Ltd	UK
Journal of Asian Earth Sciences	1367-9120	Pergamon Press	UK
Journal of Bacteriology	0021-9193	American Society for Microbiology (ASM)	USA
Journal of Bamboo and Rattan	1569-1586	VSP	Netherlands
Journal of Bamboo Research	1000-6567	China National Bamboo Research Center	China
Journal of Basic Microbiology	0233-111X	WILEY-VCH Verlag GMBH & Co. KGaA	Germany
Journal of Beijing Forestry University	1000-1522	Beijing Forestry University	China
Journal of Biogeography	0305-0270	Blackwell Publishing	UK
Journal of Biological Sciences		ANSInet, Asian Network for Scientific Information	Pakistan
Journal of Bioresource Sciences	1344-0179	Japan Society for Bioresource Sciences	Japan
Journal of Bioscience and Bioengineering	1389-1723	Society for Biotechnology	Japan
Journal of Central European Agriculture	1332-9049	Faculty of Agriculture	Croatia
Journal of Cereal Science	0733-5210	Elsevier	UK
Journal of Chemical Ecology	0098-0331	Springer Science + Business Media	Netherlands
Journal of Chemical Technology and Biotechnology	0268-2575	John Wiley & Sons	UK
Journal of China Agricultural University	1007-4333	China Agricultural University	China
Journal of Chromatographic Science	0021-9665	Preston Publications	USA
Journal of Chromatography	0021-9673	Elsevier Science Publishers B.V. Physical Sciences and Engineering Division	Netherlands
Journal of Climate	0894-8755	American Meteorological Society	USA
Journal of Coastal Conservation	1400-0350	Opulus Press	Sweden
Journal of Coastal Research	0749-0208	Coastal Education and Research Foundation	USA
Journal of Coffee Research	0374-8537	Central Coffee Research Institute, Coffee Research Station	India
Journal of Colloid and Interface Science	0021-9797	Elsevier Inc.	USA
Journal of Commodity Science	0392-064X	Cooperativa Libraria Universitaria Editrice Bologna (CLUEB)	Italy
Journal of Contaminant Hydrology	0169-7722	Elsevier	Netherlands
Journal of Contemporary Asia	0047-2336	Journal of Contemporary Asia	Philippines
Journal of Cotton Science	1524-3303	Cotton Foundation	USA
Journal of Crop Improvement	1542-7528	Food Products Press	USA
Journal of Crop Production	1092-678X	Food Products Press	USA
Journal of Culture Collections	1310-8360	National Bank for Industrial Microorganisms and Cell Cultures	Bulgaria

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Journal of Developing Areas	0022-037X	College of Business, Tennessee State University	USA
Journal of Earth System Science	0253-4126	Current Science Association	India
Journal of Eco-Physiology	0972-0413	Excellere Publication	India
Journal of Ecobiology	0970-9037	Palani Paramount Publications	India
Journal of Ecology (Oxford)	0022-0477	Blackwell Publishing	UK
Journal of Economic and Taxonomic Botany	2050-9768	Scientific Publishers (India)	India
Journal of Economic Entomology	0022-0493	Entomological Society of America	USA
Journal of Ecotoxicology & Environmental Monitoring	0971-0965	Palani Paramount Publications	India
Journal of Elementology	1644-2296	Polish Society for Magnesium Research	Poland
Journal of Environment & Development	1070-4965	Sage Publications	USA
Journal of Environmental Assessment Policy and Management	1464-3332	Imperial College Press	UK
Journal of Environmental Biology	0254-8704	Journal of Environmental Biology	India
Journal of Environmental Economics and Management	0095-0696	Elsevier Inc.	USA
Journal of Environmental Engineering	0733-9372	American Society of Civil Engineers	USA
Journal of Environmental Engineering and Science	1496-2551	National Research Council of Canada	Canada
Journal of Environmental Extension	1595-5125	Department of Agricultural Extension and Rural Development, University of Ibadan	Nigeria
Journal of Environmental Horticulture	0738-2898	Horticultural Research Institute	USA
Journal of Environmental Management	0301-4797	Elsevier	Netherlands
Journal of Environmental Monitoring	1464-0325	Royal Society of Chemistry	UK
Journal of Environmental Planning and Management	0964-0568	Routledge	UK
Journal of Environmental Quality	0047-2425	American Society of Agronomy	USA
Journal of Environmental Radioactivity	0265-931X	Elsevier	UK
Journal of Environmental Science and Health. Part A	1093-4529	Taylor & Francis	UK
Journal of Environmental Science and Health. Part C	1059-0501	Taylor & Francis	UK
Journal of Environmental Sciences	1001-0742	Science Press	China
Journal of Environmental Systems	0047-2433	Baywood Publishing Company Inc.	USA
Journal of Essential Oil-Bearing Plants	0972-060X	Har Krishan Bhalla & Sons	India
Journal of Eukaryotic Microbiology	1066-5234	Blackwell Publishing	USA
Journal of Experimental Botany	0022-0957	Oxford University Press	UK
Journal of Experimental Zoology	0972-0030	Department of Zoology	India
Journal of Forest Planning	1341-562X	Japan Society of Forest Planning, Faculty of Agriculture	Japan
Journal of Forest Science	1212-4834	Institute of Agricultural and Food Information	Czechoslovakia
Journal of Forest Science - Kangwon National University	1226-8267	Institute of Forest Science, Kangwon National University	Korea
Journal of Forestry	0022-1201	Society of American Foresters	USA
Journal of Forestry Research	1007-662X	Northeast Forestry University	China
Journal of Freshwater Ecology	0270-5060	Oikos Publishers	USA
Journal of Fruit and Ornamental Plant Research	1231-0948	Research Institute of Pomology and Floriculture	Poland
Journal of Fruit Science	1009-9980	Editorial Board of Journal of Fruit Science	China
Journal of Fujian Agriculture and Forestry University (Natural Science Edition)	1671-5470	Fujian Agriculture and Forestry University	China
Journal of Fujian College of Forestry	1001-389X	Editorial Department of Journal of Fujian College of Forestry	China
Journal of Fungal Research	1672-3538	Jilin Agricultural University	China
Journal of Geophysical Research	0148-0227	American Geophysical Union	USA
Journal of Great Lakes Research	0380-1330	International Association for Great Lakes Research	USA
Journal of Hazardous Materials	0304-3894	Elsevier	UK
Journal of Hebei Vocation-Technical Teachers College	1008-9519	Hebei Vocation Technical Teachers College	China
Journal of Herbs (Spices & Medicinal Plants)	1049-6475	Haworth Herbal Press	USA
Journal of Hill Research	0970-7050	Sikkim Science Society	India
Journal of Horticultural Science and Biotechnology	1462-0316	Headley Brothers Ltd., The Invicta Press	UK
Journal of Huazhong Agricultural University	1000-2421	Gai Kan Bianjibu	China
Journal of Hubei Agricultural College	1004-3888	Hubei Agricultural College	China
Journal of Hunan Agricultural University	1007-1032	Hunan Agricultural University	China

Journal of Hydraulic Engineering	0733-9429	American Society of Civil Engineers	USA
Journal of Hydrology (Amsterdam)	0022-1694	Elsevier	Netherlands
Journal of Hydrometeorology	1525-755X	American Meteorological Society	USA
Journal of Industrial Microbiology & Biotechnology	1367-5435	Springer-Verlag GmbH	Germany
Journal of Inorganic Biochemistry	0162-0134	Elsevier	USA
Journal of Insect Conservation	1366-638X	Springer Science + Business Media	Netherlands
Journal of Interacademicia	0971-9016	Journal of Interacademicia	India
Journal of International Development	0954-1748	John Wiley & Sons	UK
Journal of Irrigation and Drainage Engineering	0733-9437	American Society of Civil Engineers	USA
Journal of Jiangsu Forestry Science & Technology	1001-7380	Jiangsu Academy of Forestry, Jiangsu Information Centre of Forestry Science and Technology	China
Journal of Jilin Agricultural University	1000-5684	Jilin Agricultural University	China
Journal of Liquid Chromatography & Related Technologies	1082-6076	Taylor & Francis	USA
Journal of Living World		Living World Society	India
Journal of Luoyang Agricultural College	1008-1895	Chinese Academy of Agricultural Sciences (CAAS), Scientech Documentation and Information Centre	China
Journal of Maharashtra Agricultural Universities	0378-2395	Journal of Maharashtra Agricultural Universities, College of Agriculture	India
Journal of Meteorology	0307-5966	Artetech Publishing Company	UK
Journal of Microbiological Methods	0167-7012	Elsevier	UK
Journal of Microbiology	1684-1182	Scientific Communications International Limited	Taiwan
Journal of Microscopy	0022-2720	Blackwell Publishing	UK
Journal of Mountain Agriculture and Biology	1008-0475	Chinese Academy of Agricultural Sciences (CAAS), Scientech Documentation and Information Centre	China
Journal of Nanjing Agricultural University	1000-2030	Nanjing Agricultural University	China
Journal of Nanjing Forestry University (Natural Sciences Edition)	1000-2006	Nanjing Forestry University	China
Journal of Nanjing Institute of Meteorology	1000-2022	Journal of Nanjing Institute of Meteorology Editorial Department	China
Journal of Natural Resources and Life Sciences Education	1059-9053	American Society of Agronomy	USA
Journal of Natural Science of Hunan Normal University	1000-2537	Hunan Normal University	China
Journal of Near Infrared Spectroscopy	0967-0335	NIR Publications	UK
Journal of Nematology	0022-300X	Society of Nematologists	USA
Journal of Oil Palm Research	1511-2780	Malaysian Palm Oil Board (MPOB)	Malaysia
Journal of Oilseeds Research	0970-2776	Indian Society of Oilseeds Research	India
Journal of Ornamental Horticulture (New Series)	0972-0499	Indian Society of Ornamental Horticulture	India
Journal of Park and Recreation Administration	0735-1968	Sagamore Publishing	USA
Journal of Peasant Studies	0306-6150	Routledge	UK
Journal of Pesticide Reform	0893-357X	NorthWest Coalition for Alternatives to Pesticides (NCAP)	USA
Journal of Pesticide Science	1348-589x	Pesticide Science Society of Japan	Japan
Journal of Phycology	0022-3646	Blackwell Publishing	USA
Journal of Phytological Research	0970-5767	Phytological Society	India
Journal of Plankton Research	0142-7873	Oxford University Press	UK
Journal of Plant Biology	0972-3862	Society for Plant Physiology & Biochemistry	India
Journal of Plant Growth Regulation	0721-7595	Springer-Verlag	USA
Journal of Plant Nutrition	0190-4167	Taylor & Francis	USA
Journal of Plant Nutrition and Soil Science	1436-8730	WILEY-VCH Verlag GMBH & Co. KGaA	Germany
Journal of Plant Physiology	0176-1617	Elsevier GmbH	Germany
Journal of Plant Physiology and Molecular Biology	1671-3877	Science Press	China
Journal of Plant Protection Research	1427-4345	Instytut Ochrony Roslin (Institute of Plant Protection)	Poland
Journal of Plant Research	0918-9440	Botanical Society of Japan	Japan
Journal of Plant Resources and Environment	1004-0978	Institute of Botany, Jiangsu Province and the Chinese Academy of Sciences	China
Journal of Plantation Crops	0304-5242	Central Plantation Crops Research Institute (CPCRI)	India
Journal of Potassium Research	0257-4993	Potash Research Institute of India	India
Journal of Production Agriculture	0890-8524	American Society of Agronomy	USA

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Journal of Rakuno Gakuen University - Scientific Communications International Limited	0388-001X	Rakuno Gakuen University	Japan
Journal of Range Management	0022-409X	Society for Range Management	USA
Journal of Ravishankar University. B	0970-5910	Pt. Ravishankar Shukla University	India
Journal of Research and Applications in Agricultural Engineering	1642-686X	Przemyslowy Instytut Maszyn Rolniczych (PIMR), Branzowy Osrodek Informacji Naukowej	Poland
Journal of Research ANGRAU	0970-0226	Acharya N G Ranga Agricultural University	India
Journal of Research	0971-1724	Birsa Agricultural University	Birsa
Journal of Research	0048-6019	Punjab Agricultural University	India
Journal of Root Crops	0378-2409	Indian Society for Root Crops, Central Tuber Crops Research Institute	India
Journal of Rubber Research	1511-1768	Malaysian Rubber Board	Malaysia
Journal of Rural Development & Administration	0047-2751	Pakistan Academy for Rural Development	Pakistan
Journal of Rural Development (Hyderabad)	0970-3357	National Institute of Rural Development	India
Journal of Science and Technology	1027-4928	University of Gambia (UNZA)	Zambia
Journal of Science and Technology of Agriculture and Natural Resources	1028-7655	Colleges of Agriculture and Natural Resources, Isfahan University of Technology	Iran
Journal of Shandong Agricultural University	1000-2324	Shandong Nongye Daxue	China
Journal of Shanghai Fisheries University	1004-7271	Editorial Committee of Journal of Shanghai Fisheries University	China
Journal of Shanghai Jiaotong University - Agricultural Science	1671-9964	Shanghai Jiaotong University	China
Journal of Society of High Technology in Agriculture	0918-6638	British Veterinary Association	UK
Journal of Soil and Water Conservation (Ankeny)	0022-4561	Soil and Water Conservation Society	USA
Journal of Soil and Water Conservation (China)	1009-2242	Zhongguo Kexueyuan	China
Journal of Soil and Water Conservation (Taichung)	0255-5948	Soil and Water Conservation Department, National Chung Hsing University	China
Journal of Soils and Crops	0971-2836	Association of Soils and Crops Research Scientists	India
Journal of Soils and Sediments	1439-0108	Ecomed Publishers	Germany
Journal of South American Earth Sciences	0895-9811	Pergamon Press	UK
Journal of South China Agricultural University	1001-411X	South China Agricultural University	China
Journal of South Pacific Agriculture	1016-7774	Institute for Research, Extension and Training in Agriculture (IRETA)	Samoa
Journal of Southwest Agricultural University	1000-2642	Gai Kan Bian Wei Hui	China
Journal of Spices and Aromatic Crops	0971-3328	Indian Society for Spices	India
Journal of Sugar Beet Research	0899-1502	American Society of Sugar Beet Technologists	USA
Journal of Sustainable Agriculture	1044-0046	Food Products Press	USA
Journal of Sustainable Agriculture and the Environment	1119-8152	Michael Okpara University of Agriculture	Nigeria
Journal of Sustainable Forestry	1054-9811	Food Products Press	USA
Journal of Taiwan Livestock Research	0253-9209	Taiwan Livestock Research Institute	Taiwan
Journal of Tea Science	1000-369X	Tea Research Institute, CAAS	Japan
Journal of Testing and Evaluation	0090-3973	ASTM International	USA
Journal of the Agricultural Science Society of North-East India	0971-6289	Agricultural Science Society for Northeast India	India
Journal of the Air & Waste Management Association	0002-2470	Air & Waste Management Association	USA
Journal of the American Oil Chemists' Society	0003-021X	AOCS Press	USA
Journal of the American Society for Horticultural Science	0003-1062	American Society for Horticultural Science	USA
Journal of the American Water Resources Association	1093-474X	American Water Resources Association (AWRA)	USA
Journal of the Brazilian Chemical Society	0103-5053	Sociedade Brasileira de Quimica	Brazil
Journal of the Chinese Chemical Society	0009-4536	Chinese Chemical Society	Taiwan
Journal of the Chinese Society for Horticultural Science	0529-6544	Chinese Society for Horticultural Science	Taiwan
Journal of the Chinese Society of Animal Science	0253-9187	Chinese Society of Animal Science	Taiwan
Journal of the Experimental Forest of National Taiwan University	0255-6014	Experiment Forest of National Taiwan University	Taiwan
Journal of the Faculty of Agriculture	0023-6152	Kyushu University	Japan
Journal of the Faculty of Agriculture	0583-0621	Shinshu University	Japan
Journal of the Faculty of Applied Biological Science	1341-691X	Hiroshima University	Japan

Journal of the Ghana Science Association	0855-3823	Ghana Science Association	Ghana
Journal of the Graduate School of Agriculture	1345-6601	Hokkaido University	Japan
Journal of the Indian Society of Soil Science	0019-638X	Indian Society of Soil Science	India
Journal of the Japanese Forest Society	1349-8509	Japanese Forest Society	Japan
Journal of the Japanese Forestry Society	0021-485X	Japanese Forestry Society	Japan
Journal of the Japanese Society for Horticultural Science	0013-7626	Japanese Society for Horticultural Science	Japan
Journal of the Japanese Society of Agricultural Machinery	0285-2543	Japanese Society of Agricultural Machinery	Japan
Journal of the Korean Society for Horticultural Science	0253-6498	Korean Society for Horticultural Science	Korea Republic
Journal of the Korean Society of Grassland Science	1013-9354	Korean Society of Grassland Science	Korea Republic
Journal of the Royal Agricultural Society of England	0080-4134	Royal Agricultural Society of England	UK
Journal of the Royal Society of New Zealand	0303-6758	Royal Society of New Zealand	New Zealand
Journal of the Saudi Chemical Society	1319-6103	Saudi Chemical Society	Saudi Arabia
Journal of the Science of Food and Agriculture	0022-5142	John Wiley & Sons	UK
Journal of the Timber Development Association of India	0377-936X	Timber Development Association of India	India
Journal of the Torrey Botanical Society	0040-9618	Torrey Botanical Society, Allen Press Inc.	USA
Journal of the World Aquaculture Society	0893-8849	World Aquaculture Society	USA
Journal of Tourism Studies	1035-4662	School of Business, James Cook University	Australia
Journal of Toxicology and Environmental Health. Part A	1528-7394	Taylor & Francis	UK
Journal of Triticeae Crops		Editorial Department of Journal of Triticeae Crops	China
Journal of Tropical Agriculture	0971-636X	Kerala Agricultural University	India
Journal of Tropical and Subtropical Botany	1005-3395	South China Institute of Botany, Chinese Academy of Sciences	China
Journal of Tropical Ecology	0266-4674	Cambridge University Press	UK
Journal of Tropical Forest Resources	0189-3130	University of Ibadan, Department of Forest Resources Management	Nigeria
Journal of Tropical Forest Science	0128-1283	Forest Research Institute Malaysia	Malaysia
Journal of Tropical Forestry	0970-1494	Society of Tropical Forestry Scientists	India
Journal of Tropical Microbiology	1607-4106	Kenya Society of Microbiology	Kenya
Journal of Turfgrass and Sports Surface Science	1478-548X	Sports Turf Research Institute	UK
Journal of Turfgrass Science	1367-8361	Sports Turf Research Institute	UK
Journal of Vegetable Crop Production	1049-6467	Food Products Press	USA
Journal of Vegetation Science	1100-9233	Opulus Press	Sweden
Journal of Water and Health	1477-8920	IWA Publishing	UK
Journal of Water and Land Development	1429-7426	Wydawnictwo IMUZ	Poland
Journal of Water Resources Planning and Management	0733-9496	American Society of Civil Engineers	USA
Journal of Weed Science and Technology	0372-798X	Weed Science Society of Japan	Japan
Journal of Yangzhou University	1671-4652	Agricultural and Life Sciences Edition	Japan
Journal of Yangzhou University	1007-824x	Natural Science Edition	Japan
Journal of Yunnan Agricultural University	1004-390X	Yunnan Agricultural University	China
Journal of Zhejiang Forestry College	1000-5692	Zhejiang Forestry College	China
Journal of Zhejiang Forestry Science and Technology	1001-3776	Zhejiang Information Center of Forestry Science and Technology	China
Journal of Zhejiang University (Agriculture and Life Sciences)	1008-9209	Zhejiang University Press	China
Journal of Zhejiang University (Science)	1009-3095	Zhejiang University Press	China
Journal of Zoology	0952-8369	Cambridge University Press	UK
Karnataka Journal of Agricultural Sciences	0972-1061	University of Agricultural Sciences	India
Kartofel' i Ovoshchi	0022-9148	Izdatel'stvo Kolos	Russia
Kartoffelbau	0022-9156	Verlag Th. Mann	Germany
Kenya Coffee	1010-3481	Coffee Board of Kenya	Kenya
Kirkia	0451-9930	National Herbarium and Botanic Garden, Ministry of Agriculture	South Africa
Korean Journal of Biological Sciences	1226-5071	Korean Association of Biological Sciences	Korea Republic
Korean Journal of Crop Science	0252-9777	Korean Society of Crop Science	Korea Republic
Korean Journal of Environment and Ecology	1229-3857	Korean Society of Environment and Ecology	Korea Republic
Korean Journal of Horticultural Science & Technology	1226-8763	Korean Society for Horticultural Science	Korea Republic
Korean Journal of Weed Science	0253-7468	Korean Society of Weed Science	Korea Republic
Kungl. Skogs- och Lantbruksakademiens Tidskrift	0023-5350	Kungl. Skogs- och Lantbruksakademiens (Royal Swedish Academy of Agriculture and Forestry)	Sweden

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Kuwait Journal of Science & Engineering	1024-8684	Academic Publication Council	Kuwait
Lakarstwo w Polsce (Grassland Science in Poland)	1506-5162	Polskie Towarzystwo Lakarskie (Polish Grassland Society)	Poland
Lakes and Reservoirs: Research and Management	1320-5331	Blackwell Publishing	Australia
Land Contamination & Reclamation	0967-0513	EPP Publications	UK
Land Degradation & Development	1085-3278	John Wiley & Sons	UK
Land Use Policy	0264-8377	Elsevier	UK
Landbauforschung Volkenrode	0458-6859	Bundesforschungsanstalt fur Landwirtschaft (FAL)	Germany
Landlicher Raum - print	0257-5280	Bundesministerium fur Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft	Austria
Landnutzung und Landentwicklung	0934-666X	Blackwell Publishing	Germany
Landscape and Urban Planning	0169-2046	Elsevier	Netherlands
Landscape Ecology	0921-2973	Springer Science + Business Media	Netherlands
Landslides	1612-510X	Springer-Verlag GmbH	Germany
Landtechnik	0023-8082	Landwirtschaftsverlag GmbH	Germany
Landwards	1363-8300	Institution of Agricultural Engineers	UK
Laranja	0102-1907	Centro de Citricultura Sylvio Moreira - IAC	Brazil
Legume Research	0250-5371	Agricultural Research Communication Centre	India
LEISA	1569-8424	Information Centre for Low External Input Agriculture (ILEIA)	Netherlands
Louisiana Agriculture	0024-6735	Louisiana Agricultural Experiment Station	USA
LUCAS African Studies Bulletin	0024-0249	Centre for African Studies, University of Leeds	UK
Lumle Review Paper - Lumle Regional Agricultural Research Centre	1023-5132	Agricultural Research Station, Lumle	India
Lumle Technical Paper	1023-3407	Agricultural Research Station, Lumle	India
Lyonia	0888-9619	Harold L. Lyon Arboretum, University of Hawaii	USA
Macchine e Motori Agricoli	0024-8967	Gruppo Calderini Edagricole Srl	Italy
Macedonian Agricultural Review	1409-5157	Macedonian Agricultural Review, Faculty of Agriculture	Greece
Madera y Bosques	1405-0471	Instituto de Ecologia A.C., Departamento de Publicaciones	Mexico
Madras Agricultural Journal	0024-9602	Tamil Nadu Agricultural University	India
Madrono	0024-9637	California Botanical Society	USA
Magnetic Resonance Imaging	0730-725X	Elsevier	USA
Magyar Gyomkutatas es Technologia	1586-894X	Agroinform Kiado es Nyomdaipari Kft.	Hungary
Mais	0341-5155	Olah Farkas Zabo	Hungary
Malaysian Forester	0302-2935	Malaysian Forester	Malaysia
Management of Environmental Quality	1477-7835	MCB University Press Ltd	UK
Medit	1120-6403	Gruppo Calderini Edagricole Srl	Italy
Mekhanizatsiya i Elektrifikatsiya Sel'skogo Khozyaistva	0206-572X	OOO Infokholodtekh	Russia
Memoirs of the Faculty of Agriculture of Kinki University	0453-8889	Faculty of Agriculture, Kinki University	Japan
Memoirs of the Graduate School of Agriculture	1345-661x	Hokkaido University	Japan
Menara Perkebunan	0215-9318	Unit Penelitian Bioteknologi Perkebunan	Indonesia
Microbial Ecology	0095-3628	Springer-Verlag	USA
Microbiological Research	0944-5013	Elsevier GmbH	Germany
Microbiology (Moscow)	0026-2617	MAIK Nauka/Interperiodica Publishing	Russia
Microbiology (Reading)	1350-0872	Society for General Microbiology	UK
Military Medicine	0026-4075	Association of Military Surgeons of the US	USA
Minor Field Studies - International Office	1402-3237	Swedish University of Agricultural Sciences	Sweden
Miskininkyste	1392-2041	Lithuanian Forest Research Institute (Lietuvos Misku Institutas)	Lithuania
Mitigation and Adaptation Strategies for Global Change	1381-2386	Springer Science + Business Media	Netherlands
Mitteilungen aus Lebensmitteluntersuchung und Hygiene	1424-1307	Bundesamt fur Gesundheit	Switzerland
Mitteilungen der Deutschen Bodenkundlichen Gesellschaft	0343-1071	Deutsche Bodenkundliche Gesellschaft	Germany
Mitteilungen des Vereins fur Forstliche Standortskunde und Forstpflanzenzuchtung	0506-7049	Verein fur Forstliche Standortskunde und Forstpflanzenzuchtung e.V.	Germany
Monti e Boschi	0390-6736	Gruppo Calderini Edagricole Srl	Italy

Moor Journal of Agricultural Research	1595-4153	Institute of Agricultural Research and Training, Obafemi Awolowo University	South Africa
Moscow University Soil Science Bulletin	0147-6874	Allerton Press	Russia
Mountain Research and Development	0276-4741	United Nations University Press	Japan
MPOB Technology	1511-7804	Malaysian Palm Oil Board (MPOB)	Malaysia
Mutation Research	1383-5718	Elsevier	Netherlands
Mycological Research	0953-7562	Cambridge University Press	UK
Mycologist	0269-915X	Cambridge University Press	UK
Mycopathologia	0301-486X	Springer Science + Business Media	Netherlands
Mycorrhiza	0940-6360	Springer-Verlag GmbH	Germany
Mycosystema	1007-3515	Science Press	China
Mycotaxon	0093-4666	Mycotaxon Ltd	USA
Nachrichtenblatt des Deutschen Pflanzenschutzdienstes	0027-7479	Verlag Eugen Ulmer GmbH	Germany
Naga	1511-8533	International Center for Living Aquatic Resources Management	Malaysia
Native Plants Journal	1522-8339	University of Idaho Press	USA
Natura Croatica	1330-0520	Croatian Natural History Museum (Hrvatski prirodoslovni Muzej)	Croatia
Natural Areas Journal	0885-8608	Natural Areas Association	USA
Natural Resource Management	1440-1460	Australian Association of Natural Resource Management	Australia
Natural Resources Forum	0165-0203	Blackwell Publishing	UK
Natural Resources Journal	0028-0739	University of New Mexico	Poland
Natural Sciences	1505-4667	Wydawnictwo UWM, School of Law	Poland
Nature Biotechnology	1087-0156	Nature America	Germany
Nature Reviews Microbiology	1740-1526	Nature Publishing Group	UK
Naturschutz und Landschaftsplanung	0940-6808	Verlag Eugen Ulmer GmbH	Germany
Naturwissenschaften	0028-1042	Springer-Verlag GmbH	Germany
Nederlands Bosbouwtijdschrift	0028-2057	Koninklijke Nederlandse Bosbouw Vereniging	Netherlands
Nematologia Brasileira	0102-2997	Sociedade Brasileira de Nematologia	Brazil
Nematologia Mediterranea	0391-9749	Istituto per la Protezione delle Piante, Consiglio Nazionale delle Ricerche	Italy
Nematology	1388-5545	Brill Academic Publishers	Netherlands
Nematropica	0099-5444	Organizacion de Nematologos de los Tropicos Americanos (ONTA)	USA
Nendo Kagaku = Journal of the Clay Science Society of Japan	0470-6455	Clay Science Society of Japan	Japan
New Botanist	0377-1742	Today and Tomorrow's Printers & Publishers	India
New Forests	0169-4286	Springer Science + Business Media	Netherlands
New Medit	1594-5685	Istituto Agronomico Mediterraneo del CIHEAM	Italy
New Phytologist	0028-646X	Blackwell Publishing	UK
New Zealand Geographer	0028-8144	Blackwell Publishing	Australia
New Zealand Journal of Agricultural Research	0028-8233	Royal Society of New Zealand	New Zealand
New Zealand Journal of Botany	0028-825X	Royal Society of New Zealand	New Zealand
New Zealand Journal of Crop and Horticultural Science	0114-0671	Royal Society of New Zealand	New Zealand
New Zealand Journal of Forestry	1174-7986	New Zealand Institute of Forestry	New Zealand
New Zealand Journal of Forestry Science	0048-0134	New Zealand Forest Research Institute	New Zealand
Newsletter - UPASI Tea Research Foundation	0972-3145	UPASI Tea Research Foundation	India
Niger Delta Biologia	1118-8731	Rivers State University of Science and Technology, Department of Applied and Environmental Biology	Nigeria
Nigerian Agricultural Journal	0300-368X	College of Agricultural Economics, Department of Applied and Environmental Biology	Nigeria
Nigerian Journal of Soil Research	1595-6121	Institute for Agricultural Research, Ahmadu Bello University	Nigeria
Nippon Suisan Gakkaishi	0021-5392	Japanese Society of Fisheries Science	Japan
Nordic Hydrology	0029-1277	IWA Publishing	UK
North American Journal of Aquaculture	1522-2055	American Fisheries Society	USA
North American Journal of Fisheries Management	0275-5947	American Fisheries Society	USA
Northeastern Naturalist	1092-6194	Humboldt Field Research Institute	USA
Northern Journal of Applied Forestry	0742-6348	Society of American Foresters	USA
Notiziario ERSA		ERSA	Italy
Novenytermeles	0546-8191	Agroinform Kiado	Hungary
Novenyvedelem	0133-0829	Agroinform Kiado	Hungary

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
NUCIS Newsletter	1020-0797	Institut de Recerca i Tecnologia Agroalimentaries (IRTA)	Spain
Nutrient Cycling in Agroecosystems	1385-1314	Springer Science + Business Media	Netherlands
O Biologico	0366-0567	Instituto Biologico	Brazil
ODI Natural Resource Perspectives	1356-9228	Overseas Development Institute	UK
Oecologia	0029-8549	Springer-Verlag GmbH	Germany
OFI Occasional Papers	0269-5790	Oxford Forestry Institute, University of Oxford	UK
Oikos	0030-1299	Blackwell Publishing	Denmark
Oil Palm Bulletin	1511-7634	Malaysian Palm Oil Board (MPOB)	Malaysia
Okologie & Landbau	1015-2423	Stiftung Okologie & Landbau (SOL)	Germany
Olivae	0255-9994	International Olive Oil Council	Spain
Olivo & Olio	1127-0713	Gruppo Calderini Edagricole Srl	Italy
Organic Geochemistry	0146-6380	Elsevier	UK
Orman Muhendisligi	1301-3572	Orman Muhendisleri Odasi	Turkey
Oryza	0474-7615	Association of Rice Research Workers, Central Rice Research Institute	India
Pajouhesh-va-Sazandegi. In Agronomy & Horticulture	1019-9632	Ministry of Jahad Sazandegi	Iran
Pakistan Development Review	0030-9729	Pakistan Institute of Development Economics	Pakistan
Pakistan Journal of Agricultural Research	0251-0480	Pakistan Agricultural Research Council	Pakistan
Pakistan Journal of Agricultural Sciences	0552-9034	University of Agriculture, Department of Livestock Management	Pakistan
Pakistan Journal of Biological Sciences	1028-8880	ANSInet, Asian Network for Scientific Information	Pakistan
Pakistan Journal of Botany	0556-3321	Pakistan Botanical Society	Pakistan
Pakistan Journal of Forestry	0030-9818	Pakistan Forest Institute	Pakistan
Pakistan Journal of Nematology	0255-7576	Pakistan Society of Nematologists	Pakistan
Pakistan Journal of Scientific and Industrial Research	0030-9885	Pakistan Council of Scientific and Industrial Research (PCSIR)	Pakistan
Pakistan Journal of Weed Science Research	1015-3055	Weed Science Society of Pakistan, Department of Weed Science	Pakistan
Pakistan Sugar Journal	1028-1193	Shakarganj Sugar Research Institute	Pakistan
Pamphlets - NSW Agriculture		NSW Agriculture	Australia
Pasturas Tropicales	1012-7410	Centro Internacional de Agricultura Tropical (CIAT)	Colombia
PAV-Bulletin Vollegrondsgroenteteelt	1385-5301	PAV, Praktijkonderzoek voor de Akkerbouw en de Vollegrondsgroenteteelt	Poland
PE&RS (Photogrammetric Engineering & Remote Sensing)	0099-1112	American Society for Photogrammetry and Remote Sensing	US
Peckiana	1618-1735	Staatliches Museum fur Naturkunde Gorlitz	Germany
Pedobiologia	0031-4056	Elsevier GmbH	Germany
Pedologist	0031-4064	Japanese Society of Pedology	Japan
Pedosphere	1002-0160	Science Press	China
Periodicum Biologorum	0031-5362	Hrvatsko Prirodoslovno Drustvo	Croatia
Permafrost and Periglacial Processes	1045-6740	John Wiley & Sons	UK
Perspectives in Plant Ecology	1433-8319	Elsevier GmbH	Germany
Perspectives on Global Development and Technology	1569-1500	Brill Academic Publishers	Netherlands
Pesquisa Agropecuaria Brasileira	0100-204X	Empresa Brasileira de Pesquisa Agropecuaria	Brazil
Pesquisa Agropecuaria Gaucha	0104-9070	Fundacao Estadual de Pesquisa Agropecuaria (FEPAGRO)	Brazil
Pesquisa Agropecuaria Pernambucana	0100-8501	Empresa Pernambucana de Pesquisa Agropecuaria	Brazil
Pesquisa em Andamento da Embrapa Semi-Arido	1516-1625	Embrapa Semi-Arido	Brazil
Pest Management and Economic Zoology	0971-5703	Indian Society of Pest Management and Economic Zoology	India
Pest Management Science	1526-498X	John Wiley & Sons	UK
Pesticidas - Revista de Ecotoxicologia e Meio Ambiente	0103-7277	Universidade Federal do Parana, Setor de Tecnologia	Brazil
Pesticide Biochemistry and Physiology	0048-3575	Elsevier	Netherlands
Pesticide Outlook	0956-1250	Royal Society of Chemistry	UK
Pesticide Research Journal	0970-6763	Society of Pesticide Science India	India
Pflanzenschutz-Nachrichten Bayer	0340-1723	Bayer CropScience AG	Germany
Philippine Agricultural Scientist	0031-7454	College of Agriculture, University of the Philippines at LosBanos (UPLB)	Philippines
Philippine Journal of Science	0031-7683	Science and Technology Information Institute	Philippines
Philosophical Transactions of the Royal Society of London. Series A	0080-4614	Royal Society	UK

Philosophical Transactions of the Royal Society of London. Series B	0962-8436	Royal Society	UK
PHM Revue Horticole	0031-5087	Royal Society	UK
Photosynthesis Research	0166-8595	Springer Science + Business Media	Netherlands
Photosynthetica	0300-3604	Institute of Experimental Botany, Academy of Sciences of the Czech Republic	Czechoslovakia
Phycological Research	1322-0829	Blackwell Publishing	Australia
Physiologia Plantarum	0031-9317	Blackwell Publishing	Denmark
Physiological Entomology	0307-6962	Blackwell Publishing	UK
Physiology and Molecular Biology of Plants	0971-5894	Prof. H.S. Srivastava Foundation for Science and Society	India
Phytochemistry	0031-9422	Elsevier	Netherlands
Phytocoenologia	0340-269X	Gebruder Borntraeger Verlagsbuchhandlung	Germany
Phytomorphology	0031-9449	International Society of Plant Morphologists	India
Phyton (Buenos Aires)	0031-9457	Fundacion Romulo Raggio	Argentina
Phyton (Horn)	0079-2047	Verlag Ferdinand Berger & Sohne	Austria
Phytopathologia Mediterranea	0031-9465	Mediterranean Phytopathological Union	Italy
Pig News and Information	0143-9014	CABI Publishing	UK
PKV Research Journal	0378-813X	PKV Research Journal	India
Plant and Cell Physiology	0032-0781	Oxford University Press	UK
Plant and Soil	0032-079X	Springer Science + Business Media	Netherlands
Plant Archives	0972-5210	Dr R.S. Yadav	India
Plant Biology	1435-8603	Georg Thieme Verlag	Germany
Plant Biosystems	1126-3504	Taylor & Francis	UK
Plant Ecology	1385-0237	Springer Science + Business Media	Netherlands
Plant Growth Regulation	0167-6903	Springer Science + Business Media	Netherlands
Plant Molecular Biology	0167-4412	Springer Science + Business Media	Netherlands
Plant Nutrition and Fertilizer Science	1008-505X	Editorial Department of Plant Nutrition and Fertilizer Science	China
Plant Physiology	0032-0889	American Society of Plant Biologists	USA
Plant Physiology and Biochemistry	0981-9428	Elsevier SAS	France
Plant Physiology Communications	0412-0922	Chinese Academy of Agricultural Sciences (CAAS), Scientech Documentation and Information Centre	China
Plant Production Science	1343-943X	Crop Science Society of Japan	Japan
Plant Protection Bulletin (Faridabad)	0378-0449	Directorate of Plant Protection, Quarantine and Storage	India
Plant Protection Bulletin (Taipei)	0577-750X	Plant Protection Society of the Republic of China	Taiwan
Plant Protection Quarterly	0815-2195	R.G. and F.J. Richardson	Australia
Plant Science	0168-9452	Elsevier	UK
Plant Species Biology	0913-557X	Blackwell Publishing	Australia
Plant	0140-7791	Blackwell Publishing	UK
Planta	0032-0935	Springer-Verlag GmbH	Germany
Planta Daninha	0100-8358	Sociedade Brasileira da Ciencia das Plantas Daninhas	Brazil
Planter	0126-575X	Incorporated Society of Planters	Malaysia
Plodovodstvo	0134-9759	Belorusskii Nauchno-Issledovatel'skii Institut Plodovodstva (Belorussian Research Institute for Fruit Growing)	Belarus
Pochvovedenie	0032-180X	MAIK Nauka/Interperiodica Publishing	Russia
Pochvovedenie i Agrokhimiya		Belorusskii Ordena Trudovogo Krasnago Znameni, Nauchno-Issledovatel'skii Institut Pochov'edeniya i Agrokhimii	Russia
Pochvoznanie	0861-9425	National Centre for Agrarian Sciences in Bulgaria	Bulgaria
Polish Journal of Environmental Studies	1230-1485	HARD	Poland
Polish Journal of Soil Science	0079-2985	Ossolineum, Publishing House of the Polish Academy of Sciences	Poland
Prace Vyzkumneho Ustavu Lesniho Hospodarstvi a Myslivosti	0139-5807	Vyzkumny Ustav Lesniho Hospodarstvi a Myslivosti (VULHM) (Forestry & Game Management Research Institute)	Czechoslovakia
Prace z Zakresu Nauk Lesnych	0079-4708	Wydawnictwo Poznanskiego Towarzystwa Przyjaciol Nauk	Poland
Prace z Zakresu Nauk Rolniczych	0079-4708	Wydawnictwo Poznanskiego Towarzystwa Przyjaciol Nauk	Poland
Pratacultural Science	1001-0629	Editorial Board of Pratacultural Science	China
Precision Agriculture	1385-2256	Springer Science + Business Media	Netherlands
Probleme de Agrofitotehnie Teoretica si Aplicata	0254-7279	Institutul de Cercetari pentru Cereale si Plante Tehnice (Research Institute for Cereals and Industrial Crops)	Romania

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Problemy Inzynierii Rolniczej	1231-0093	Blackhorse Scientific Publishers	Poland
Proceedings - International Fertiliser Society	1466-1314	International Fertiliser Society	UK
Proceedings - Soil and Crop Science Society of Florida	0096-4522	Soil and Crop Science Society of Florida	USA
Proceedings of the Florida State Horticultural Society	0886-7283	Florida State Horticultural Society	USA
Proceedings of the Indiana Academy of Science	0073-6767	Indiana Academy of Science	USA
Proceedings of the Japan Academy. Series B	0386-2208	Japan Academy	Japan
Proceedings of the Japanese Society of Sugar Beet Technologists	0912-1048	Kanmi Shigen Shinkokai (Sugar Crop Development Fund)	Japan
Proceedings of the National Academy of Sciences India. Section B	0369-8211	National Academy of Sciences	USA
Proceedings of the National Academy of Sciences of the United States of America	0027-8424	National Academy of Sciences	USA
Proceedings of the New Zealand Grassland Association	0369-3902	New Zealand Grassland Association	New Zealand
Proceedings of the New Zealand Society of Animal Production	0370-2731	New Zealand Society of Animal Production	New Zealand
Proceedings of the Royal Society of London. Series B - Biological Sciences	0962-8452	Royal Society	UK
Proceedings of the Royal Society of Queensland	0080-469X	Royal Society of Queensland Inc.	Australia
Process Biochemistry	1359-5113	Elsevier	UK
Process Safety and Environmental Protection	0957-5820	Institution of Chemical Engineers	UK
Proeftuinnieuws		European Vegetable R&D Centre	Belgium
Progres Agricole et Viticole	0369-8173	Progres Agricole et Viticole	France
Progress in Environmental Science	1460-4094	Arnold	UK
Progress in Plant Protection	1427-4337	Instytut Ochrony Roslin (Institute of Plant Protection)	Poland
Progressive Agriculture	0972-6152	Society for Recent Development in Agriculture	India
Progressive Horticulture	0970-3020	Horticultural Experiments and Training Centre	India
Public Administration and Development	0271-2075	John Wiley & Sons	UK
Publicacion Especial - Estacion Experimental Agroindustrial Obispo Colombres de Tucuman	0328-7300	Estacion Experimental Agroindustrial 'Obispo Colombres'	Argentina
Quarterly Journal of International Agriculture	0049-8599	DLG-Verlag	Germany
Quarterly Newsletter - Tea Research Foundation (Central Africa)	0040-0378	Tea Research Foundation (Central Africa)	Malawi
Quarterly Sugar Industry Report	0023-138X	Sugar Refining Industry Association	Japan
Quaternary Research	0033-5894	Elsevier Inc	USA
Quimica Nova	0100-4042	Sociedad Brasileira de Quimica	Brazil
RABSU - Revista de Agricultura y Biologia de Suelos	0351-1693	Instituto Universitario de Technologia Jose Antonio Anzoategui (IUTJAA)	Venezuela
Radiation and Environmental Biophysics	0301-634X	Springer-Verlag GmbH	Germany
Radiocarbon	0033-8222	Department of Geosciences, University of Arizona	USA
Radovi - Sumarski Institut Jastrebarsko	0351-1693	Sumarski Institut, Forest Research Institue	Croatia
Radovi Poljoprivrednog Fakulteta Univerziteta u Sarajevu (Works of the Faculty of Agriculture University of Sarajevo)	0033-8583	Univerzitet u Sarajevu, Poljoprivredni Fakultet	Bosna Hercegovina
Range Management and Agroforestry	0971-2070	Range Management Society of India	India
Rangeland Journal	1036-9872	Australian Rangeland Society	Australia
Rangelands	0190-0528	Society for Range Management	USA
RAP Publication	1014-191X	FAO Regional Office for Asia and the Pacific	Thailand
Rapport - Fodevareokonomisk Institut	0106-1291	Fodevareokonomisk Institut	Denmark
Rapport fra Skogforskningen	0803-2858	Norsk Institutt for Skogforskning (Norwegian Forest Research Institute)	Norway
Rapporti ISTISAN - Istituto Superiore di Sanita	1123-3117	Istituto Superiore di Sanita	Italy
Remote Sensing of Environment	0034-4257	Elsevier	USA
Renewable Agriculture and Food Systems	0889-1893	CABI Publishing	UK
Renewable Resources Journal	0738-6532	Renewable Natural Resources Foundation (RNRF)	USA
Report - SkogForsk	1103-6648	SkogForsk (Forestry Research Institute of Sweden)	Sweden

Report of the Kyushu Branch of the Crop Science Society of Japan	0285-3507	Kyushu Branch of the Crop Science Society of Japan	Japan
Report of the Taiwan Sugar Research Institute	0257-5493	Taiwan Sugar Research Institute	Taiwan
Reproductive Toxicology	0890-6238	Elsevier	USA
Research Bulletin of the Aichi-ken Agricultural Research Center	0388-7995	Aichi-ken Agricultural Research Center	Japan
Research Bulletin of the Hokkaido National Agricultural Experiment Station	0367-5955	Hokkaido National Agricultural Experiment Station	Japan
Research Bulletin of the Hokkaido University Forests	1347-0981	Hokkaido University Forests	Japan
Research Bulletin of the Niigata University Forests	0918-3302	Faculty of Agriculture, Niigata University	Japan
Research Bulletin of the Tottori University Forests	0082-5379	Tottori University Forests	Japan
Research in Agricultural Engineering	1212-9151	Ustav Zemedelskych a Potravinarskych Informaci	Czechoslovakia
Research in Microbiology	0923-2508	Elsevier SAS	France
Research of Agricultural Modernization	1000-0275	Changsha Institute of Agricultural Modernization, Chinese Academy of Sciences	China
Research on Crops	0972-3226	Gaurav Society of Agricultural Research Information Centre	India
Research Paper - State Forests of New South Wales	1324-3829	State Forests of New South Wales, Research and Development Division	Australia
Research Report - European Forest Institute (EFI)	1238-8785	European Forest Institute (EFI)	Netherlands
Research Report - International Water Management Institute	1026-0862	International Water Management Institute	Sri Lanka
Resource	1076-3333	American Society of Agricultural Engineers	USA
Resources	0921-3449	Elsevier	USA
Restoration Ecology	1061-2971	Blackwell Publishing	USA
Resultat - SkogForsk	1103-4173	SkogForsk (Forestry Research Institute of Sweden)	Sweden
Results - SkogForsk	1103-6222	SkogForsk (Forestry Research Institute of Sweden)	Sweden
Review of Development Economics	1363-6669	Blackwell Publishing	UK
Review of Palaeobotany and Palynology	0034-6667	Elsevier	Netherlands
Review of Urban & Regional Development Studies	0917-0553	Blackwell Publishing	Australia
Reviews of Environmental Contamination and Toxicology	0179-5953	Springer-Verlag	USA
Revista - Facultad Nacional de Agronomia Medellin	0304-2847	Universidad Nacional de Colombia	Colombia
Revista Argentina de Microbiologia	0325-7541	Asociacion Argentina de Microbiologia	Argentina
Revista Argentina de Produccion Animal	0326-0550	Asociacion Argentina de Produccion Animal	Argentina
Revista Arvore	0100-6762	Sociedade de Investigacoes Florestais	Brazil
Revista Biologia (Habana)	0864-3490	Universidad de la Habana	Cuba
Revista Brasileira de Agrociencia	0104-8996	Faculdade de Agronomia Eliseu Maciel, Universidade Federal de Pelotas	Brazil
Revista Brasileira de Botanica	0100-8404	Sociedade Botanica de Sao	Brazil
Revista Brasileira de Ciencia do Solo	0100-0683	Sociedade Brasileira de Ciencia do Solo	Brazil
Revista Brasileira de Engenharia Agricola e Ambiental	1415-4366	Departamento de Engenharia Agricola, Universidade Federal da Paraiba	Brazil
Revista Brasileira de Fruticultura	0100-2945	Sociedade Brasileira de Fruticultura	Brazil
Revista Brasileira de Milho e Sorgo	1676-689X	Associacao Brasileira de Milho e Sorgo	Brazil
Revista Brasileira de Oleaginosas e Fibrosas	1415-6784	Embrapa Algodao	Brazil
Revista Brasileira de Plantas Medicinais	1516-0572	Fundacao do Instituto de Biociencias	Brazil
Revista Brasileira de Sementes	0101-3122	Associacao Brasileira de Tecnologia de Sementes ABRATES	Brazil
Revista Brasileira de Zootecnia	1516-3598	Sociedade Brasileira de Zootecnia	Brazil
Revista Ceres	0034-737X	Editora UFV, Universidade Federal de Vicosa	Brazil
Revista Chapingo. Serie Ciencias Forestales y del Ambiente	0186-3231	Universidad Autonoma Chapingo	Mexico
Revista Chapingo. Serie Horticultura	0186-3231	Universidad Autonoma Chapingo	Mexico
Revista Chapingo. Serie Ingenieria Agricola	0186-3231	Universidad Autonoma Chapingo	Mexico
Revista Chapingo. Serie Ingenieria Agropecuaria	0186-3231	Universidad Autonoma Chapingo	Mexico
Revista Chilena de Historia Natural	0716-078X	Sociedad de Biologia de Chile	Chile
Revista Ciencia Agronomica	0045-6888	Centro de Ciencias Agrarias da Universidade Federal do Ceara	Brazil
Revista Cientifica Agropecuaria	0329-3602	Facultad de Ciencias Agropecuarias, Universidad Nacional de Entre Rios	Brazil
Revista Cientifica Rural	1413-8263	INTEC	Brazil
Revista de Agricultura (Piracicaba)	0034-7655	Revista de Agricultura	Brazil

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Revista de Biologia (Lisboa)	0034-7736	Museu, Laboratorio e Jardim Botanico	Portugal
Revista de Biologia Tropical	0034-7744	Universidad de Costa Rica	Costa Rica
Revista de Ciencias Agrarias	1517-591X	Faculdade de Ciencias Agrarias do Para, Ministerio da Educacao	Brazil
Revista de la Ciencia del Suelo y Nutricion Vegetal	0717-635X	Sociedad Chilena de la Ciencia del Suelo	Chile
Revista de la Facultad de Agronomia (La Plata)	0041-8676	Facultad de Ciencias Agrarias y Forestales, Universidad Nacional de La Plata	Argentina
Revista de la Facultad de Agronomia (Universidad de Buenos Aires)	0325-9250	Facultad de Agronomia, Universidad de Buenos Aires	Argentina
Revista de la Facultad de Agronomia	0041-8285	Universidad Central de Venezuela	Venezuela
Revista do Instituto Adolfo Lutz	0073-9855	Instituto Adolfo Lutz	Brazil
Revista Espanola de Estudios Agrosociales y Pesqueros	1575-1198	Ministerio de Agricultura, Pesca y Alimentacion	Spain
Revista Fitotecnia Mexicana	0187-7380	Sociedad Mexicana de Fitogenetica	Mexico
Revista Forestal Centroamericana	1021-0164	Centro Agronomico Tropical de Investigacion y Ensenanza	Costa Rica
Revista Forestal Venezolana	0556-6606	Facultad de Ciencias Forestales y Ambientales, Universidad de Los Andes	Venezuela
Revista Forestal Yvyrareta Pais de Arboles	0328-8854	Facultad de Ciencias Forestales	Argentina
Revista Fruticola	0716-534X	Copefrut S.A.	Chile
Revista Industrial y Agricola de Tucuman	0370-5405	Estacion Experimental Agroindustrial ‘Obispo Colombres’	Argentina
Revista Internacional de Contaminacion Ambiental	0188-4999	Universidad Autonoma de Tlaxcala	Mexico
Revista Latinoamericana de Microbiologia	0034-9771	Asociacion Latinoamericana de Microbiologia	Mexico
Revista Padurilor	1583-7890	Ministerul Industrializarii Lemnului si Materialelor de Constructii (MILMC)	Romania
Revista Universidade Rural. Serie Ciencias da Vida	0104-7264	Universidade Federal Rural do Rio de Janeiro (UFRRJ)	Brazil
Revista Universidade Rural. Serie Ciencias Exatas e da Terra	1414-0578	Universidade Federal Rural do Rio de Janeiro (UFRRJ)	Brazil
Revue Agricole et Sucriere de l’Ile Maurice	0370-3576	Societe de Technologie Agricole et Sucriere de l’Ile Maurice	Mauritius
Revue Forestiere Francaise	0035-2829	Ecole Nationale du Genie Rural des Eaux et des Forets (ENGREF)	France
Revue Horticole Suisse	0370-5323	Revue Horticole Suisse, Centre de Lullier	Switzerland
Revue Suisse d’Agriculture	0375-1325	Station Federale de Recherches Agronomiques de Changins	Switzerland
Rivista di Agronomia	0035-6034	Gruppo Calderini Edagricole Srl	Italy
Rivista di Economia Agraria	0035-6190	Societa Editrice il Mulino	Italy
Rivista di Frutticoltura e di Ortofloricoltura	0016-2310	Gruppo Calderini Edagricole Srl	Italy
Rivista di Idrobiologia	0048-8399	Universita degli Studi di Perugia, Dipartimento di Biologia Animale ed Ecologia	Italy
Rivista di Ingegneria Agraria	0304-0593	Universita di Bologna, Facolta di Agraria	Italy
Rivista di Viticoltura e di Enologia	0370-7865	Unione ex Allievi della Scuola di Viticoltura e di Enologia di Conegliano	Italy
Roczniki Naukowe Zootechniki	0137-1657	Instytut Zootechniki	Poland
Roczniki Panstwowego Zakladu Higieny	0035-7715	Panstwowy Zaklad Higieny	Poland
Romanian Agricultural Research	1222-4227	Institutul de Cercetari pentru Cereale si Plante Tehnice (Research Institute for Cereals and Industrial Crops)	Romania
Rosliny Oleiste	1233-8273	Instytut Hodowli i Aklimatyzacji Roslin	Poland
Rostlinna Vyroba	0370-663X	Ustav Zemedelskych a Potravinarskych Informaci	Czech Republic
Rozprawy - Akademia Rolnicza w Szczecinie	0239-6467	Wydawnictwo Akademii Rolniczej	Szczecin
Rozprawy i Monografie/Dissertations and Monographs	1509-3018	Wydawnictwo UWM	Poland
Rural Eco-Environment	1001-5906	China Environmental Science	China
Rural Sociology	0036-0112	Rural Sociological Society	USA
Russian Agricultural Sciences	1068-3674	Allerton Press	USA
Russian Journal of Ecology	1067-4136	MAIK Nauka/Interperiodica Publishing	Russia
Russian Journal of Plant Physiology	1021-4437	International Academic Publishing Company Nauka/Interperiodica	Russia
Russian Meteorology and Hydrology	1068-3739	Allerton Press	USA
SA Fruit Journal	1683-4577	Deciduous Fruit Producers Trust	South Africa
SA Waterbulletin	0258-2244	Water Research Commission	South Africa
Sarhad Journal of Agriculture	1016-4383	NWFP Agricultural University	Pakistan
Scandinavian Journal of Forest Research	0282-7581	Taylor & Francis	UK
Schriften aus der Forstlichen Fakultat der Universitat Gottingen und der Niedersachsischen Forstlichen Versuchsanstalt	0344-5666	J.D. Sauerlander’s Verlag	Germany

Schriftenreihe der Eidgenossischen Forschungsanstalt fur Agrarwirtschaft und Landtechnik	0257-9200	Eidgenossische Forschungsanstalt fur Agrarwirtschaft und Landtechnik (FAT)	Switzerland
Schriftenreihe der Forschungsgesellschaft fur Agrarpolitik und Agrarsoziologie e.V. Bonn	0179-4485	Forschungsgesellschaft fur Agrarpolitik und Agrarsoziologie e.V.	Germany
Schweizerische Zeitschrift fur Forstwesen	0036-7818	Schweizerischer Forstverein	Switzerland
Science Bulletin of the Faculty of Agriculture	1347-0159	Kyushu University Faculty of Agriculture Publications	Japan
Science for Conservation	1173-2946	Department of Conservation	New Zealand
Science in China Series C - Life Sciences	1006-9305	Science in China Press	China
Science in New Guinea	0310-4303	University of Papua New Guinea	Papua New Guinea
Science of the Total Environment	0048-9697	Elsevier	Netherlands
Scientia Agraria	1519-1125	Universidade Federal do Parana	Brazil
Scientia Agraria Paranaensis	1677-4310	EDUNIOESTE	Brazil
Scientia Agricola	0103-9016	Universidade de Sao Paulo, Escola Superior de Agricultura Luiz de Queiroz (ESALQ)	Brazil
Scientia Agricultura Sinica	0578-1752	Chinese Academy of Agricultural Sciences (CAAS), Scientech Documentation and Information Centre	China
Scientia Agriculturae Bohemica	0582-2343	Ceska Zemedelska Univerzita v Praze	Czechoslovakia
Scientia Forestalis	1413-9324	Instituto de Pesquisas e Estudos Florestais (IPEF)	Brazil
Scientia Horticulturae	0304-4238	Elsevier	Netherlands
Scientia Silvae Sinicae	1001-7488	Chinese Academy of Forestry	China
Scientific Horticulture		Scientific Publishers (India)	India
Scientific Journal of King Faisal University (Basic and Applied Sciences)	1658-0311	King Faisal University Press	Saudi Arabia
Scottish Forestry	0036-9217	Royal Scottish Forestry Society	UK
Selbyana	0361-185X	Marie Selby Botanical Gardens	USA
Selected Bibliography on Irrigation and Water Resources Management	1015-1680	International Irrigation Management Institute (IIMI)	Sri Lanka
Selskostopanska Tekhnika	0037-1718	Akademiya na Selskostopanskite Nauki	Bulgaria
Serie de Documents de Travail - Agropolis International		Agropolis International	France
Serie Divulgativa - CENICANA	0121-6457	Centro de Investigacion de la Cana de Azucar de Colombia	Colombia
Sherwood - Foreste ed Alberi Oggi	1590-7805	Compagnia delle Foreste	Italy
Silva Balcanica	1311-8706	Bulgarian Academy of Sciences, Forest Research Institute	Bulgaria
Silva Fennica	0037-5330	Finnish Society of Forest Science	Finland
Silva Gandavensis	0587-1476	Laboratory of Forestry, University of Gent	Belgium
Silva Lusitana	0870-6352	Estacao Florestal Nacional	Portugal
Ethiopian Journal of Science	0379-2897	Faculty of Science	Ethopia
Singapore Journal of Primary Industries	0129-6485	Agri-Food and Veterinary Authority of Singapore	Singapore
Sistemas de Producao - Embrapa Agropecuaria Oeste	1676-4129	Embrapa Agropecuaria Oeste	Brazil
Small Fruits Review	1522-8851	Food Products Press	USA
Social Studies of Science	0306-3127	Sage Publications	USA
Societe et Environnement	1370-6233	FUSAGx	Belgium
Society & Natural Resources	0894-1920	Routledge	UK
Sociologia Ruralis	0038-0199	Blackwell Publishing	UK
Sodininkyste ir Darzininkyste	0208-4212	Lietuvos Sodininkystes ir Darzininkystes Institutas (Lithuanian Institute of Horticulture)	Lithuania
Sodobno Kmetijstvo	0350-1655	CZD Kmecki Glas	Slovenia
Soil & Sediment Contamination	1058-8337	Taylor & Francis	USA
Soil & Tillage Research	0167-1987	Elsevier	Netherlands
Soil Biology & Biochemistry	0038-0717	Elsevier Ltd	UK
Soil Microorganisms	0912-2184	Japanese Society of Soil Microbiology	Japan
Soil Science	0038-075X	Lippincott Williams & Wilkins	USA
Soil Science and Plant Nutrition	0038-0768	Japanese Society of Soil Science and Plant Nutrition	Japan
Soil Science Society of America Journal	0361-5995	Soil Science Society of America Inc.	USA
Soil Survey Horizons	NA	Soil Science Society of America Inc.	USA
Soil Use and Management	0266-0032	CABI Publishing	UK
Soils and Fertilizers (Beijing)	1002-0616	Editorial Department of Soils and Fertilizers	China
South African Journal of Botany	0254-6299	NISC Pty Ltd	South Africa

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
South African Journal of Enology and Viticulture	0253-939X	South African Society for Enology and Viticulture	South Africa
South African Journal of Plant and Soil	0257-1862	Forum Press International	South Africa
South African Journal of Science	0038-2353	Academy of Science of South Africa (ASSAf)	South Africa
South Asian Anthropologist	0257-7348	Serials Publications	India
South China Fruits	1001-4195	Citrus Research Institute	India
South Indian Horticulture	0038-3473	South Indian Horticultural Association, CAAS	India
Southeastern Naturalist	1528-7092	Humboldt Field Research Institute	USA
Southern African Forestry Journal	0038-2167	Southern African Institute of Forestry, Suider-Afrikaanse Instituut van Boswese	South Africa
Southern Journal of Applied Forestry	0148-4419	Society of American Foresters	USA
Southwest China Journal of Agricultural Sciences	1001-4829	Editorial Department of Southwest China Journal of Agricultural Sciences	China
Southwestern Naturalist	0038-4909	Southwestern Association of Naturalists	USA
Soybean Science	1000-9841	Heilongjiang Academy of Agricultural Sciences	China
Spanish Journal of Agricultural Research	1695-971X	Spanish National Institute for Agricultural and Food Research and Technology (INIA)	Spain
Special Circular - Ohio Agricultural Research and Development Center	0736-8003	Ohio Agricultural Research and Development Center, Ohio State University	USA
Spiegel der Forschung	0176-3008	Justus-Liebig-Universitat Giessen	Germany
Sri Lanka Journal of Tea Science	1010-4208	Tea Research Institute of Sri Lanka	Sri Lanka
Sri Lankan Journal of Agricultural Sciences	1013-8137	National Agricultural Society of Sri Lanka	Sri Lanka
Sudan Journal of Agricultural Research	1561 - 770X	Agricultural Research Corporation	Sudan
Suelos Ecuatoriales	0562-5351	Sociedad Colombiana de la Ciencia del Suelo	Colombia
Sugar Cane International	0265-7406	Agra Europe (London) Ltd	UK
Sugar Journal	0039-4734	Kriedt Enterprises Ltd	USA
Sugar Tech	0972-1525	Society for Sugar Research and Promotion	India
Sultan Qaboos University Journal for Scientific Research - Agricultural and Marine Sciences	1026-0544	Sultan Qaboos University	Oman
Sumarski List	0373-1332	Hrvatsko Sumarsko Drustvo (Croatian Forestry Society)	Croatia
Summa Phytopathologica	0100-5405	Grupo Paulista de Fitopatologia	Brazil
Suo	0039-5471	Suoseura - Finnish Peatland Society	Finland
Sustainable Development	0968-0802	John Wiley & Sons	UK
Sveriges Utsadesforenings Tidskrift	0039-6990	Sveriges Utsadesforening	Sweden
Swaziland Sugar Journal		Swaziland Sugar Association	Swaziland
Sylvatrop	0015-0022	Ecosystems Research and Development Bureau	Philippines
Sylwan	0039-7660	Polskie Towarzystwo Lesne	Poland
Symbiosis (Rehovot)	0334-5114	Balaban Publishers	Israel
Systematic and Applied Microbiology	0723-2020	Elsevier GmbH	Germany
Systematics and Geography of Plants	1374-7886	Jardin Botanique National de Belgique	Belgium
Tabacco	1124-3791	Istituto Sperimentale per il Tabacco	Italy
Taiwan Journal of Forest Science	1026-4469	Taiwan Forestry Research Institute	Taiwan
Taiwan Sugar	0492-1712	Taiwan Sugar Corporation	Taiwan
Taiwanese Journal of Agricultural Chemistry and Food Science	1605-2471	Agricultural Chemical Society of Taiwan and Taiwan Association for Food Science and Technology	Taiwan
Talanta	0039-9140	Elsevier	Netherlands
Tanzania Journal of Agricultural Sciences	0856-664X	Faculty of Agriculture, Sokoine University of Agriculture	Tanzania
Tanzania Journal of Science	0856-1761	University of Dar es Salaam, Faculty of Science	Tanzania
TAO - Terrestrial	1017-0839	Chinese Geoscience Union	China
Tarim ve Koy	1300-8331	Yayin Dairesi Baskanligi	Turkey
Tasforests	1033-8306	Forestry Tasmania, Division of Forest Research and Development	Australia
Tea	1015-7174	Tea Research Foundation of Kenya	Kenya
Tearmann	1649-1009	Faculty of Agriculture, University College Dublin	UK
Technical Report - Koninklijk Nederlands Meteorologisch Instituut	0169-1708	Koninklijk Nederlands Meteorologisch Instituut	Netherlands
Technical Reports Series - International Atomic Energy Agency	0074-1914	International Atomic Energy Agency (IAEA)	Austria

Technote (Darwin)	0158-2755	Department of Industries & Development, Northern Territory	Australia
Tekhnika v Sel'skom Khozyaistve	0131-7105	Mezhdunarodnyi Tsentr Nauchnoi i Tekhnicheskoi Informatsii	Russia
Teknik Bulten - Orman Bakanligi Dogu Akdeniz Ormancilik Arastirma Enstitusu	1300-7912	Dogu Akdeniz Ormancilik Arastirma Enstitusu	Turkey
Tellus A	0280-6495	Blackwell Publishing	Denmark
Tellus B	0280-6509	Blackwell Publishing	Denmark
Termeszetvedelmi Kozlemenyek	1216-4585	Magyar Biologiai Tarsasag	Hungary
Terra	0187-5779	Sociedad Mexicana de la Ciencia del Suelo A.C.	Mexico
Tests of Agrochemicals and Cultivars	0951-4309	Association of Applied Biologists	UK
Thai Journal of Agricultural Science	0049-3589	Agricultural Science Society of Thailand	Thailand
Theoretical and Applied Climatology	0177-798X	Springer-Verlag	Austria
Tobacco Research	0379-055X	Indian Society of Tobacco Science	India
Tohoku Journal of Crop Science	0911-7067	Tohoku Branch, The Crop Science Society of Japan	Japan
Toxicological Sciences	1096-6080	Oxford University Press	USA
Toxicology	0300-483X	Elsevier Ireland	Irish Republic
Toxicology Letters	0378-4274	Elsevier Ireland	Irish Republic
Toxicon	0041-0101	Elsevier	Netherlands
Traktory i Sel'skokhozyaistvennye Mashiny	0235-8573	Mashinostroenie	Russia
Transactions of the ASAE	0001-2351	American Society of Agricultural Engineers	USA
Transactions of the Chinese Society of Agricultural Engineering	1002-6819	Chinese Society of Agricultural Engineering	China
Transactions of the Estonian Agricultural University	1406-4049	Eesti Pollumajandusulikool	Estonia
Transport in Porous Media	0169-3913	Springer Science + Business Media	Netherlands
Tree Physiology	0829-318X	Heron Publishing	Canada
Tree Planters' Notes	0096-8714	United States Department of Agriculture, Forest Service	USA
Trees: Structure and Function	0931-1890	Springer-Verlag GmbH	Germany
Trends in Biotechnology	0167-7799	Elsevier	UK
Trends in Ecology & Evolution	0169-5347	Elsevier Ltd	UK
Tropenlandwirt	0173-4091	Verband der Tropenlandwirte Witzenhausen	Germany
Tropical Agricultural Research	1016-1422	Postgraduate Institute of Agriculture (PGAI), University of Peradeniya	Sri Lanka
Tropical Agriculture	0041-3216	University of the West Indies Press	Trinidad and Tobago
Tropical Agriculture Association Newsletter	0954-6790	Tropical Agriculture Association	UK
Tropical Agriculture Technical Memorandum	1329-6671	CSIRO Tropical Agriculture	Australia
Tropical and Subtropical Agroecosystems	1870-0462	Facultad de Medicina Veterinaria y Zootecnia, Universidad Autonoma de Yucatan	Mexico
Tropical Ecology	0564-3295	International Society for Tropical Ecology	India
Tropical Forestry	0910-5115	Japan International Forestry Promotion and Cooperation Center	Japan
Tropical Grasslands	0049-4763	Tropical Grassland Society of Australia	Australia
Tropical Science	0041-3291	Whurr Publishers	UK
Tropicultura	0771-3312	AGRI-Overseas	Belgium
Tuexenia	0722-494X	Floristisch-Soziologische Arbeitsgemeinschaft e.V.	Germany
Turf Professional	0031-224X	Nelson Communications Ltd.	UK
Turkish Journal of Agriculture and Forestry	1300-011X	TUBITAK	Turkey
Turkish Journal of Botany	1300-008X	TUBITAK	Turkey
Turkish Journal of Field Crops	1301-1111	Society of Field Crop Science	Turkey
Umweltwissenschaften und Schadstoff-Forschung	0934-3504	Ecomed Publishers	Germany
Unasylva (English ed.)	0041-6436	Food and Agriculture Organization of the United Nations (FAO)	Italy
University of Aden Journal of Natural and Applied Sciences	1606-8947	University of Aden	Yemen
Uspekhi Sovremennoi Biologii	0042-1324	MAIK Nauka/Interperiodica Publishing	Russia
Uttar Pradesh Journal of Zoology	0256-971X	Uttar Pradesh Zoological Society	India
Vadose Zone Journal	1539-1663	Soil Science Society of America Inc.	USA
Vaekst	0109-4947	Hedeselskabet	Denmark
Van Vigyan	0970-3071	Society of Indian Foresters	India
Vaniki Sandesh	0972-5598	State Forest Research Institute (SFRI)	India
Vegetable Crops Research Bulletin	1506-9427	Instytut Warzywnictwa (Research Institute of Vegetable Crops RIVC)	Poland
Vegetable Science	0970-6585	Indian Society of Vegetable Science	India

(Continued)

Table J2 (Continued)

Title	ISSN	Publisher	Publisher country
Vegetation History and Archaeobotany	0939-6314	Springer-Verlag GmbH	Germany
Verbondsnieuws	0771-3851	Belgische Sierteelt en Groenvoorziening	Belgium
Visnik Agrarnoi Nauki	0868-8532	Agrarna Nauka	Ukraine
Vitis	0042-7500	Royal Botanic Gardens	UK
WANATCA Yearbook	0312-8997	West Australian Nut and Tree Crop Association	Australia
Wasser und Abfall	1436-9095	Friedr. Vieweg & Sohn Verlagsgesellschaft mbH	Germany
Waste Management & Research	0734-242X	Friedr. Vieweg & Sohn Verlagsgesellschaft mbH	Poland
Wastelands News	0970-9762	Society for Promotion of Wastelands Development	India
Water and Environmental Management	0951-7359	Institution of Water and Environmental Management	UK
Water Environment Research	1061-4303	Water Environment Research Foundation	USA
Water International	0250-8060	International Water Resources Association (IWRA)	USA
Water Policy	1366-7017	IWA Publishing	UK
Water Quality Research Journal of Canada	1201-3080	Canadian Association on Water Quality	Canada
Water Reports	1020-1203	Food and Agriculture Organization of the United Nations (FAO)	Italy
Water Research (Oxford)	0043-1354	Elsevier	UK
Water Resources Management	0920-4741	Springer Science + Business Media	Netherlands
Water Resources Research	0043-1397	American Geophysical Union	USA
Water SA	0378-4738	Water Research Commission	South Africa
Water Science and Technology	0273-1223	IWA Publishing	UK
Water Science and Technology: Water Supply	1606-9749	IWA Publishing	UK
Water Wheel	0258-2244	Water Research Commission	South Africa
Weed Biology and Management	1444-6162	Blackwell Publishing	Australia
Weed Research (Oxford)	0043-1737	Blackwell Publishing	UK
Weed Science	0043-1745	Weed Science Society of America	USA
Weed Technology	0890-037X	Weed Science Society of America	USA
Western Journal of Applied Forestry	0885-6095	Society of American Foresters	USA
Western North American Naturalist	1527-0904	Brigham Young University	USA
Wetlands	0277-5212	Society of Wetland Scientists	USA
Wetlands Ecology and Management	0923-4861	Springer Science + Business Media	Netherlands
Wiadomosci Botaniczne	0043-5090	W. Szafer Institute of Botany, Polish Academy of Sciences	Poland
Wiadomosci Instytutu Melioracji i Uzytkow Zielonych	0509-6677	Wydawnictwo IMUZ	Poland
Wildlife Research	1035-3712	CSIRO Publishing	Australia
Willdenowia	0511-9618	Botanischer Garten und Botanisches Museum Berlin-Dahlem	Germany
Wissenschaftliche Zeitschrift der Technischen Universitat Dresden	0043-6925	Technischen Universitat Dresden	Germany
Woda Srodowisko Obszary Wiejskie	1642-8145	Instytut Melioracji i Uzytkow Zielonych (Institute for Land Reclamation and Grassland Farming)	Poland
Wood and Fiber Science	0735-6161	Society of Wood Science and Technology	USA
Wool Technology and Sheep Breeding	0043-7875	University of New England	Australia
World Journal of Microbiology & Biotechnology	0959-3993	Springer Science + Business Media	Netherlands
World Soil Resources Reports	0532-0488	Food and Agriculture Organization of the United Nations (FAO)	Italy
World Water and Environmental Engineering	1354-313X	Faversham House Group Ltd	UK
Wuhan University Journal of Natural Sciences	1007-1202	Wuhan University Journal	China
WWT - Water & Waste Treatment	0950-6651	Faversham House Group Ltd	UK
Zahradnictvi (Horticultural Science)	0862-867X	Ustav Zemedelskych a Potravinarskych Informaci	Czechoslovakia
Zeitschrift fur Bewasserungswirtschaft	0049-8602	DLG-Verlag	Germany
Zeitschrift fur Geomorphologie	0044-2798	Gebruder Borntraeger Verlagsbuchhandlung	Germany
Zeitschrift fur Naturforschung. Section C - Biosciences	0939-5075	Verlag der Zeitschrift fur Naturforschung	Germany
Zeitschrift fur Okologie und Naturschutz	0940-5178	Urban & Fischer Verlag GmbH & Co. KG	Germany
Zeitschrift fur Pflanzenkrankheiten und Pflanzenschutz	0340-8159	Verlag Eugen Ulmer GmbH	Germany
Zoologicheskii Zhurnal	0044-5134	Nauka	Russia
Zootecnia Tropical	0798-7269	Fondo Nacional de Investigaciones Agropecuarias (FONAIAP)	Venezuela

*Abstracted from CABI Publishing (http://www.cabi-publishing.org/AboutUs.asp).

reasons and this information must be ferreted out by diligent researchers. Many examples could be cited where critical data were published in rather obscure sources, only to be ‘discovered’ later and finally put to good use. Such is the case no doubt with many of the journals listed in Table J2 that are relatively unknown in developed countries where busy researchers have little time to scan the world literature. It is thus hoped that the list in Table J2 will serve as an eye opener and heads-up alert not only to soil scientists but other researchers in related fields who may not be aware of efforts in developing nations or sources of information in rather specialized journals in related disciplines.

Charles W. Finkl

K

KAME

A ridge of badly sorted sand and gravel, originally deposited from meltwater running on the upper surface of a glacier. A rudimentary bedding is normally seen, commonly disrupted by the disappearance of the ice, which originally supported the deposit.

Cross-reference

Ice Erosion

KARST

A type of landscape characteristic of regions underlain by relatively soluble rock, most notably limestone. Solution of the rock leads to a topography marked by numerous abrupt ridges, fissures, channels, sink-holes, swallow-holes and caverns. Little or no surface water is evident and where streams occur they tend to be intermittent, and in some cases disappear down swallow-holes. Virtually all water-circulation and drainage is underground and soil and vegetation is scanty. The name comes via German from the Serbo-Croat *Kras*, used of a high barren limestone region south of Ljubljana in the Balkans. Figure K1 is of giant karst from the vicinity of the Grasberg Mine in West Papua. Karst landscapes are like immense flow through tea bags. Any water added to the surface rapidly descends through fissures and caves. Soil particles may be carried downwards too, so that erosion is essentially vertical, rather than lateral as is usually the case in water and wind erosion. The leading authority is Ford and Williams (2007).

Bibliography

Ford, D.C., and Williams, P.W., 2007. *Karst Geomorphology and Hydrology.* Chichester, UK: Wiley, 576 pp.

KASTANOZEMS

Kastanozems are grassland soils like the chernozems but from the drier, short grass regions. The surface horizons are humus-rich and brownish (“chestnut”) colored, with secondary calcite in the subsurface. This article is based on FAO (2001).

Connotation. From the Latin for chestnut *castanea*, combined with the Russian *zemlja*, earth, land.

Definition. FAO (2001) defines Kastanozems as having

1. a mollic horizon with a moist chroma of more than 2 to a depth of at least 20 cm, or having this chroma directly below the depth of any plow layer, and
2. concentrations of secondary carbonates within 100 cm from the soil surface, and
3. no diagnostic horizons other than an argic, calcic, cambic, gypsic, petrocalcic, petrogypsic or vertic horizon.

Parent material. Kastanozems have formed on a wide variety of surficial sediments, with post-glacial loess being particularly characteristic.

Environment. Kastanozems are found in the drier parts of the major grasslands such as the European steppe, the North American prairie and the South American pampas. Climatic gradients in the Kastanozem have a pronounced effect on their physical appearance. In Russia, for example, wetter conditions in the north produce darker and thicker horizons than those found in Kastanozems in the more arid south.

Distribution. There are about 465 million ha of Kastanozems worldwide. In temperate regions they border the wetter areas where Chernozems are found, and are associated with Gypsisols and Calcisols in drier parts, bordering on alkali soils in the driest. In the tropics they are associated with Phaeozems. Figure K2 shows the global distribution.

Characteristics. Kastanozems mostly develop into AhBC profiles with a brown Ah-horizon of medium depth (50 cm or so) and a granular or fine blocky structure. The rest of the profile is lighter in color, typically a cinnamon to pale yellow, massive to coarsely prismatic cambic or argic B horizon, with

Figure K1 Giant karst, Grasberg Mine, West Papua. The horizontal dimension of the photograph is approximately 20 metres.

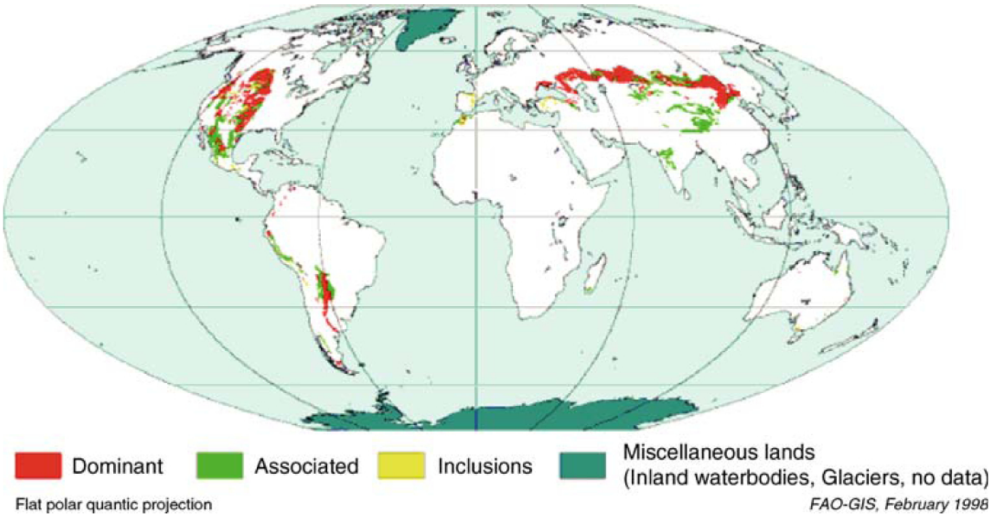


Figure K2 Global distribution of Kastanozems.

a secondary accumulation of calcite and/or gypsum within or below it. This feature is shared with the Chernozems, but distinguishes them from the Phaeozems. The northern Eurasian Kastanozems have Ah-horizons some 50 cm thick, dark brown and with a granular or fine blocky structure, grading into cinnamon or pale yellow massive to coarse prismatic B horizons. Argic B horizons are reported to be more intense in coloration in Luvic compared with other Kastanozems. Dark Kastanozems grade morphologically into Chernozems, whereas light Kastanozems grade into Calcisols.

Krotovinas occur in almost all Kastanozems but less abundantly than in chernozems.

Kastanozems are similar to chernozems in physical properties, though a lower humus content in the surface layer (more pronounced in the lighter Kastanozems) leads to a weaker microaggregation. This soil is consequently denser packed, with a smaller total pore volume (40–55%), and capacity for storing water, and a lower permeability to water. Kastanozems dry out to great depth in the dry season. In the wet season they may be incompletely moistened even after heavy rains on account of low porosity. A 'physiologically dead' horizon occurs below the limit of wetting, receiving neither water from above, nor from below by capillary rise.

Kastanozems are chemically rich soils with a pH slightly above neutral hear the surface, rising to as much as 8.5 at depth. The cation exchange capacity is 25–30 cmol(+)/kg dry soil, with Ca^{2+} and Mg^{2+}-ions as the dominant ions on the exchange complex. The organic soil fraction of the surface horizon has a C/N ratio around 10 (comparable to chernozems). The soil-pH is slightly above 7.0 but may increase to a value around 8.5 at some depth. Accumulations of lime and gypsum have already been noted. At greater depth there may be accumulations of more soluble salts, but not normally to the degree where plant growth is inhibited.

The typical short grass vegetation of the Kastanozems has low biodiversity and is dominated by ephemera (early ripening species). Aboveground the dry biomass is only between 0.8–1 t ha^{-1}, while the dry root mass lies between 3–4 t ha^{-1}. More than 50% of all roots are concentrated in the upper 25 cm and few roots extend down to deeper than 1 m. Most of grass vegetation dies each season. The Ah horizon of Kastanozems has an organic matter content of about 2 to 4%. It seldom exceeds 5%.

Origin. The principal genetic feature to be explained is the presence of secondary calcite in the B horizon, commonly with gypsum deeper down and salt even deeper. The components of these secondary materials are leached by water percolating downwards in the wet season. In wetter regions the calcite precipitates approximately 1 m down, gypsum accumulates at about 150 to 200 cm in drier regions, and in the driest climates salt may accumulate below. In some situations, notably in western Canada, the salt may originate in ground waters that have traveled long distances.

Argic B horizons are found in some Kastanozems and are somewhat enigmatic. They may be fossil, be normally translocated, or, less likely, the result of the destruction of clay high in the profile followed by its reconstitution at depth.

Use. The main obstacle to the agricultural use of these potentially rich soils is drought. Irrigation, with the threat of secondary salinization, is almost always necessary for high yields. The principal crops are small grains, and where irrigation is practiced vegetable. A major problem, especially under fallow, is wind erosion. Another serious problem on Kastanozems is overgrazing, extensive grazing being another important use for these soils.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 p.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag. 130 pp.

Cross-references

Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils

KOPPEN

See *Climate* and *Factors of Soil Formation*.

KROTOVINAS

Or Crotovinas. An animal burrow that has become filled with organic matter and soil material generally common in grassland soils: Chernozems, Kastanozems, Phaeozems.

KUBIENA BOX

See *Micromorphology*.

L

L HORIZON

See *Horizon*, *Profile*, *Horizon Designations*.

LABILE POOL

The labile pool may be best defined as an arbitrary measure of the ions in the solid phase which may exchange rapidly with ions of the same element in solution, so as to replace these ions in solution as they become lost from the system through plant uptake, leaching, or other methods. The labile pool of a nutrient should not be confused with the plant available nutrient pool but should rather be thought of as a portion of it. The labile pool usually represents the portion of the nutrient held in the solid phase of soil by adsorption to surfaces of the particulate matter (including precipitates). Therefore, a labile pool would exist for most of the plant nutrients, which are adsorbed on surfaces in the soil. While research exists on many of these nutrients (Dyanand and Sinha, 1985; Lopez and Graham, 1972), the primary nutrient studied is phosphorus (P) and much of the following discussions will focus on P.

Concepts

Consider the following equilibria (Larsen, 1967) between pools or reservoirs of P in soil:

Soil solution P ↔ labile soil P ↔ nonlabile P

The equilibrium is very rapid between labile and soil solution P whereas true equilibrium is seldom, if ever, established between labile and nonlabile pools of soil P. The equilibrium of one system is related to the equilibrium of the other due to the dynamic nature of the two systems. When phosphate is added or removed from the system, it drives the equilibrium reaction between solution P and labile P, which in turn, drives the reaction between labile P and nonlabile P (Barber, 1995). The former proceeds very quickly whereas the latter proceeds quite slowly. For this reason, it is arbitrary to compartmentalize soil P in his manner, since exact boundaries cannot be determined (Olsen and Khasawneh, 1980). They discuss the relationship between labile and nonlabile pools as being a kinetic, and differentiate a separate, mechanistic point of view of adsorbed versus crystalline P. Adsorbed refers to P held on active surfaces in the soil, whereas crystalline P refers to P compounds either as reaction products or as structurally part of the soil matrix. They report that the two classification systems are not equivalent, although a great deal of overlap exists.

Measuring labile pool nutrients

Labile pool is usually defined as the fraction of the solid phase of soils, which is occupied by a particular nutrient, as measured by radioactive isotopic substitution with a carrier-free isotope of the nutrient added to soil solution (Barber, 1995). In the case of P, the key is the length of time allowed for the equilibrium reaction to proceed. This is rapid and commonly occurs within 24 to 48 hours and is usually arbitrarily set at one of these two time intervals. It is the arbitrary nature of the measurement that leads most authors to agree that the definitive value is that which is obtained through isotopic substitution.

The use of isotopic tracers is discussed by several authors including Barber (1995), Mengel (2001), and Olsen and Khasawneh (1980) along with other methods of approximating labile pool measurements. These methods include resin-extraction, chemical extractants and adsorption experiments.

For P, the tracer technique involves the isotopic exchange between soil P and labeled ^{32}P for a specific time and for a specific set of conditions (reviewed by Fried and Broeshart (1967) and Olsen and Khasawneh (1980)). When isotopically exchangeable P is determined by field studies (crop removal during a growing season) the resulting value is referred to as the *L* value. The laboratory equivalent of the *L* value is the *E* value and is measured over a specific (but shorter) time period. *E* values are usually expressed as E_t where t = time of equilibration.

Another method of estimating the labile pool of P involves a saturated anion-exchange resin, which is added to the soil in sufficient quantity to lower solution P levels to near zero. This results in P desorption (Barber, 1995). Again a standard length of time and experimental conditions are critical. It is argued by Barber that the resin would act as a sink for P similar to plant roots and therefore, resin exchange would be a close approximation of P uptake by plants during the growing season. Olsen and Khasawneh (1980) report that resin-extractable P is only a fraction of labile P but these two measurements are highly correlated.

A third method of estimating labile P is by adsorption experiments. These basically work in reverse of the desorption created by resin exchange. Adsorption experiments measure the amount of P that disappears from solution when varying levels of P are supplied and relate what has disappeared to what is left in solution. Adsorption estimation of labile P is reviewed by Olsen and Khasawneh (1980) who report that the adsorption isotherm is not the same as the desorption isotherm and throws doubt into the usefulness of using adsorption experiments for determining labile P.

Kamprath and Watson (1980) provide a review of the fourth method of estimating labile pool – chemical extraction. Chemical extraction was developed out of a need for soil testing for nutrient levels that would correlate with plant growth and fertilizer response. Because of the dynamic nature of soil P pools (solution vs labile vs nonlabile), extractants usually measure all or a part of each of these pools. This relates back to the earlier discussion of plant removal of solution P leading to movement of P out of the labile P, which in turn leads to movement of nonlabile P. Plant response correlations were best, obtained when some portion of the nonlabile pool was extracted. While this system is not a good measure of the labile pool, it does provide insight for plant responses to fertilizers and there is a good correlation between labile P and extractable P for many closely related soils (Olsen and Khasawneh, 1980). The best use of extraction techniques is for recently fertilized fields where the equilibrium relationships are transient because of the disequilibrium caused by the addition of a highly soluble P source greatly increasing solution P.

Importance to crop production

Soil solution P is the readily available source of P to plants. Soil solution P is maintained by equilibrium exchange with labile P. The same would be true for other essential plant nutrients. The ability of crops to take up nutrients such as P from the soil is related to the concentration of P in soil solution (referred to as the intensity factor or I) and the amount of P in reserve that is used to replenish and maintain the solution P concentration. The reserve P is referred to as the quantity factor (Q). Q is a measurement of the equilibrium relationship between soil solution P and labile P but must also include the influence of nonlabile P in replenishing labile P. The relation between the concentration of P in solution and those adsorbed on the solid phase is commonly referred to as buffer power of the soil (Barber, 1995). Barber reports that desorption measurements may be the best way to measure buffer power where plant removal is being studied.

Because of the influence of nonlabile P on maintaining labile P, the best correlations to plant growth response to soil P often involve chemical extractants that extract some portion of the nonlabile pool. Several factors influence the ability of extraction techniques leading to high correlations with plant growth and nutrient uptake. A full discussion of these factors is provided by Kamprath and Watson (1980).

S. A. Ebelhar

Bibliography

Barber, S.A., 1995. *Soil Nutrient Bioavailablity.* New York: Wiley & Sons, 414 pp.

Dyanand, S., and Sinha, M.K., 1985. Labile pool and selective distribution of iron in calcareous and sodic soils. *Plant Soil*, **88**: 11–21.

Fried, M., and Broeshart, H., 1967. *The Soil–Plant System in Relation to Inorganic Nutrition.* New York: Academic Press, 358 pp.

Kamprath, E.J., and Watson, M.E., 1980. Conventional soil and tissue tests for assessing the phosphorus status of soils. In Khasawneh, F.E., Sample, E.C., and Kamprath, E.J., eds., *The Role of Phosphorus in Agriculture.* Madison, WI: American Society of Agronomy, pp. 433–469.

Larsen, S., 1967. Soil phosphorus. *Adv. Agron.*, **19**: 151–210.

Larsen, S., and Widdowson, A.E., 1971. Ageing of phosphate added to soil. *J. Soil Sci.*, **22**: 5–7.

Lopez, P.L., and Graham, E.R., 1972. Labile pool and plant uptake of micronutrients: 1. Determination of labile pool of Mn, Fe, Zn, Co, and Cu in deficient soils by isotopic exchange. *Soil Sci.*, **114**: 295–299.

Mengel, K., 2001. *Principles of Plant Nutrition.* Dordrecht, Holland: Kluwer, 849 pp.

Olsen, S.R., and Khasawneh, F.E., 1980. Use and limitations of physical–chemical criteria for assessing the status of phosphorus in soils. In Khsawneh, F.E., Sample, E.C., and Kamprath, E.O., eds., *The Role of Phosphorus in Agriculture.* Madison, WI: American Society of Agronomy, pp. 361–410.

Cross-references

Buffers, Buffering
Macronutrients
Plant Nutrients
Sorption Phenomena

LACUSTRINE

Pertaining to a lake or lakes. Processes and deposits characteristic of the lake-environment. Used in combinations such as lacustrine sands, lacustrine terraces, lacustrine plain, lacustrine fauna. Lacustrine sedimentary deposits generally range from sands to clays in grain size, so that derived soils range in texture from light (e.g., Arenosols) to heavy (e.g., Vertisols).

LAGOON

Lagoons are generally shallow, elongated, lake-like strips of water, separated from a larger water-body by a low ridge or bank of sand, gravel, or other loose material. Marine lagoons, such as those in the neighborhood of Venice (Figure L1) and other regions along the Adriatic coast of Italy, contain salt or brackish water. Freshwater lagoons may be associated with lakes and large rivers. The water bodies enclosed in an atoll, or by a barrier reef are also referred to as lagoons. Usage has also been extended to artificial bodies of water constructed as repositories of liquid wastes, slurries, or runoff, originating in urban, agricultural and industrial activities. On emergent coasts, highly reduced lagoonal sediments may be exposed, and sulfidic soils may form.

Figure L1 Lagoon of Venice (ESA Satellite Proba, 1 July 2005).

LAND

In its most general sense, the solid portion of the surface of the Earth, as opposed to the sea. In soil science commonly used with a defining word to designate a region with specific properties, particularly in an agricultural sense: for example *arable land*, *corn-land*, *plow-land*, *stubble land*. *Champion land* was a usage common in Medieval and Early Modern periods to designate open field, arable land as opposed to woodland. Land is also used in an ecological sense (the "land organism" of Aldo Leopold, 1949) to mean the complex of soils, waters, organisms, local climate and topography that interact at the Earth's land surface. Leopold's concept anticipates later ideas about Gaia and environmental health.

Bibliography

Leopold, A., 1949. *A Sand County almanac, and Sketches here and there.* New York, Oxford University Press, 226 pp.

LANDFILL

The solid wastes and refuse disposed of by burial in pits constructed for the purpose, natural depressions, or abandoned quarries or other artificial excavations. Localities used in this way are called landfill sites. As it is added, the waste is periodically covered by soil and when full a final layer of soil is laid down, cultivated and planted with a vegetative cover. Soils constructed in this manner are Technosols.

Cross-reference

Technosols

LANDSCAPE

In general, any part of the land surface characterized in terms of its visual impact, for example its topography (shape, relief, etc.), vegetation cover (forest, grassland etc.), surface waters (lakes, streams), and so on, and by the web of ecological processes that create and maintain this macroscopic appearance. Since the Industrial Revolution, *Homo sapiens* has become the most notable agent modifying the landscape, especially over the last 10 000 yr by the activities of deforestation and farming (Ruddiman, 2007) and the resulting urbanization and industrialization. Human-modified landscapes may be referred to as cultural landscapes, with the cultural landscape of a given historical period superimposed and partially obliterating earlier cultural landscapes. In any one region, the palimpsest so produced may be deciphered to yield a valuable record of human activities in that region.

Bibliography

Ruddiman, W.F., 2007. *Plows, Plagues, and Petroleum*. New Jersey: Princeton. Princeton University Press. 224 pp.

LANDSCAPE AND SOILS

Processes that affect landscapes also affect soils, and vice versa (Birkeland, 1999). Geomorphologists are concerned with "the mobilization, transportation and redeposition of materials by overland flow, throughflow and mass movements" on the land (Conacher and Dalrymple, 1977), all of which involve, modify, and are modified by, the soil. In fact, the relationship of topography and soil has been well recognized in pedology, at least from the time of Dokuchaev in the nineteenth century. It is implicit in the concept of catena – "a repeated sequence of soil profiles geographically related to and associated with relief features" (Gregorich et al., 2001). Figure L2 is an example of a catena on a podzolized hillslope in Somerset, England. Park and Burt (1999) from whom the example is taken tracked the distribution of secondary Fe oxides in the catena, and their results clearly demonstrate the importance of lateral and downslope movements in soil genesis. In other words pedogenesis is not simply a matter of vertical movements.

The catenary approach to the relationship of topography and soil was elaborated into a nine-unit land-surface model by Conacher and Dalrymple (1977). Energy and mass pass ("cascade") from one unit into the next, each unit being equivalent to a process-response subsystem in Chorley and Kennedy's (1971) terminology. The nine units are defined in terms of *distinguishing* rather than *dominant* processes (Table L1). Thus, the processes considered as being definitive of units 1, 2, 3, 5, and 6 actually occur in varying combinations and intensities in nearly every unit.

The model is illustrated in three dimensions in Figure L3, while Figure L4 provides details in cross-section.

Relative differences in type and intensity of the pedomorphic processes will also be a function of other soil-forming factors that affect the relationship of soil and topography, the most notable one being the linked factor climate-vegetation.

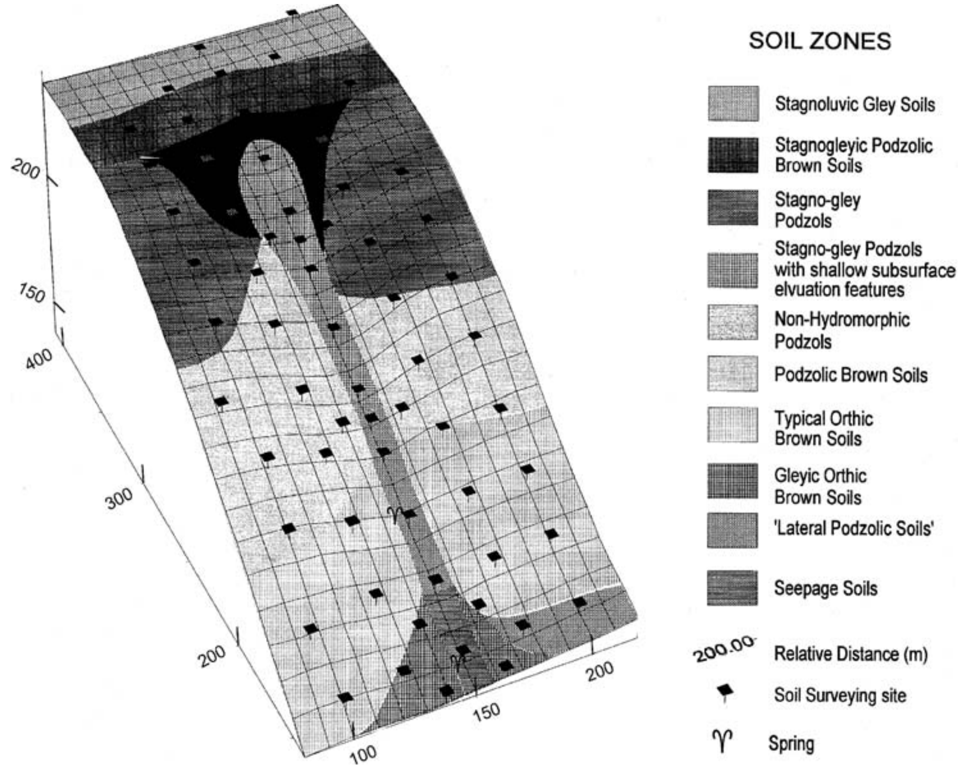


Figure L2 Landscape with podzolic soils from the Quantock Hills in the southwest of England. An example of the relationship of soils with landform (Park and Burt, 1999).

Table L1 Definitions of the component units of the nine unit landsurface model (Conacher and Dalrymple, 1977)

Land surface unit	Abbreviated definition
1	Interfluve, with predominant pedogeomorphic processes being those resulting from vertical (both up and down) soil-water movements
2	Responses to mechanical and chemical eluviation by lateral subsurface soil-water movements, either predominate, or serve to distinguish this unit from other units on the catena
3	Convex slope element where soil creep is the predominant process producing lateral movement of soil materials
4	Slope greater than 45° characterized by the processes of fall and rock-slide
5	Response to transportation of a large amount of materials downslope, relative to other units, by flow, slump, slide, raindrop impact, surface wash, and human cultivation practices
6	Response to colluvial redeposition from upslope
7	Response to redeposition from upvalley of alluvial materials
8	Channel wall, distinguished by lateral corrasion by stream action
9	Stream channel bed, with transportation of material down-valley by stream action being the predominant process

Some of the translocations of materials between pedons in a catena, under different climatic-vegetation regimes are shown in Table L2. Details of the geomorphological context are included where known.

Time is a soil forming factor that also needs to be taken into account, and a convenient framework in which to consider time is the tectonic structure of the lithosphere. The youthful features of the Earth's surface are found at plate margins, specifically at constructive margins (rift systems) and at destructive ones (subduction zones). Rift systems, either in an oceanic or a continental setting, provide a variety of morphogenetic settings for soil genesis, ranging from the extensive quasi-planar landscapes of flood basalts, through the relatively gentle relief of shield volcanoes, to the accentuated relief of fault scarps and of the great stratovolcanoes built up of alternating flows and pyroclastics (an additional feature leading to catenary variability in the landscape). Subduction zones are the site of explosive andesitic volcanism, in which the classical cone-shaped volcanoes are constructed, and also of linear mountain belts, where the greatest relief and, in general, the greatest area of young soils are found, with parent material regularly being exposed to weathering and erosion in upslope positions, and incipient soils being constantly buried in colluvium, downslope. Weatherable primary minerals are common in the soils of these youthful landscapes, and the clay fraction, which usually contains secondary amorphous phases and materials exhibiting short-range order (allophane, imogolite, ferrihydrite, for example) rather than well-developed crystallinity, is commonly less than five percent.

Away from the plate margins, older parts of the continent are exposed, including older mountain belts and (in the oldest parts) the craton. This is where relief is least and where erosional processes are relatively quiescent. It is on the cratonic landscapes of the tropics, undisturbed by recent glaciations, that the oldest and most weathered soils occur. Ferralitic catenas dominate the landscape, commonly with gibbsitic soils in the most leached, upper parts, grading through kaolinitic soils on gentle slopes, to smectite-bearing Vertisols in poorly drained localities in stream valleys. The complete downhill sequence marks the path of migration of Si, Ca, Mg, Na, and K, relative to Fe and Al. Primary minerals other than quartz, are generally absent.

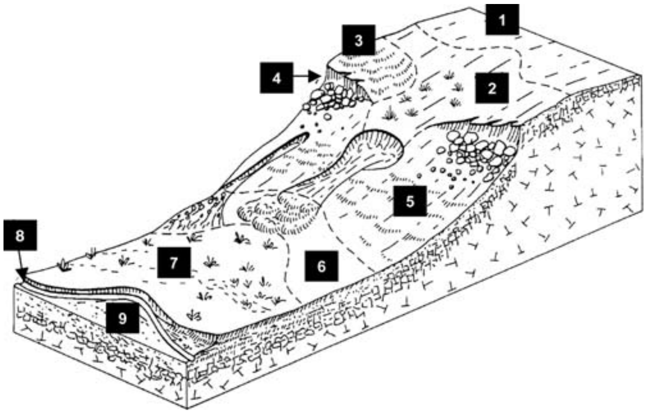


Figure L3 Conacher and Dalrymple's (1997) nine unit model.

Finally, Erhart (1963, 1964, 1967) recognizes two types of weathering regime on continents, the distinction between the two being fundamentally one of the stability of landform. His idea, reinterpreted in terms of plate tectonics, is essentially as follows. In continental regions distant from plate boundaries, and unaffected by recent events such as major glaciations capable of remodeling the landscape wholesale, relief tends to be unemphatic and a climax vegetation is established over mature, deeply weathered soils. The Amazon and Congo basins are examples, and the dominant ferralitic soils may be 100 m thick, or more. Erhart calls this a state of biostasis, where the erosional load reaching the adjacent ocean is relatively low in clastic materials and high in dissolved, mobile elements such as Ca, Mg, Na and K. According to Erhart, these are conditions favoring the formation of limestones in the geological record. He gives the name rhexistasis to the contrasted state found near

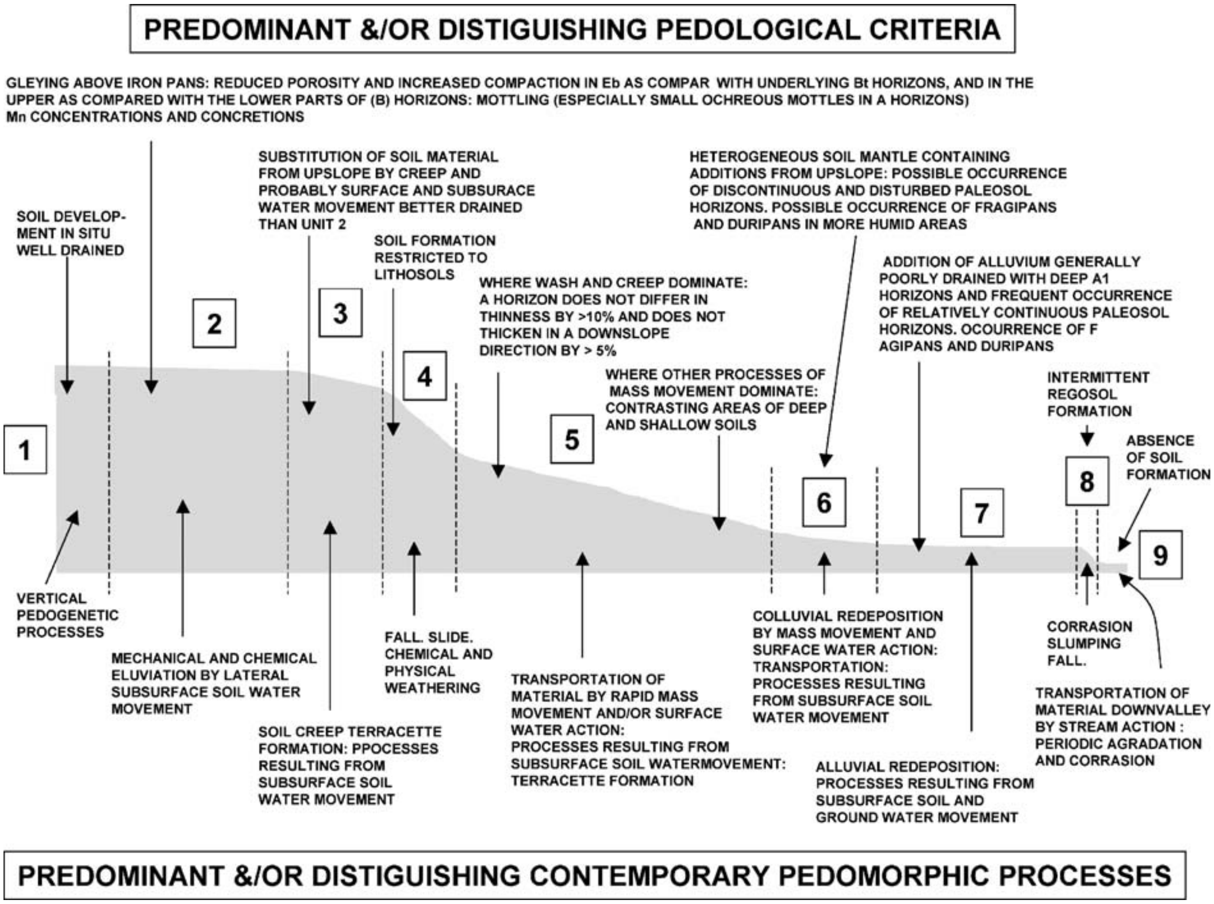


Figure L4 Details of the nine-unit model in cross section.

Table L2 Catenas in climatic zones from circum-polar to tropical regions, on a variety of landform units, and with material translocations between soil types (Soil Taxonomy usage) in the catena. Adapted from Sommer and Schlichting (1997) where individual references will be found. DOC is dissolved organic carbon

Climate / Vegetation	Geomorphic unit	Catenary sequence of soils	Materials translocated
(Ant-)Arctic	Closed basin of granodiorite moraine	Cryorthents?	Soluble salts, gypsum
	Terraces	Cryorthents'!	Carbonates
	Closed basin?	Cryorthents?	Soluble salts
	Fluvial terraces	Cryaquepts, -umbrepts, -hemists, -fluvents	N, P
Subarctic	Plains of (fluvio-)glacial sediments	Spodosols	Humus
	Hillslope of diabasic porphyrite	Spodosols	Humus, Al
Alpine	Cirque of biotite gneiss	Cryochrepts-cryumbrepts	Si, K, Na, Ca, Mg, Al
	Acid granite moraines	Spodosols, albaqualfs	Humus
	Granitic gneiss moraines	Cryumbrepts	Al
Boreal	Hillslope of calcareous shales and slates	Spodosols-endoaquepts	Mg, K, Al
	Hummocky moraines	Cryoboralfs-albaqualfs	DOC, P
Temp, / Boreal	Hillslope of calcareous, clayey till	Glossoboralfs-paleboralfs-argiborolls	Bases
Temperate-humid	Moraines and fluvioglacial sands	Spodosols-endoaquepts	Fe, Mn, P, Co, Mo
	Marly ridge	Dystrochrepts-epiaquepts-Endoaquepts	Carbonates
	Loessial plateau	Haplaquolls-albaqualfs	P
	Hillslopes of mudstones and shales	Spodosols-inceptisols	Fe
	(Clayey) Sandstone-plateau	Epiaquepts-andic dystrochrepts	Mn, Fe, P
	Dunes + fluvioglacial sands	Haplorthod-endoaquod-histosols	Ca, Mg, K
	Hillslopes of gneiss debris	Fragiorthods-fragiumbrepts	Al, Fe, bases
Continental	Plains of fluvial clays and loams	Mollisols-solonetz-solonchak / histosols	I
	Plains of sandstones + shales	Argiborolls-natrargids	Na, soluble salts
	Hummocky moraine	Argi- / haplaquolls-calci- / Haplaquolls-fluvaquents	Carbonates, soluble salts
	Loessial plateau	Haploborolls-natriborolls	Mo, Y, Sc
	Plains of tertiary continental sediments	Natriborolls-entisols	Carbonates, gypsum, soluble salts
Mediterranean	Hillslopcs of tonalite	Xerochrepts-haploxeralfs-natrixeralfs-haploxererts	Na
	Hillslopes of basalt, dolomite, limestone	Orthents-xererts, xeralfs	Mn
	Basalt mesas with shallow, depressions	Orthents-xeralfs-xererts	Mn
Medit. / arid	Closed basin with alluvium	Haploxeralfs-natrargids	Carbonates, gypsum, Na
(Semi-)Arid	Dissected laterites	?	Soluble salts
	Dissected laterites	?	Soluble salts
Subtropical-subhumid	Hillslopes of basalt	Oxisols-molli- / vertisols	Ca, Mg, Si
	Basin of shales, lime-, sandstones	Oxisols-vertisols	Mn
	Hillslopes on a doleritic plateau	Mollisols-vertisols	Mg, Si, carbonates
	Hillslopes of granite / acid volcanic rocks	Solods-solodized solonetz	Na, Mg
	?	Paleudults-quartzipsamments	P
	Clay- / sandstone plateaus (shallow depressions)	Lixisols-planosols	Al, P
Tropical-humid	Dissected laterites	?	Fe, Mn
	Valleyslopes of Tertiary sediments	Oxisols-ultisols-spodosols	Humus
	Valleyslopes of Tertiary arenites and argilites	Oxisols-ultisols-spodosols	Humus, Al
	Pediment of granitic gneiss	Acrorthox-paleudults (-alfs)	Fe, Mn, Si, bases
	Hillslopes of basaltic tuff	Palehumults	Bases
	Hillslopes of serpentinized dunite	Haploperox-dystrochrepts-duraquepts	Si

plate boundaries where relief is usually high, and erosion consequently much more active. The landscape is unstable and soils are young, as previously stated. Voluminous clastic sediments are added to the ocean, and the great thicknesses of greywackes and associated sedimentary rocks (12 thousand meters or more in particular occurrences) are the result. Even after half a century, Erhart's ideas are controversial, but the relationship between regimes of soil formation on land and sediment type and sedimentary style in the sea is a fruitful area for future research at the boundary between pedology and geology.

Ward Chesworth

Bibliography

Birkeland, P., 1999. *Soils and Geomorphology*, 3rd edn. New York: Oxford University Press, 430 pp.

Chorley, R.J., and Kennedy, B.A., 1971 *Physical Geography: A Systems Approach*. London: Prentice-Hall, 370 pp.

Conacher, A.J., and Dalrymple, J.B., 1977. The nine unit land surface model. An approach to pedogeomorphic research. *Geoderma*, **18**: 1–154.

Erhart, H., 1963. Sur le cycle de la silice hydrate dans la biosphere. *C.R. Acad. Sci.*, **256**: 3731–3734.

Erhart, H., 1964. Consequences logiques de la bio-rhexistasie sur le chimisme des mers anciennes et sur les sediments qu'elles ont engendres. *C.R. Acad. Sci.*, **259**: 2669–2671.

Erhart, H., 1967. *La Genese des Sols en tant que Phenomene Geologique*. Paris: Masson, 177 pp.

Gregorich, E.G., Turchenek, L.W., Carter, M.R., and Angers, D.A., 2001. *Soil and Environmental Science Dictionary*. Boca Raton, FL: CRC Press, 577 pp.

Park, S.J., and Burt, T.P., 1999. Identification of throughflow using the distribution of secondary iron oxides in soils. *Geoderma*, **93**: 61–84.

Sommer, M., and Schlichting, E., 1997. Archetypes of catenas with respect to matter – a concept for structuring and grouping catenas. *Geoderma*, **76**: 1–33.

LATERITE

A general term for the red, iron (and commonly aluminum) rich, highly weathered and leached material, found in tropical and sub-tropical regions, and formed under a hot, humid climate. Soils with these characteristics were formerly known as lateritic soils and are now classed as Ferralsols and Plinthosols (WRB) or oxisols (USDA). The processes by which laterites and related soils form are collectively known as lateritization. This involves not only the removal of the relatively easily mobilized cations of Ca, Mg, K, and Na, but also, over the long term (order of millions of years) of the removal of Si relative to Fe and Al. This gives rise to a humus-poor surface horizon, called plinthite, rich in iron oxide or hydroxide, kaolinite and possibly gibbsite. This horizon hardens irreversibly to a hardpan or to nodular masses when exposed (by removal of vegetation for example) to repeated wetting and drying.

Bibliography

Aleva, G.J.J., 1994. In Creutzberg, D., eds., Aleva, G.J.J. (compiled) *Laterites: Concepts, Geology, Morphology, and Chemistry*, Wageningen, the Netherlands: International Soil Reference and Information Center. 169 p.

Cross-references

Ferralsols
Plinthosols
Tropical Soils

LAW OF THE MINIMUM

The "Law of the Minimum" is a conjecture about crop response to growth factors formulated in the middle of the nineteenth century. This hypothesis is commonly associated with the name of Justus von Liebig, a German chemist of world renown. According to Russell (1912, p. 11), the initial formulation of the "Law of the Minimum" appeared in 1843, in the third edition of von Liebig's *Chemistry in its Applications to Agriculture and Physiology*. Russell's translation of the relevant passage gives the following definition of the law of the minimum: "by the deficiency or absence of one necessary constituent, all others being present, the soil is rendered barren for all those crops to the life of which that one constituent is indispensable." The same theme is expounded by von Liebig in his *Die Grundsätze der Agricultur-Chemie* published in 1855, where it is written that

> If one of the participating nutritive constituents of the soil or atmosphere be deficient or wanting or lacking in assimilability, either the plant does not grow or its organs develop only imperfectly. The deficient or lacking constituent makes those that are present inactive or lessen their activity. If the deficient or lacking be added to the soil or if occurring in insoluble form it be made soluble, then the other nutrients become active (p. 22–23).
>
> The productivity of a field is in direct relation to the necessary constituent contained in the soil in smallest amount (p. 105).

A more elaborate and informative statement of von Liebig's conjecture can be found in his 1862 book entitled *Die Naturgesetze des Feldbaues* (edited in English by J. Blyth in 1863 with the title of *The Natural Laws of Husbandry*) where, on page 223, it is written that

> Every field contains a *maximum* of one or several, and a *minimum* of one or several different nutrients. The yields of crops stand in relation (Verhältnis) to this *minimum*, be it lime, potash, nitrogen, phosphoric acid, magnesia, or any other mineral constituent; this minimum governs and controls the level and the persistence of yields.
>
> Should this minimum for example be lime or magnesia, the yield of grain and straw, of turnips, potatoes or clover will remain the same and be no greater even though the amount of potash, silica, phosphoric acid, etc., already in the soil be increased a hundred times. The crop yields on this field, however, will be increased by a simple fertilization with lime.

The explanation of the law of the minimum continues on page 227:

> In order to understand these facts correctly, it must be remembered that the law of the minimum does not apply only to one nutrient, but to all. If in a given field the yields of a crop are limited by a minimum of phosphoric acid, these yields can be increased by applications of phosphoric acid up to the point where the added phosphoric acid stands in the right relation to the minimum that is now present of another nutrient.
>
> If the added phosphoric acid exceeds the corresponding quantity, for instance, of potash or ammonia in the soil, this excess then will have no effect. Before the application of phosphoric acid, the amount of potash or ammonia was a little larger than the amount of phosphoric acid in the soil and, therefore, this excess had no effect. It was activated by the application of phosphoric acid the excess of which then became inactive, in the same way as the previous excess of potash.
>
> While the crop yield before was in relation to the minimum of phosphoric acid, it is now in relation to the minimum of either potash or ammonia, or both alkalies.

In modern terms, the mathematical specification of von Liebig's law of the minimum can be stated as

$$y = \min\{f_N(N), f_P(P), f_K(K), \ldots, f_L(L)\} \qquad (1)$$

where y stands for crop yield while N, P, K, W and L stand for nitrogen, phosphorus, potassium, water and the "last" growth factor, respectively. The functions f_N, f_P, f_K, f_W, and f_L represent the potential yield responses to the corresponding nutrients. The "min" operator selects the level of crop yield that is associated with the limiting nutrient, as declared by the von Liebig's conjecture.

The publication of the law of the minimum gave rise to a controversy that has lasted to the present time. Von Liebig accompanied the explanation of his conjecture with invectives, scorn and sarcasm directed toward the plant physiologists of his time. In turn, he was attacked by his contemporaries and successors who, in large part, did not accept his "law."

One aspect of the controversy over the von Liebig's hypothesis deals with the interpretation and the translation of a single word (Verhältnis) used more than once by von Liebig to describe the dependence of crop yield on limiting nutrients. In German, the word *Verhältnis* means *relation*, any sort of relation. Regretfully, several English translators of von Liebig's works elected to give a more specific interpretation to the word "relation" such as, for example, a "proportional relation." Consider the following statement made by von Liebig on page 227 of his *Die Naturgesetze des Feldbaues:*

> Während vorher die Ernte im *Verhältnis* stand zu dem Minimum an Phosphorsäure, steht sie jetzt im *Verhältnis* zu dem Minimum an Kali oder Ammoniak, oder zu beiden.

In 1863, his English editor, J. Blyth, translated this passage as (p. 210):

> Whilst the produce before was *proportionate* to the minimum of phosphoric acid, it is now in *proportion* to the minimum of potash or ammonia, or both alkalies.

From then on, several other Anglo-Saxon authors used the word *proportion* instead of *relation* to translate von Liebig's *Verhältnis*. It is imperative to make absolutely clear that a *proportional relation* is the most restrictive type of relation (even more restrictive than a linear relation). Since 1863, therefore, von Liebig was erroneously charged with asserting that yields are proportional to limiting inputs, a proposition that cannot be found in his writings.

Another nontrivial reason for the obstacles encountered by von Liebig's law of the minimum is that it was an idea far ahead of its time. For instance, it was far ahead of the mathematical ability of von Liebig and his colleagues who could not have been expected to express the "law" in a meaningful and general mathematical specification. As will be shown further on, the mathematical and statistical apparatus for estimating a relation such as Equation (1) became available only after 1950. Rigorous statistical tests of the law of the minimum vis-a-vis alternative specifications of response hypotheses were never carried out during the first 140 years of its formulation. These tests began with Lanzer and Paris (1979) and continued with Ackello-Ogutu et al. (1981), Sadi et al. (1987), and Paris (1992). These studies indicate that, at least for a limited number of data samples, the law of the minimum is capable of interpreting experimental results of crop response to fertilizers better than either polynomial or Mitscherlich-Baule specifications. Although much work remains to be done before declaring (or rejecting) the generalized validity of the law, it is possible to envision a renewed interest in the law of the minimum by agronomists, soil scientists and economists.

A family of von Liebig models expressing the law of the minimum

Relation (1) embodies all the essential features of the law of the minimum but it is too general for any empirically useful application. To begin with, we must limit the number of growth factors examined at any one time. Suppose, therefore, to be interested in studying the response of a crop, say corn, to variable levels of nitrogen (N) and phosphorus (P), while all other nutrients (K, W, …, L) are held at non limiting levels. In other words, these nutrients are arbitrarily fixed at levels presumed to be sufficiently high for causing either N or P to be limiting factors. In this case, the corn response function formulated according to the law of the minimum exhibits a plateau effect (m) such as

$$y_i = \min\{f_N(N_i), f_P(P_i), m\} + u_i \tag{2}$$

where

$$m = \min\{f_K(\bar{K}), f_W(\bar{W}), \ldots, f_L(\bar{L})\}$$

and

$$\bar{K},\ \bar{W}, \ldots, \bar{L}$$

are the fixed levels of the growth factors that are beyond the scope of the study. A random error u_i is added to the model in order to represent the statistical error associated with a crop response experiment which is assumed to consists of I observations, $i = 1, \ldots, I$. The functions f_N and f_P can assume either linear or nonlinear specifications. The linear specification of f_N and f_P gives rise to the linear-response and plateau (LRP) model expressed as

$$y_i = \min\{a_N + b_N N_i, a_P + b_P P_i, m\} + u_i \tag{3}$$

where a_N, a_P, b_N, b_P and m are parameters to be estimated statistically. Figure L5 illustrates the geometric shape of a LRP model. This specification of the von Liebig hypothesis has been criticized for its inability to express a declining phase of the crop yields due either to excessive quantities of nutrients N and P or to the presence of injurious factors in the soil. This criticism is unwarranted because, when such a declining phase is important, model (3) can be modified quite easily to account for the declining yields:

$$y_i = \min\{a_N + b_N N_i, a_P + b_P P_i, m, c + d_N N_i + d_P P_i\} + u_i \tag{4}$$

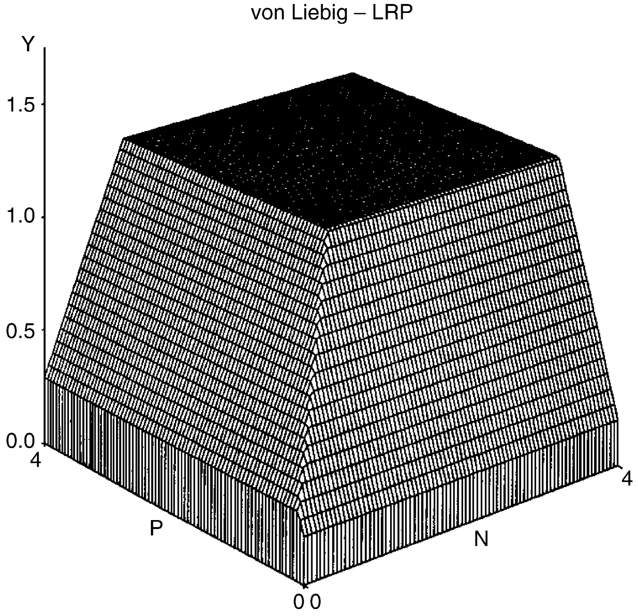


Figure L5 A von Liebig model with linear regimes.

where $c \geq m$ and $d_N \leq 0$, $d_P \leq 0$. These conditions guarantee that the additional regime in N and P, $c + d_N N_i + d_P P_i$, constitutes a plane with a negative slope, as required by the declining yield portion of the experimental results. Figure L6 illustrates the geometric shape of model (4). If desired, the additional regime can be specified in a more flexible formulation such as a polynomial function. Another admissible version of the declining portion of the response surface may be expressed by two orthogonal planes.

The nonlinear specification of functions f_N and f_P in model (2) can assume several different versions. An exponential formulation of each function joins together von Liebig's and Alfred von Mitscherlich's ideas about crop response:

$$y_i = \min\{m[1 - k_N \exp(-b_N N_i)], m[1 - k_P \exp(-b_P P_i)]\} + u_i \tag{5}$$

where m is the asymptotic plateau common to each potential yield function and exp is the exponential operator. Figure L7 illustrates the geometric shape of model (5). This figure shows that the law of the minimum can represent scenarios of decreasing marginal products and of decreasing returns to scale.

When the exponential regimes of model (5) are replaced with square-root polynomial formulations, model (2) assumes the following specification

$$y_i = \min\{a_N + b_N N_i + d_N N_i^{0.5}, a_P + b_P P_i + d_P P_i^{0.5}, m\} + u_i \tag{6}$$

The square-root polynomial function is a very flexible specification capable of interpreting a wide range of crop responses. It possesses rising and declining yield phases without requiring their symmetry. Figure L8 illustrates the geometric shape of model (6).

A version of the law of the minimum more elaborate than any of those presented above assumes that each potential yield function is associated with a specific experimental error. In this case, a linear version of the relevant specification assumes the form of a switching regression model such

$$y_i = \min\{a_N + b_N N_i + u_{Ni}, a_P + b_P P_i + u_{Pi}, m + u_{mi}\} \tag{7}$$

while a nonlinear formulation is specified as

$$y_i = \min\{m[1 - k_N e^{-b_N N_i}] + u_{Ni}, m[1 - k_P e^{-b_P P_i}] + u_{Pi}\} \tag{8}$$

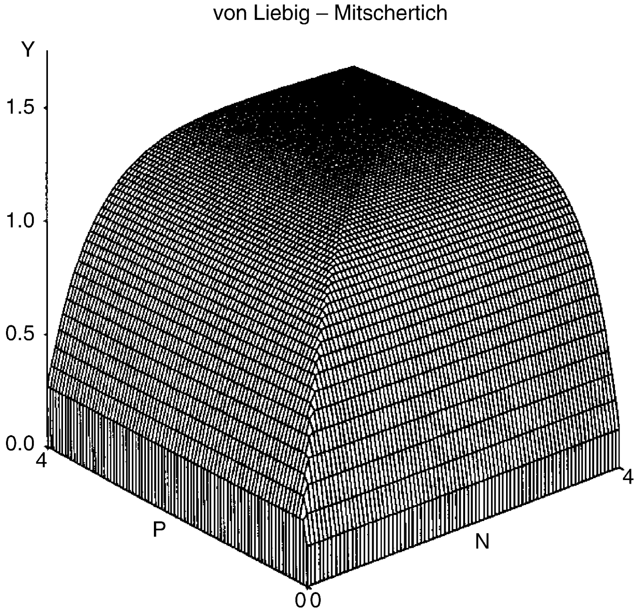


Figure L7 A von Liebig model with Mitscherlich regimes.

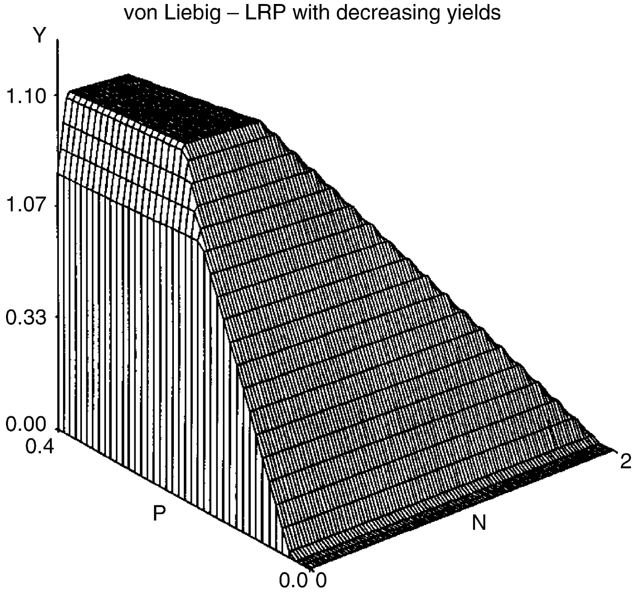


Figure L6 A von Liebig model with linear regimes and declining yields.

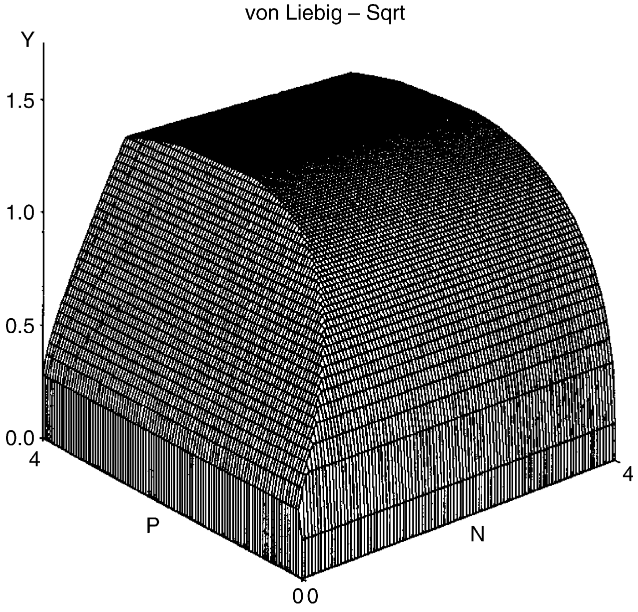


Figure L8 A von Liebig model with square-root regimes.

The distinguishing feature of models (7) and (8) is represented by the presence of experimental error terms that are subject to the minimum operator. The justification for advancing this statistical specification of the error term is inspired by the agronomic variability usually observed in vegetative regimes governed by limiting nutrients such as nitrogen and phosphorus (or any other growth factor). Each nutrient has different implications for the vegetative as well as the maturity and productive stages of a crop. The influence of a limiting nutrient, therefore, is likely to be reflected also in the variability of the experimental error associated with different regimes.

Von Liebig's law of the minimum and Mitscherlich's law of physiological relations

All the previous models adhere strictly to the traditional interpretation of the law of the minimum characterized by the twin notion of nonsubstitution between growth factors and of a plateau. As shown in the next section, this rigorous formulation of the law of the minimum is capable to interpret the crop response phenomenon to a considerable degree of precision. Very few contemporaries and successors of von Liebig, however, accepted a strict interpretation of the law of the minimum as a plausible empirical law. To complicate this lack of understanding, von Liebig never presented a mathematical specification of his hypothesis. The first attempt to interpret the law of the minimum with a functional specification is attributed to the German agronomist Alfred Mitscherlich who in 1909 published a remarkable study showing that crop response is likely to follow an exponential specification. This study is also taken to be the first empirical verification of the law of diminishing returns. Although the mathematical formulation of Mitscherlich does not contain the "*minimum*" operator required to express von Liebig's hypothesis correctly, it was regarded, nevertheless, as its first analytical specification. In the words of Lang (1924, p. 103):

> Mitscherlich thought to obtain the most accurate expression for the behavior of yield increase, designated by the law mentioned, by giving the *qualitative* formulation of Liebig's law of the minimum – dependence of plant yield on the minimum factor – a *quantitative* form; that is, by determining exactly to what degree plant yield is dependent on the vegetative factor present in minimum.

The successors of Lang rejected this interpretation of Mitscherlich's exponential function as representing von Liebig's law of the minimum in *quantitative form*. Mitscherlich's contribution has been (wrongly) interpreted ever since as a negation of von Liebig's hypothesis. Even the reviewer of Lang's book, J. D. Black (1925, p. 275), misinterpreted his writing:

> Liebig stated his law as follows: "The productivity of a field is in direct relation to the necessary constituent contained in smallest quantity." Now such a statement is obviously inconsistent with the principle of diminishing returns as ordinarily understood .... It is even more obviously inconsistent with the whole marginal productivity theory of value so generally taken as the starting point in value theory today. All the years from 1839 to the present, the soil and plant chemists have struggled with this law of the minimum trying to reconcile it with the results of practical field experience. It has remained for Mitscherlich in a series of experiments, the first results of which were published in 1909, to resolve this difficulty by showing that Liebig's law of the minimum is wrong, and that the principle of diminishing returns is the true principle involved .... The law of the minimum made the increase in yield proportional to the increase in the minimum factor – a straight line would express the results. Mitscherlich demonstrated that a logarithmically decreasing curve expresses the results, within the usual reaches of experience, with a surprising degree of exactness.

All these assertions by J. D. Black regarding von Liebig's law of the minimum are incorrect. As stated by Lang (1924, p. 115), neither diminishing returns nor decreasing marginal products are inconsistent with the law of the minimum:

> These two examples show, with all the clarity one might wish, that Mitscherlich's quantitative formulation of the law of the minimum is at the same time the best imaginable expression for our Law of Diminishing Soil Returns.

The fact that authoritative scientists such as J. D. Black were unable to understand what was being proposed by Mitscherlich and by Lang is a sign of the confusion that has surrounded von Liebig's hypothesis from the start. In reality, Lang is not entirely correct in his assertion that Mitscherlich's exponential function represents a mathematical formulation of the law of the minimum. This is the case only when Mitscherlich's exponential function is embedded into von Liebig's models as specified in relations (5) and (8). These two models indicate that both Liebig and Mitscherlich were working, in ways that were complementary and never antagonistic, toward the same goal of discovering a functional relation between crop yield and factors of growth.

The experimental work provided Mitscherlich with a keen scientific insight into the laws governing plant growth. Lang gives again a very informative account of Mitscherlich's thought process (p. 137):

> From all these results, Mitscherlich draws the conclusion that the old Liebig Law of the Minimum, according to which yield is dependent on the vegetative factor which is at the minimum, is not justified by facts, at least not in this strict statement of it. In fact, "the magnitude of the yield is governed by all the growth factors together." But since each of the many factors exerts the greater influence on yield increase – the yield increase is all the more rapid – the less there is present of the requisite quantity of the factor in question, we are after all not so far from the Liebig Law. Apparently this law might be justified; but in reality it is inconsistent with the new knowledge; not only may yield be materially increased by the minimum factor but also by every other factor present in insufficient quantity.

Lang's oscillation between recognizing some residual validity to the "old" Liebig law and accepting a novel formulation brought about by the empirical evidence accumulated so painstakingly by Mitscherlich, constitutes a scientific tale of great intellectual beauty. Once again, the mathematical expertise common to agronomists in those years could not accommodate properly the discoveries made in the field. Lang continued to perorate Mitscherlich's new discoveries in an important footnote (p. 137):

> The above principles explain the practice of farmers in fertilizing their fields during the war: of the three leading fertilizer ingredients, nitrogen, phosphoric acid, and potash, the first two had become rather scarce during the war, while an abundance of the last was available, and it was used in greater quantities than usual. Nitrogen, especially – German farmers had for years before the war been storing the soil with an excess of phosphoric acid – necessarily became deficient, relatively and absolutely. Although nitrogen finally became in reality strongly in the minimum, a fact easily discerned by the appearance of the crops, yet the practice of farmers in the matter of potash fertilizer was entirely correct, under the conditions the only possibility, as a means of obtaining increased yields – in spite of the clearly recognized minimum factor – a practice which would have had to be condemned, at least theoretically, on the basis of previous ideas.

The above considerations lead Mitscherlich to the formulation of the "Law of Physiological Relations (Gesetz der Physiologischen Beziehungen)" which, in the translation by Lang (p. 141), reads: "*The magnitude of the yield is conditioned by* *all the factors of growth. Each single factor exercises the greater limiting influence on yield the nearer it is to the minimum.*" It has become common ever since to express this law mathematically as the product of a series of exponential terms, each of them representing the effect of one vegetative factor. This formulation relaxes somewhat the strict requirements of the law of the minimum. It is possible, however, to propose an alternative mathematical formulation of Mitscherlich's law which complements von Liebig's hypothesis:

$$y_i = \min\left\{f_{N/P,K,\ldots,L}(N_i),\ f_{P/N,K,\ldots,L}(P_i),\ f_{K/N,P,\ldots,L}(K_i)\right\} + u_i \tag{9}$$

where each potential yield function is conditioned by all the other growth factors, as stated by Mitscherlich's law of physiological relations. The essence of von Liebig's law of the minimum is maintained in model (9) as the general framework within which a multitude of specifications can be articulated to represent the potential yield functions. The implementation of the above specification for a two-input (N and P) model of the square-root type assumes the following structure (Kreuz, 1993):

$$y_i = \min\left\{\alpha_N(P) + \beta_N(P)N_i + \gamma_N(P)N_i^{0.5},\ \alpha_P(N) + \beta_P(N)P_i + \gamma_P(N)P_i^{0.5},\ m\right\} + u_i \tag{10}$$

Model (10) expresses the idea that the parameters of each potential yield function depend on the conditioning levels of the other growth factors. Assuming a linear dependence of the parameters such as $\alpha_N = a_{N1} + a_{N2}P$, $\beta_N = b_{N1} + b_{N2}P$, $\gamma_N = c_{N1} + c_{N2}P$, etc., the final specification of the generalized von Liebig model which is suitable for estimation appears as

$$\begin{aligned}
y_i &= \min\{Y_{Ni}, Y_{Pi}, Y_{mi}\} + u_i\\
Y_{Ni} &= [a_{N1} + a_{N2}P_i] + [b_{N1} + b_{N2}P_i]N_i + [c_{N1} + c_{N2}P_i]N_i^{0.5}\\
Y_{Pi} &= [a_{P1} + a_{P2}N_i] + [b_{P1} + b_{P2}N_i]P_i + [c_{P1} + c_{P2}N_i]P_i^{0.5}\\
Y_{mi} &= m
\end{aligned} \tag{11}$$

In specifying the conditioning process brought about by Mitscherlich's law of physiological relations, it is essential to assure the identification of each potential yield functions. In the next section, the von Liebig's law of the minimum will be empirically illustrated in its numerous specifications elaborated above.

Empirical Results of the Law of the Minimum

All the von Liebig models discussed in the preceding sections were estimated by means of maximum likelihood methods as shown by Paris (1992). Two samples of experimental data were used for this purpose. The first sample was collected by Heady et al. (1955) and deals with response of corn to applied nitrogen (N) and phosphorus (P) on a calcareous Ida silt loam soil in western Iowa. Nine levels of N and P were selected with two replications for a total of 114 treatment plots. The crop population was chosen at 18 000 plants per acre. The range of N and P treatments varies from 0 to 320 pounds per acre for the purpose of detecting a phase of yield decline, if it exists. The estimates of a von Liebig model corresponding to a linear-response and plateau type are presented in Table L3 under model (3). The predicted surface corresponding to this model is presented in Figure L5.

Table L3 Estimation of von Liebig models

Model (3): Linear von Liebig (LRP)

$$\begin{aligned}
y_i &= \min\{Y_{Ni}, Y_{Pi}, Y_{mi}\} + u_i\\
Y_{Ni} &= \underset{(0.042)}{0.2904} + \underset{(0.097)}{0.9601}N_i\\
Y_{Pi} &= \underset{(0.042)}{0.2004} + \underset{(0.078)}{1.2219}P_i\\
Y_{mi} &= \underset{(0.023)}{1.2461}
\end{aligned}$$

$\log L = 65.221$ $\hat{\sigma} = 0.137$ $R^2 = 0.912$ $df = 109$

Model (4): Linear von Liebig with declining yields

$$\begin{aligned}
y_i &= \min\{Y_{Ni}, Y_{Pi}, Y_{mi}, Y_{Di}\} + u_i\\
Y_{Wi} &= \underset{(0.063)}{-0.151} + \underset{(0.410)}{5.563}W_i\\
Y_{Ni} &= \underset{(0.025)}{0.763} + \underset{(0.529)}{3.680}N_i\\
Y_{mi} &= \underset{(0.125)}{1.190}\\
Y_{Di} &= \underset{(0.183)}{1.486} - \underset{(0.276)}{0.367}W_i - \underset{(0.353)}{0.726}N_i
\end{aligned}$$

$\log L = 43.915$ $\hat{\sigma} = 0.045$ $R^2 = 0.973$ $df = 18$

Model (5): Nonlinear von Liebig with Mitscherlich regimes

$$\begin{aligned}
y_i &= \min\{Y_{Ni}, Y_{Pi}\} + u_i\\
Y_{Ni} &= \underset{(0.028)}{1.291}[1 - \underset{(0.029)}{0.791}\exp(-\underset{(0.226)}{1.734}N_i)]\\
Y_{Pi} &= \underset{(0.028)}{1.291}[1 - \underset{(0.033)}{0.870}\exp(-\underset{(0.309)}{2.286}P_i)]
\end{aligned}$$

$\log L = 76.060$ $\hat{\sigma} = 0.124$ $R^2 = 0.928$ $df = 109$

Model (6): Nonlinear von Liebig with Square-Root regimes

$$\begin{aligned}
y_i &= \min\{Y_{Ni}, Y_{Pi}, Y_{mi}\} + u_i\\
Y_{Ni} &= \underset{(0.035)}{0.280} + \underset{(0.267)}{0.618}N_i + \underset{(0.215)}{0.296}N_i^{0.5}\\
Y_{Pi} &= \underset{(0.037)}{0.161} - \underset{(0.059)}{0.432}P_i + \underset{(0.227)}{1.396}P_i^{0.5}\\
Y_{mi} &= \underset{(0.040)}{1.276}
\end{aligned}$$

$\log L = 83.462$ $\hat{\sigma} = 0.116$ $R^2 = 0.936$ $df = 107$

Statistics in parentheses are standard errors.

A von Liebig specification with Mitscherlich regimes is presented under model (5) in Table L5. The improvement over the LRP version is negligible when measured in terms of the coefficient of determination. Although the parameters of the two models belong to different spaces, the value of the logarithm of the likelihood function shows a remarkable increase of about 11 points. A non-nested hypothesis test carried out by Paris (1992) showed that the von Liebig model with Mitscherlich regimes is a superior specification when compared to the von Liebig model of the LRP type. The predicted surface generated by model (5) is illustrated in Figure L7.

As anticipated above, a square-root specification of potential yield functions provides a flexible way to interpret crop

Table L4 Estimation of von Liebig models as switching regressions

Model (7): von Liebig with linear regimes

$$y_i = \min\{Y_{Ni}, Y_{Pi}, Y_{mi}\}$$

$$Y_{Ni} = \underset{(0.038)}{0.289} + \underset{(0.084)}{0.984}\,N_i + u_{Ni}$$

$$Y_{Pi} = \underset{(0.095)}{0.264} + \underset{(0.134)}{0.934}\,P_i + u_{Pi}$$

$$Y_{mi} = \underset{(0.014)}{1.268} + u_{mi}$$

$$\log L = 70.514 \quad \hat{\sigma}_N = 0.130 \quad \hat{\sigma}_P = 0.237 \quad \hat{\sigma}_m = 0.094 \quad df = 106$$

Model (8): von Liebig with Mitscherlich regimes

$$y_i = \min\{Y_{Ni}, Y_{Pi}\}$$

$$Y_{Ni} = \underset{(0.024)}{1.373}[1 - \underset{(0.028)}{0.802}\,\exp(-\underset{(0.157)}{1.544}\,N_i)] + u_{Ni}$$

$$Y_{Pi} = \underset{(0.024)}{1.373}[1 - \underset{(0.041)}{0.873}\,\exp(-\underset{(0.212)}{1.962}\,P_i)] + u_{Pi}$$

$$\log L = 79.598 \quad \hat{\sigma}_N = 0.123 \quad \hat{\sigma}_P = 0.143 \quad df = 107$$

Statistics in parentheses are standard errors.

Table L5 Estimation of a Generalized von Liebig Model

von Liebig Model (10) incorporating Mitscherlich's Law of Physiological Relations

$$y_i = \min\{Y_{Ni}, Y_{Pi}, Y_{mi}\} + u_i$$

$$Y_{Ni} = \underset{(0.029)}{0.303} - \underset{(0.056)}{0.508}\,N_i + \underset{(0.079)}{1.140}\,N_i^{0.5} + \underset{(0.069)}{0.570}N_iP_i$$

$$Y_{Pi} = \underset{(0.025)}{0.156} - \underset{(0.064)}{0.544}\,P_i + \underset{(0.121)}{0.973}\,P_i^{0.5} + \underset{(0.028)}{0.108}P_i^{0.5}N_i$$

$$Y_{mi} = \underset{(0.016)}{1.285}$$

$$\log L = 89.679 \quad \hat{\sigma} = 0.110 \quad df = 105$$

Statistics in parentheses are standard errors.

response data. The estimates of a similar model are presented in Table L3 under model (6). Once again, the coefficient of determination shows only a modest gain over either of the two previous models. The value of the logarithm of the likelihood function, however, exhibits a dramatic improvement. The predicted surface of this specification is presented in Figure L8.

The sample of data utilized in the estimation of these three models did not show any decline of crop yield. A second sample of experimental information was chosen for this purpose. It deals with the response of cotton lint to N and irrigation water W and was analyzed by Hexem and Heady (1978). This cotton experiment was conducted in 1969 on Panoche clay loam soil at the West Side Field Station, Fresno County, California. This sample of experimental data shows a distinct phase of declining yields. A von Liebig model similar to specification (4) was suited, therefore, to interpret the data. The estimates of this model are presented in Table L3 under model (4). The predicted surface corresponding to this model is illustrated in Figure L6.

The estimation of models (7) and (8) was carried out according to maximum likelihood procedures discussed by Paris (1992) using the same sample of corn data collected by Heady et al. The corresponding estimates are presented in Table L4.

An estimated model that incorporates Mitscherlich's law of physiological relations is presented in Table L5. Also this model was estimated using the sample of corn response to N and P. The dependence of each potential yield function on the other nutrient is validated by the significant estimates of all the coefficients. The estimates of Table L5 can be directly compared with those of model (6) in Table L4. As before, while the improvement in the coefficient of determination is negligible, the gain in the logarithm of the likelihood function is significant. This discussion shows that the *R*-squared is an irrelevant statistic for hypothesis testing and for model selection.

Conclusion

The Law of the Minimum is a famous conjecture with a troubled history. Its enunciation opened the modern era for agricultural practices based upon a mineral theory of plant nutrition. Its author, Justus von Liebig, could not give it a convincing mathematical formulation and, in the end, his critics defined "the Law of the Minimum" for him. His translators from the German interpreted his writing as stating that yields were *proportional* to the limiting input. This interpretation was devastating for the von Liebig's hypothesis because many empirical findings did not conform to such a formulation.

A re-evaluation of the Law of the Minimum undertaken in recent years has revealed two facts: von Liebig did not state his hypothesis in terms of proportionality relations; when analyzed with correct and rigorous statistical procedures, experimental data of crop response tend to validate the Law of the Minimum.

At the turn of the century, Blackman (1905) gave the Law of the Minimum a dynamic formulation, although little scientific and empirical consequence followed his statement (p. 289): "When a process is conditioned as to its rapidity by a number of separate factors, the rate of the process is limited by the pace of the 'slowest' factor." A mathematical formulation of this proposition may take the following structure:

$$\frac{\partial Y}{\partial t} = \min\{g_1(t), g_2(t), \ldots, g_n(t)\}$$

$$Y(t) = \int_{t_0}^{t_1} \min\{g_1(\tau), g_2(\tau), \ldots, g_n(\tau)\}\mathrm{d}\tau$$

where $g_i(\tau)$ is the growth rate of the *i*th factor. This formulation of the Law of the Minimum requires some knowledge of calculus of variations, a requirement that attests to the richness of the hypothesis to interpret scientific scenarios of many different types.

Quirino Paris

Bibliography

Ackello-Ogutu, C., Paris, Q., and Williams, W.A., 1985. Testing a von Liebig crop response function against polynomial specifications. *Am. J. Agric. Econ.*, **67**: 873–880.

Black, J.D., 1925. Book review of the law of diminishing returns by W.J. Spillman and E. Lang. *J. Farm Econ.*, **7**: 274–280.

Blackman, F.F., 1905. Optima and Limiting Factors. *Ann. Bot.*, **19**: 281–295.

Grimm, S.S., Paris, Q., and Williams, W.A., 1987. A von Liebig model for water and nitrogen crop response. *West. J. Agric. Econ.*, **12**: 182–192.

Holloway, G., and Paris, Q., 2002. Production efficiency in the von Liebig model. *Am. J. Agric. Econ.*, **84**: 1271–1278.

Heady, E.O., Pesek, J.T., and Brown, W.G., 1955. Corn response surfaces and economic optima in fertilizer use. *Iowa State Experiment Station Research Bulletin 424*.
Hexem, R.W., and Heady, E.O., 1978. *Water Production Functions for Irrigated Agriculture.* Ames: Iowa State University Press.
Kreuz, C., 1993. von Liebig models with decreasing yields, Mitscherlich's law of physiological relations, and the relative yield hypothesis. Unpublished Ph.D. dissertation, Universidade Federal de Santa Catarina, Brazil.
Lang, E., 1924. The Law of the soil. In Spillman, W.J., and Lang, E., eds., *The Law of Diminishing Returns.* New York: World Book Company.
Lanzer, E.A., and Paris, Q., 1981. A New analytical framework for the fertilization problem. *Am. J. Agric. Econ.*, **63**: 93–103.
von Liebig, J., 1843. *Die Chemie in ihrer Anwendung auf Agricultur und Physiologie*. 3e Aufl., Braunschweig: F. Vieweg und Sohn.
von Liebig, J., 1862. *Die Naturgesetze des Feldbaues*. 7e Aufl., Vol. II. Braunschweig: F. Vieweg und Sohn.
von Liebig, J., 1863. *The Natural Laws of Husbandry.* Blyth, J., ed., New York: D. Appleton and Company.
von Liebig, J., 1955. *Die Grundsätze der Agricultur-Chemie: mit Rücksicht auf die in England angestellen Untersuchungen*. Braunschweig: F. Vieweg und Sohn.
Mitscherlich, E.A., 1909. Das Gesetz des Minimums und das Gesetz des abnehmenden Bodenertrages. *Landwirtschaftlische Jarbücher*, **38**: 537–552.
Paris, Q., 1992. The von Liebig hypothesis. *Am. J. Agric. Econ.*, **74**: 1019–1028.
Russell, E.J., 1912. *Soil Conditions and Plant Growth.* London: Longmans, Green and Co.

Cross-references

Fertilizers
Plant Nutrients
Soil Fertility

LEACHING

To subject a material such as a soil or other weathered deposit to the action of percolating water, which removes soluble substances and transports them away under the influence of gravity: a major mechanism in the evolution of soil. Lixiviate is a synonym used especially when the leaching is employed to obtain soluble salts from solid materials (wood ashes, for example).

Cross-references

Soil
Weathering Systems in Soil Science

LEPTOSOLS

Leptosols are very shallow soils with minimal development, formed typically on hard rock or highly calcareous materials. They also include deeper soils on gravelly and/or stony parent materials lacking fine earth. With an incomplete solum and/or without clearly expressed pedogenetic features, Leptosols qualify as azonal soils in the pre-Soil Taxonomy terminology of the USDA. This article is based on the descriptions in FAO (2001 and 2006).

Connotation. Shallow soils; from Gr. *leptos*, thin.

Synonyms. Leptosols are equivalent to lithosols in many classifications (Soil Taxonomy, FAO for example) and with 'lithic' subgroups in other soil groupings. In many systems, rendzina is the name applied to Leptosols on calcareous parent materials, while ranker is used for Leptosols on acid rocks.

Definition. Leptosols have

1. either continuous hard rock within 25 cm from the soil surface; or a 10 to 25 cm thick mollic horizon with a thickness between directly overlying material with a calcium carbonate equivalent of more than 40%, or less than 10% (by weight) fine earth from the soil surface down to a depth of 75 cm; and
2. no diagnostic horizons other than a mollic, ochric, umbric, or yermic horizon.

In point 1 of the definition, the stipulation of hard rock within 25 cm of the surface excludes cemented layers such as a petrocalcic or petroplinthic horizon. However, soils deeper than 25 cm may be included if they contain less than 10% fine earth down to at least 75 cm.

Parent material. Various kinds of hard bedrock or unconsolidated calcareous and other materials with less than 10% fine earth.

Environment. Leptosols are a very diverse group of soils found from the poles to the equator in environments conducive to youthful soils e.g., on the erodible slopes of mountain belts, and in situations such as the active flood plains of river systems where fresh additions of alluvium are found.

Distribution. With an areal extent of 1 655 million ha, Leptosols are the most extensive reference soil group on Earth. They occur in all climatic zones, especially in mountains, associated with river systems, lake shores and sea coasts, in recently glaciated regions such as the Canadian Shield, and in the extensive desert regions of north Africa and southwest Asia, coasts extending over approximately. Lithic Leptosols are particularly extensive in mountain belts, and less so in cratonic regions. Figure L9 shows the global distribution of this group.

Characteristics. Leptosols are azonal soils with an incomplete solum and/or without clearly expressed morphological features. Weakly expressed A(B)R or A(B)C horizonation is common, though Rendzic and Mollic Leptosols have a more pronounced morphology, with a dark brown to black calcareous, organo-mineral surface horizon with a stable crumb or granular structure, or with a vermicular structure with abundant earthworm casts. In addition Rendzic Leptosols have visually obvious white limestone fragments. At the base of the solum, the change to bedrock is abrupt, or at most is marked by a thin transitional horizon. Because of the wide variety of pedogentic environments and parent materials in which leptosols form, the soils are very variable in their physical, chemical and biological properties. They are commonly free draining, though some hyperskeletic leptosols have groundwater at shallow depth, while (exceptionally) some leptosols in poorly drained localities (shallow slopes and declivities for example) may develop stagnic properties. Leptosols on calcareous parent materials generally have better physical and chemical properties than non-calcareous ones and are also more uniform as a group. The natural vegetation on leptosols varies with the climate but is generally richer and more diverse on calcareous leptosols than on acid ones. Earthworms, enchytraeid worms and arthropods are the main faunal species, and in dry periods they may become temporarily inactive.

Origin. Soil formation is at an early stage, normally with a thin A horizon overlying an incipient B horizon or lying

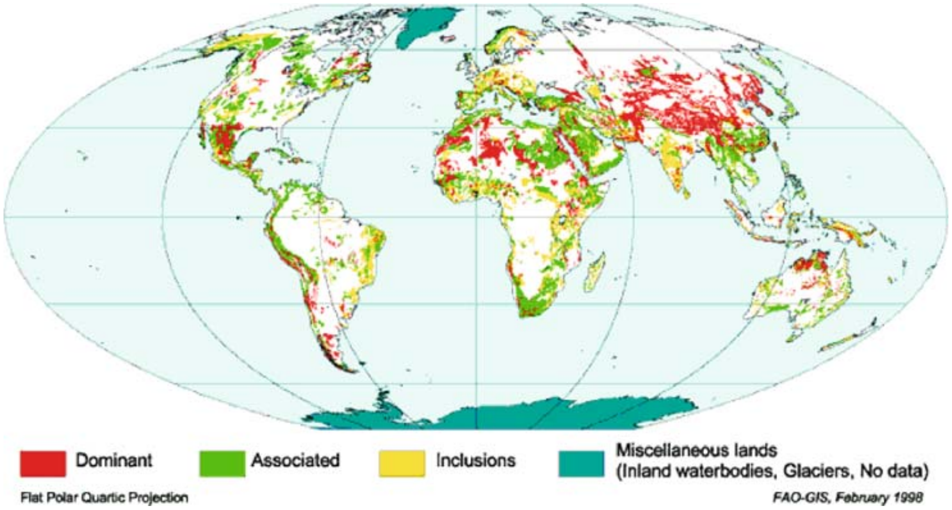


Figure L9 Global distribution of Leptosols.

directly over parent material. The principal soil forming process in rendzic and mollic leptosols is the destruction of carbonates and the removal of the products of dissolution. The scarce, remaining residue is well mixed with stable humifying organic matter and, in rendzic leptosols, with fragments of limestone. Smectites in the clay fraction produce a dominant blocky structure in the soil, by swelling and shrinking. Pedogenesis of predominantly siliceous parent materials in mountainous regions with a combination of relatively cool climate and high precipitation produces Umbric Leptosols.

Use. Shallowness and/or stoniness, with consequent low water holding capacity and excessive drainage leading to drought, tend to be the most severe limitations to the use of Leptosols. They may, however have potential for grazing during the wet season, and for forestry. Plantations of teak and mahogany are maintained on Rendzic Leptosols in Southeast Asia, while in the temperate zone similar soils mostly support deciduous mixed forest. Also in temperate regions, acid lithic, umbric and Dystric Leptosols are commonly under pine forest. Leptosols on hill slopes tend to be more fertile than those on flat lands, though erosion may be a considerable problem on the former, especially where population pressure is high. Removal of the forest cover by over-exploitation, or by environmental pollution serves to increase the threat of erosion. Historically, in cultures such as Southeast Asia, and pre-Columbian South America, the problem has been dealt with by terracing. Agroforestry systems also offer some control.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FAO, 2006. World reference base for soil resources. World Soil Resources Report 103. Rome: Food and Agriculture Organization of the United Nations, 132 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science*, 2nd edn., Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W. and Hintermaier-Erhard, G. 2008. Soils of the world. Heiderberg, Berlin: Springer-Verlag. 130 pp.

Cross-references

Biomes and their Soils
Classification of soils: World Reference Base (WRB) for soil resources
Classification of soils: World Reference Base (WRB) Soil Profiles
Geography of Soils

LESSIVAGE

The downward movement in a soil, of clay particles suspended in water, resulting in the formation of argillans and the formation of a relatively clay-rich horizon at a lower level of the profile. Horizons of clay accumulation so formed, affect the hydrodynamics of a soil, and in the extreme restrict drainage sufficiently to cause gleying (Zaidel'man, 2007). See *Eluviation*, *Illuviation*.

Bibliography

Zaidel'man, F.R., 2007. Lessivage and its relation to the hydrological regime of soils. *Eurasian Soil Sci.*, **40**: 115–125.

Cross-references

Cutan
Gleysols
Water Movement

LFH HORIZON

See *Horizon*, *Profile*, *Horizon Designations*.

LIGHT FRACTION

Plant debris and other organic components of a soil lying in the density range 1.5 to 2 Mg m^{-3}. Separated from the heavier fraction by flotation in a liquid of appropriate density.

LIME

Calcium oxide (CaO) also called quick lime, obtained by the de-carbonation of calcium carbonate in the form of limestone, by roasting in a kiln. The oxide is caustic and combines exothermically with water, to form the hydroxide $Ca(OH)_2$ (slaked lime). In agriculture limestone itself is referred to as lime and, with other materials with an alkaline reaction, is used in the process of liming to combat acidity in soil. The term is also loosely used as a synonym for calcium as in the outdated term carbonate of lime for $CaCO_3$.

Bibliography

Adams, F., 1984. *Soil Acidity and Liming*, 2nd edn. Madison, WI: American Society of Agronomy, 380 pp.

Cross-reference

Carbonates

LIQUEFACTION

In absolute terms: the reduction of a solid or a gas to a liquid state. In geotechnical terms the word is used to describe the fluid behavior of a clay-rich, water-saturated soil or other surficial deposit, when subjected to a sudden shock such that the shear strength of the deposit is lost. Major landslides have been effected in water-saturated marine clays deposited in the Northern Hemisphere during the period of deglaciation, that began about 15,000 years ago.

Cross-references

Andosols
Thixotropy, Thixotropism

LITHIC

Of or pertaining to rock or stone. In the WRB system, a soil qualifies as lithic when it has continuous hard rock within 10 cm of the soil surface.

LITHOSEQUENCE

A sequence of soils in which the dominant variable accounting for any physical, chemical and biological differences is the nature of the parent rock over which the sequence has developed.

LITTER

The decomposing but still recognizable organic debris that has accumulated as a distinct horizon at a soil surface. It is derived from the standing biomass. Leaf-litter, as the name implies, is largely composed of leaves. A litter horizon is designated L in several national soil classifications. In the German system for example, the L horizon is distinguished from the other organic-rich surface horizons: F (fermentation horizon), H (humification horizon), and M (living moss layer).

Bibliography

Boden, A.G., 1994. *Bodenkundliche Kartieranleitung*, 4th edn. Stuttgart: E. Schweizerbart'sche-Verlagsbuchhandlung, 392 pp.

LIXISOLS

Lixisols are strongly weathered soils in which clay has washed out of an upper, down to a lower horizon. The clays are of low activity, and a moderate to high level of base saturation. This account is taken from FAO (2001 and 2006).

Connotation. Strongly weathered soils in which clay is washed down from the surface soil (eluviation) to an accumulation horizon (illuviation) at some depth; from L. *lixivia*, washed-out substances.

Synonyms. They have been known in the past as 'red and yellow earths' and as 'latosols'. Other classifications are 'red-yellow podzolic soils' (e.g., Indonesia), 'podzolicos vermelho-amarello eutroficos a argila de atividade baixa' (Brazil), 'Sols ferralitiques faiblement désaturés appauvris' and 'Sols ferrugineux tropicaux lessivés' (France), shortlands (South Africa), In Soil Taxonomy, they key out as subgroups of alfisols.

Definition. FAO (2001) define Lixisols as soils with an argic horizon starting within 100 cm of the soil surface, or within 200 cm of the soil surface if the argic horizon is overlain by loamy sand or coarser textures throughout.

Parent material. Unconsolidated, strongly weathered and strongly leached, finely textured materials.

Environment. Regions with a tropical, subtropical or warm temperate climate with a pronounced dry season, notably on old erosional or depositional surfaces. Many Lixisols are (surmised to be) polygenetic soils with characteristics formed under a more humid climate in the past. They are a kind of tropical equivalent of the Luvisol, more weathered and with a higher ratio of Al and Fe oxides to silica.

Distribution. Lixisols cover about 435 million ha of the Earth's land surface, with more than half in sub-Sahelian and East Africa, about a quarter in South and Central America and the rest on the Indian subcontinent, in Southeast Asia and in Australia. Figure L10 shows their approximate global extent.

Characteristics. ABtC-profiles. On slopes and on other surfaces subject to erosion, the argic accumulation horizon may be exposed or at shallow depth.

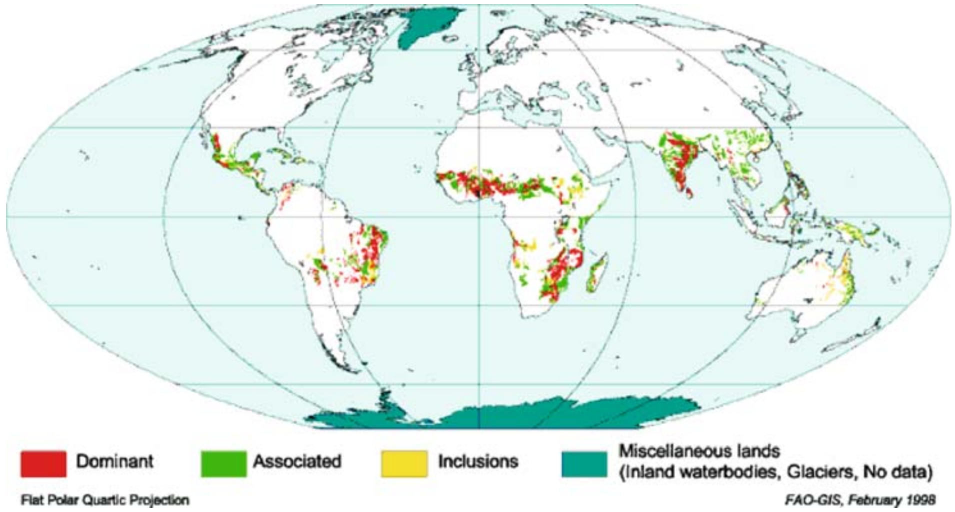


Figure L10 Global distribution of lixisols.

Origin. There are indications Lixisols began their development under a wetter climate than at present. Initial intense weathering and leaching, appears to have been followed by chemical enrichment more recently, i.e., after the climate had changed towards an annual evaporation surplus. Fossil *plinthite* and/or coarse reddish mottles or indurate iron nodules in the subsurface soil of many Lixisols also hint at wetter conditions in the past. There are indications that base-rich aeolian deposits enriched (some) Lixisols whereas others could have been improved by biological activity (import of bases from the deeper subsoil) or by lateral seepage of water. The reddish or yellow colors of many Lixisols (notably in argic horizons) are the result of '*rubefaction*' brought about by dehydration of iron compounds in long dry seasons.

Use. Most 'unreclaimed' Lixisols are under savannah or open woodland vegetation. Such areas are often used for low volume grazing. Perennial crops or forestry are suitable land uses; arable farming requires recurrent inputs of fertilizers and/or lime. The unstable surface soil structure makes Lixisols prone to slaking and erosion in sloping land.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FAO, 2006. World reference base for soil resources. World Soil Resources Report 103. Rome: Food and Agriculture Organization of the United Nations, 132 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science*, 2nd edn., Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2008. *Soils of the World*. Heidelberg Berlin: Springer-Verlag. 130 pp.

Cross-references

Biomes and their Soils
Classification of soils: World Reference Base (WRB) for soil resources
Classification of soils: World Reference Base (WRB) Soil Profiles
Geography of Soils

LOADING

In environmental science the amount of a substance added to an ecosystem or to the soil, surface waters, or other parts of an ecosystem, by natural or (increasingly) by human activities. In mechanics, the weight that a surface such as the soil is subjected to.

LOAM

See *Particle Size Distribution*.

LOESS

See *Biomes and their Soils*, *Ice Erosion* (see map), *Silt*, *Wind Erosion*.

LUVISOLS

Luvisols are soils in which high activity clay has migrated from the upper part of the profile, generally grayish in color, to be deposited in an argic B horizon, commonly of a browner hue. The following account is from FAO (2001, 2006).

Connotation. Soils in which clay is washed down from the surface soil to an accumulation horizon at some depth; from L. *luere*, to wash.

Synonyms. ‘Alfisols’ (Soil Taxonomy), ‘gray brown podzolic soils’ (earlier USA terminology), ‘pseudo-podzolic soils’ (Russia), ‘sols lessivés’ (France), ‘Parabraunerde’ (Germany),

Definition. Luvisols are soils that have an argic horizon with a cation exchange capacity (in 1 M NH_4OAc at pH 7.0) equal to or greater than 24 cmol(+) kg^{-1} clay. The argic horizon starts either within 100 cm of the soil surface or within 200 cm of the soil surface if the argic horizon is overlain by material that is loamy sand or coarser throughout.

In terms of negative properties, they lack the abrupt textural change of Planosols, albeluvic tonguing as in Albeluvisols, a mollic surface horizon as in steppe soils, and the alic properties of Alisols

Parent material. Luvisols form on a wide variety of unconsolidated materials: glacial till, and aeolian, alluvial and colluvial deposits, for example. Chemically the parent materials are base-rich, with calcite (and/or dolomite) commonly in evidence.

Environment. Usually found on flat or gently sloping land in cool temperate regions and in warm areas with contrasted dry and wet seasons (as in the Mediterranean region for example).

Distribution. There are more than 500 to 600 million ha of Luvisols, globally. These are mostly in the temperate zone, for example in west/central Russia, Europe including the Mediterranean region, southern Ontario and adjacent parts of northeastern USA and in southern Australia. They also occur in the tropics and subtropics, mostly on young land surfaces. Figure L11 shows the global distribution.

Characteristics. The general pattern of horizonation is ABtC. Since the soils form on a wide variety of parent materials in many environments, Luvisols are a very diverse group. An albic horizon is sometimes present and a gradation toward the Albeluvisol reference group is not uncommon. Brown hues are the predominant colors, and are normally more reddish in warmer regions.

Luvisols are at an intermediate stage of weathering (with a SiO_2/Al_2O_3 ratio greater than 2.0). Weatherable minerals from the parent material are still present in the solum, and 2:1 sheet silicates (smectites) are the common constituents of the clay fraction. As a consequence Luvisols tend to have a high inherent fertility. Where formed on calcareous parent materials, decalcification is usual in the surface horizon (which thereby has a slightly acid reaction) and may extend down to the C horizon, depending on the age and climatic history of the soil. The chemical properties of Luvisols vary with parent material and pedogenetic history.

Luvisols are generally porous and well aerated, with a granular or crumb structure in the surface horizons. The argic horizon has a stable, blocky structure, with the greatest capacity for available water storage (15 to 20 vol.-%).

Drainage is not normally a problem except in landscape depressions with shallow groundwater, where gleyic soil properties may develop in and below the argic horizon. If the Bt is dense enough to impede drainage for extended periods of time, stagnic properties may result.

Origin. Illuviation of clay from the upper part of the soil, to accumulate as an argic B horizon is the chief physical characteristic of Luvisols. Clay cutans are commonly formed. The process of clay-movement involves three steps

1. clay, occurring in aggregates in surface soil, is dispersed and thereby mobilized;
2. it is transported downwards in aqueous suspension;
3. the transported clay is immobilized by re-aggregation and/or by simple filtration in fine pores, to accumulate in its new locality.

In the language of colloid chemistry the significant processes are the peptization of clay (step 1, above), followed after transport, by flocculation (step 3). Which process dominates depends upon the ionic properties of the system, in particular: ionic strength of the soil solution, composition of the ions adsorbed at the exchange complex, and specific charge characteristics of the clay in the soil. Generally, high concentrations of electrolyte favor flocculation, while low concentrations favor dispersion. In terms of the electrical double layer model, a low electrolyte concentration widens the double layer while a high concentration compresses it. Dispersion becomes more likely as it widens.

Soil-pH has a significant influence. At pH values below 5 (measured in water 1:1), there is a sufficiently high concentration

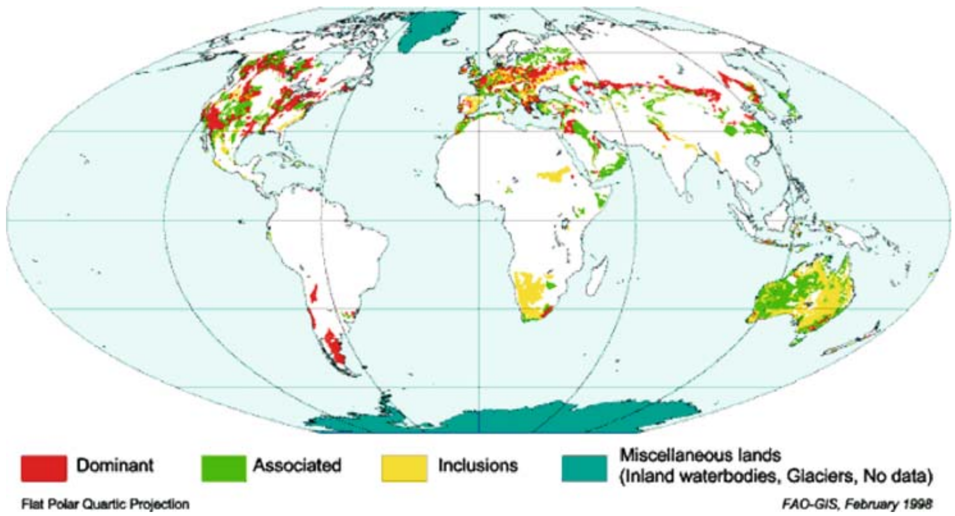


Figure L11 Global distribution of Luvisols.

of Al^{3+} in the soil solution to keep the clay flocculated. Between pH 5.5 and 7.0, the content of exchangeable aluminum is much lower and provided that divalent ions are in low concentration, clay can disperse. At still higher pH values, divalent ions such as Ca^{2+} will normally keep the clay flocculated unless there is a strong dominance of Na^+ in the soil solution.

Many Luvisols have formed from pre-existing Albeluvisols by anthropogenic activities, in Western Europe for example, where cultivation has been practiced extensively over some three or four thousands of years. The pedological transformation has been brought about by agriculturally induced erosion leading to the *truncation* of the Ah- and E-horizons, as well as most of the albeluvic tongues. A significant role has also been played by increased *homogenization* by soil fauna (worms in particular), encouraged by liming and/or fertilization over the long term.

Use. Most Luvisols are at an intermediate stage of weathering and so are generally of a high inherent fertility. Provided they have good drainage characteristics, they are suitable for many agricultural uses.

In temperate climates small grains, sugar beet and fodder are grown with orchards and grazing on erodible slopes. In the Mediterranean region, where chromic, calcic and Vertic Luvisols are common in colluvial deposits of limestone weathering, the lower slopes are commonly sown to a combination of wheat and/or sugar beet on lower slopes and extensive grazing or tree crops on eroded upper slopes, is common in the Mediterranean region.

Structural deterioration is a potential problem. Luvisols with a high silt content at the surface may be sensitive to slaking and erosion. Tillage of the soils when wet, or with heavy machinery may be deleterious. Also, a platy structure may develop in the upper, eluviated part of the profile, leading to the acquisition of stagnic properties. Consequently, Luvisols that have been truncated by erosion can be better soils in an agricultural sense than the non-eroded variety.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FAO, 2006. World reference base for soil resources. World Soil Resources Report 103. Rome: Food and Agriculture Organization of the United Nations, 132 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science*, 2nd edn., Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2008. *Soils of the World*. Heidelberg, Berlin: Springer-Verlag. 130 pp.

Cross-references

Biomes and their Soils
Classification of soils: World Reference Base (WRB) for soil resources
Classification of soils: World Reference Base (WRB) Soil Profiles
Geography of Soils

M

MACRONUTRIENTS

Introduction

Essential elements for plant growth are commonly classified as macronutrients or micronutrients based on the amount of the element required for normal growth of plants (Allaway, 1975; Epstein and Bloom, 2005). Macronutrients are required in large amounts and normally constitute 1 000 mg kg^{-1} (0.1%) or more of the dry weight of the plant. Micronutrients are required in relatively small amounts and normally make up less than 500 mg kg^{-1} (0.05%) of the dry plant weight. Plants contain small amounts of 90 or more elements, but only 16 are known to be essential to higher plants (Epstein and Bloom, 2005; Finkl, 1988). An element is not considered to be essential unless a deficiency of it makes it impossible for the plant to complete its life cycle. Carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg) and sulfur (S) are classified as *macronutrients* and zinc (Zn), iron (Fe), manganese (Mn), copper (Cu), molybdenum (Mo), boron (B) and chlorine (Cl) are classified as *micronutrients*. The macronutrients, their chemical symbols, the ionic or molecular form(s) commonly available to the plant from the air or soil solution, and the year each element was proven to be essential, are presented in Table M1. The macronutrients can be further subdivided based on the source of each of the elements. Carbon, H, and O are largely obtained by the plant from air and water while N, P, K, Ca, Mg and S come primarily from the soil and are absorbed by the plant through the root system. Nitrogen can be supplied to the plant in relatively large quantities from both the air and soil. *Rhizobia* bacteria, found in nodules on the roots of legumes, are able to fix dinitrogen (N_2) from the air and convert it into inorganic forms for plant use.

Macronutrients in soil

Plant nutrient elements are released to the soil from rocks, organic matter or other parent materials by weathering and soil-forming processes. Macronutrients are normally present in the soil in complex organic or inorganic combinations that must be converted to simpler compounds and then to ionic forms prior to their uptake by plants (Table M2). All of the macronutrients, except K, are found in the soil in both organic and inorganic combination. Potassium is found only in inorganic combinations (Haby et al., 1990). Approximately 97 to 99 percent of soil N is present in soil organic matter (Dahnke and Johnson, 1990) largely in proteins and amino acids. Phosphorus is present as a constituent of many inorganic compounds as well as organic combinations such as phytin and nucleic acids. Potassium is largely present in soils in the primary minerals, feldspar and mica, and in secondary clay minerals such as illite. Primary inorganic sources of Ca in soil are feldspars, hornblende, calcite and dolomite. Magnesium is present in significant amounts in mica, hornblende, dolomite, and serpentine as well as certain clay minerals. Sulfur can be found in organic form as a constituent of proteins and in inorganic minerals such as pyrite and gypsum. Over the life cycle of a field crop, most of the K, Mg and Ca would be supplied by ions adsorbed to the exchange complex of clay minerals, N would be supplied from organic sources and both P and S would be supplied from adsorbed anions ($H_2PO_4^{2-}$ and SO_4^{2-}, respectively) and organic sources. If the concentrations of macronutrients in a readily available form are inadequate, then commercial fertilizers can be applied to insure an adequate supply of readily available nutrient for plant utilization.

There is a broad range in concentration of the macronutrients in soils. The total concentration of the elements is not considered as important in their availability to plants as their chemical form. Under natural conditions, the major factors affecting macronutrient availability to plants are: (1) concentration in the soil solution; (2) degree of interaction with, and rate of release from, the solid phases of the soil; (3) activity of soil microorganisms; and (4) discrimination by the plant root during ion uptake (Bohn et al., 2001).

Macronutrients in plants

Carbon, H, and O are the primary elements needed to build structural units in plants. These elements make up 94 to 99 percent of the fresh plant tissue weight and are important in energy storage and metabolism. With the exception of C,

Table M1 The macronutrient elements, their chemical symbols, their ionic or molecular form(s) commonly absorbed by plants from the air or soil, and the year that each nutrient was proven to be essential for plant growth and reproduction

Element	Symbol	Ion or molecule	Year proved essential	Primary sources(s) and absorbing plant organ
Carbon	C	CO_2	1882	Air; leaves
Hydrogen	H	H_2O	1882	Water; roots
Oxygen	O	H_2O, CO_2 through leaves	1804	Soil and air; mostly
Nitrogen	N	NH_4^+, NO_3^-, N_2 through roots	1872	Soil and air; mostly
Phosphorus	P	$H_2PO_4^-$, HPO_4^{2-}	1903	Soil; roots
Potassium	K	K^+	1890	Soil; roots
Calcium	Ca	Ca^{2+}	1856	Soil; roots
Magnesium	Mg	Mg^{2+}	1906	Soil; roots
Sulfur	S	SO_4^{2-}	1911	Soil; roots

Table M2 Chemical forms of the macronutrients and the common range of each in soil

Common forms in soil		Concentration range in soil mg kg^{-1}
Soil organic matter-proteins, amino acids,nucleic acids	Nitrogen	200–4 000
Apatite, complex calcium, iron, and aluminum phosphates; soil organic matter-phytins and nucleic acids	Phosphorus	100–5 000
Primary minerals feldspar and mica and secondary alumino silicate minerals	Potassium	400–5 000
Largely from feldspars, horneblende, dolomite and calcite	Calcium	400–35 000
Primary minerals mica, hornblende, dolomite and serpentine and from the secondary aluminosilicate minerals	Magnesium	600–15 000
Mineral combinations such as pyrite and gypsum; soil organic matter	Sulfur	100–10 000

H, O and N from biological N-fixing systems, all other essential nutrients come primarily from the soil. The main function of the mineral macronutrients, N, P, and S in the plant is as a constituent of proteins and nucleic acids. Nitrogen is also a structural component of chlorophyll and is important in cation-anion balance and osmoregulation. Phosphorus also forms energy-rich bonds and is involved in energy storage and transfer in the plant. An adequate supply of P is essential for seed formation and stimulation of root growth. Phosphorus is associated with early maturity in crops. Sulfur is a constituent of the amino acids, cysteine and methionine, and hence of proteins. It is also a structural constituent of several coenzymes and prosthetic groups such as ferredoxin, biotin (vitamin H), and thiamine pyrophosphate (vitamin B1). Sulfur deficiency inhibits the synthesis of these compounds. Potassium is the only macronutrient that is not a constituent of organic structures in plants and functions mainly in the maintenance of electrochemical equilibria in cells, the regulation of enzyme activities and osmoregulation in plant cells and stomata (Marschner, 1986). Magnesium is an integral part of the structure of the chlorophyll molecule and also functions as a constituent of activator enzyme molecules, where it is directly or indirectly involved in the catalytic function of the enzymes. Calcium is bound in an exchangeable form to cell walls and at the exterior surface of the plasma membrane. Most of its activity is apparently related to its capacity for coordination, by which it provides stable but reversible intermolecular linkages, predominantly in the cell walls and at the plasma membrane. Calcium is intimately involved in cell extension and root extension ceases within a short period of time in the absence of Ca. The role of Ca in cell extension is not yet clear, however, there are indications that it is required for the incorporation of material into the cell walls (Marschner, 1986).

Sources of macronutrients

Soil serves as a storehouse for plant nutrients and normally provides a substantial amount of the crop nutrient requirements. Total and available concentrations of nutrients vary greatly between soils and crops. Under most conditions, however, crop production can be enhanced by application of supplemental macronutrients. Data presented in Table M3 give typical total concentrations of macronutrients in soil (Lindsay, 2001; Clarke and Washington, 1924), representative concentrations of the macronutrients in field crops, and the annual uptake of each nutrient required in the above ground portion of a crop to produce 10 000 kg of dry matter per hectare. An enrichment ratio is also calculated and shown in Table M3 for the macronutrients. Enrichment ratios of >1 (N and P) indicate that the plant must produce dry matter with relatively higher concentrations of the nutrient than the total amount found in soil. Enrichment ratios of ~1 (K, Ca and S) indicate that the plant will produce dry matter with approximately the same relative nutrient concentration as the soil. Magnesium has an enrichment ratio of 0.2 indicating a much lower nutrient concentration in plant tissue compared to soil. Another interpretation may be that the higher the enrichment ratio the more likely a soil will have to be supplemented with nutrients to produce a crop.

Different crops and plants contain varying concentrations of the macronutrients in their tissue and will produce a range of dry matter per hectare, therefore, the values given in Table M3 will be expected to vary with the type of crop, dry matter production and the fertility of the soil.

Table M3 Typical concentrations of macronutrients in soils and plants and annual plant uptake

Macronutrient	Concentration soil mg kg^{-1}		Enrichment plant ratio†	Annual plant uptake† kg ha^{-1} yr^{-1}
Nitrogen	2 000	10 000	5.0	100
Phosphorus	400	2 000	5.0	20
Potassium	15 000	10 000	0.7	100
Calcium	24 000	17 000	0.7	170
Magnesium	9 000	1 500	0.2	15
Sulfur	1 600	1 500	0.9	15

†The enrichment ratio is defined as the ratio of plant to soil concentrations, with both expressed in the same units.
†Annual plant uptake per hectare based on an annual dry matter production of 10 000 kg ha^{-1}.

Any material containing one or more of the essential nutrients that is added to the soil or applied to plant foliage for the purpose of supplementing the plant nutrient supply can be called a fertilizer. The earliest fertilizer materials were animal manures, plant and animal residues, ground bones and potash salts derived from wood ashes. Although these natural materials are still used to supplement soil nutrient levels, the majority of supplemental macronutrients are supplied to soils from commercial fertilizer sources. Three major developments in the nineteenth century were the forerunners of the modern fertilizer industry: the discovery of potassium salt deposits in the German states in 1839, the treatment of ground rock phosphate with sulfuric acid to form superphosphate in 1842 and the development of the theoretical principles for combining hydrogen and atmospheric nitrogen to form ammonia in 1884 (Boswell, 1985). The basic concepts of fertilizer manufacture have not changed much from those original developments but the level of sophistication in fertilizer technology has changed tremendously. The primary sources of the three major elements supplied in commercial fertilizer sources today are from the synthetic fixation of elemental N (from atmospheric N_2) to produce anhydrous ammonia, acidification of rock phosphate to produce phosphoric acid (H_3PO_4), and mined KCl and K_2SO_4 as direct application K sources. Calcium, Mg and S needs of crops are commonly met by applying calcite, $CaCO_3$, dolomite, $CaMgCO_3$, and gypsum, $CaSO_4$.

L. R. Hossner

Bibliography

Allaway, W.H., 1975. The effects of soils and fertilizers on human and animal nutrition. U.S.D.A. Agr. Inf. Bull. No. 378, Washington, DC.
Bohn, H.L., McNeal, B.L., and O'Connor, G.A., 2001. *Soil Chemistry.* New York: Wiley & Sons, 307 pp.
Boswell, F.C., ed., 1985. *Fertilizer Technology and Use.* Madison, WI: Soil Science Society of America, 633 pp.
Clarke, F.W., and Washington, J.S., 1924. The composition of the earth's crust. U.S. Geol. Survey Paper 127. Washington, DC.
Dahnke, W.C., and Johnson, G.V., 1990. Testing soils for available nitrogen. In Westerman, R.L., ed., *Soil Testing and Plant Analysis.* Madison, WI: Soil Science Society of America, pp. 127–139.
Epstein, E., and Bloom, A.J., 2005. *Mineral Nutrition of Plants: Principles and Perspectives.* New York: Wiley & Sons, 400 pp.
Finkl, C.W., Jr., 1979. Macronutrients. In Finkl, C.W., Jr., ed., *The Encyclopedia of Soil Science.* New York: Van Nostrand Reinhold, pp. 274–276.
Haby, V.A., Russelle, M.P., and Skogley, E.O., 1990. Testing soils for potassium, calcium and magnesium. In Westerman, R.L., ed., *Soil Testing and Plant Analysis.* Madison, WI: Soil Science Society of America, pp. 181–227.
Lindsay, W.L., 2001. *Chemical Equilibria in Soils.* Caldwell, NJ: Blackburn Press, 449 pp.
Marschner, H., 1986. *Mineral Nutrition in Higher Plants.* New York: Academic Press, 674 pp.
Sposito, G., 1989. *The Chemistry of Soils.* New York: Oxford University Press, 277 pp.

MANGAN

See *Cutan*.

MANURE

Dung, commonly with the addition of barnyard wastes and stable litter, used to fertilize soil and to raise the organic matter content. Less commonly used in older literature as a synonym for fertilizer. A major problem in modern animal feeding operations is holding sufficient land to spread manure so that water and air quality are not compromised (Ribaudo et al., 2003). Regular soil processes are the first line of defence in preventing pollution from these and other sources (such as municipal and industrial sludges) though the amount of manure produced has overtaxed land disposal systems in the US, UK, Holland, Canada and other developed nations in the recent past.

Bibliography

Ribaudo, M.N., Gollehon, and Agapoff J., 2003. "Land Application of Manure by Animal Feeding Operations: Is More Land Needed?" Journal of Soil and Water Conservation **58**(1): 30–38.

Cross-references

Sludge Disposal
Soil Fertility

MARGINAL LAND

Borderline land that is on or close to a physical or chemical limit below or beyond which agricultural use ceases to be possible or leads to undesirable consequences, such as excessive erosion. Marginal land tends to be brought into production principally by population pressure, but also by such forces as demand for food in wartime (Europe in WWII for example), and the urge to profit from agricultural subsidies. Destruction of wildlife habitat is a significant collateral effect of the push to exploit the soils of marginal lands.

Bibliography

Bethke, Raymond, W., and Nudds, Thomas D., 1995. Effects of climate change and land use on duck abundance in Canadian prairie-parklands. *Ecological Applications* 5: 588–600.

MARL

A crumbly, sedimentary deposit consisting essentially of clay and calcium carbonate, used as a manure and to improve the texture of sandy soil, especially to relieve the problem of excessive drainage. Marl was used on the sandy soils of the northwest of England from Medieval times until well into the 20th century. It was readily available and found in pockets at no great depth on the landscape. The present day rural landscape of Cheshire for example is dotted with old extraction pits, now full of water (Davies, 1960). They are recognized by having a sloping side where wagons were loaded and a vertical face where excavation ended. Sandy soils of the region of Delamere Forest, which were marled over several centuries, now have a horizon of clay accumulation in the B horizon, locally known as the fox bench.

Bibliography

Davies, C. Stella. 1960. Agricultural History of Cheshire. Manchester: Chetham Society. 230 pp.

MARSH

A marsh is a well-buffered wetland, with relatively strong water-flow and large seasonal fluctuations in water level. Trees are lacking, and eutrophic conditions allow a high production of vascular plants, while prohibiting a well-developed bryophyte layer. A salt marsh is one affected by sea-water.

Cross-reference

Wetland

MASS MOVEMENT

Displacement of a mass of soil or other unconsolidated material, including loose rock bodies, under the influence of gravity down sloping topography. Slower motions are referred to as creep, more rapid ones as slides, slumps or superficial faults. Mass movement may be a consequence of water-saturation, of neotectonic movements, or of anthropic activities, all of which may have been operative in the example illustrated of a slope failure in the Himalayas of Nepal (Figure M1).

Figure M1 Slope failure in the Himalayas, Nepal.

Cross-reference

Mechanical Weathering

MATRAN

See *Cutan*.

MATRIC POTENTIAL

The amount of work required to move a unit quantity of water reversibly into a soil from a reservoir of pure water, at the same temperature and at an equivalent gravitational position (elevation). It is a function of the soil matrix, and the water in question is the layer, no more than a few molecules thick, that coats particulate matter in the soil.

Cross-reference

Water Content and Retention

MATRIX

The enclosing mass of finer grained materials of a soil in which skeletal grains, gravel, pebbles or larger particles, are embedded. The undifferentiated groundmass of the soil.

Cross-reference

Micromorphology

MEADOW

A permanent or semi-permanent field of grass and other herbaceous plants, cropped for hay. A water meadow is grassland close to a river and commonly subject to seasonal flooding. Pasture and hay production are the common uses (Larin, 1965).

Bibliography

Larin, I.V., 1965. *Advances in Pasture and Hay-meadow Management*. Jerusalem, Israel Program for Scientific Translations. 479 p.

MECHANICAL WEATHERING

Mechanical (or physical) weathering is the process by which physical forces break down rock, minerals and soil into finer particles. This article treats mechanical weathering as being separate from chemical weathering, even though both types of alteration occur concurrently in nature. Following Yatsu (1988), the processes of mechanical (or physical) weathering are classified according to the kind of stresses established in geological materials. The pedological context is stressed.

Mechanical weathering due to phase changes

Frost weathering and salt weathering are considered to be caused by phase changes.

Frost weathering

This is also known as congelifraction, gelifraction, frost wedging, frost riving, frost shattering and frost splitting, all of which imply the forcing apart of materials, commonly rock, by expansion of water upon freezing in pore spaces, cracks or other gaps in the solid (Washburn, 1979, p. 73). It is common in the high latitudes and at high altitudes, where sub-zero weather may be expected.

Many factors contribute to the effect, such as the geometry of cracks, porosity and strength of rocks, rate of cooling, water content in rock pore space, transportation of water to ice formation, etc., are involved that weathering due to ice is exceedingly complicated and a number of hypotheses have been advanced to explain it. McGreevy (1981) reviewed five existing working hypotheses: (*a*) volumetric expansion of water on freezing, (*b*) crystallization pressure of ice, (*c*) the capillary theory of frost damage, (*d*) the ordered water hypothesis and (*e*) the hydraulic pressure hypothesis.

Of fundamental importance in discussing frost weathering is the pressure-temperature (PT) diagram of the one component system H_2O, first determined by Bridgeman (1912). A modern version is presented as Figure M2. The salient feature in the present context is the 9 percent increase in volume that takes place when liquid water cools to 0° C at 100 kPa pressure and becomes ice. This is capable of exerting a destructive force on any solid in which freezing takes place, and is the primary phenomenon that accounts for frost weathering. However it does not act alone, processes such as the concentration of mechanical stress around the tip of a microcrack, stress corrosion, and crystal growth among others, add to the effect.

Frost action in a pedological context is a feature of Cryosols especially.

Salt weathering

The term salt fretting is often used as a synonym for salt weathering. However the former implies the appearance of a whitish efflorescence, while the latter indicates the process itself. Salt weathering may include three types of stress: (1) pressure due to crystal growth from solution, (2) stresses exerted by the expansion of many salts in confined spaces upon heating (see under thermal stress, below) and (3) stresses caused by hydration (gaining of structural water).

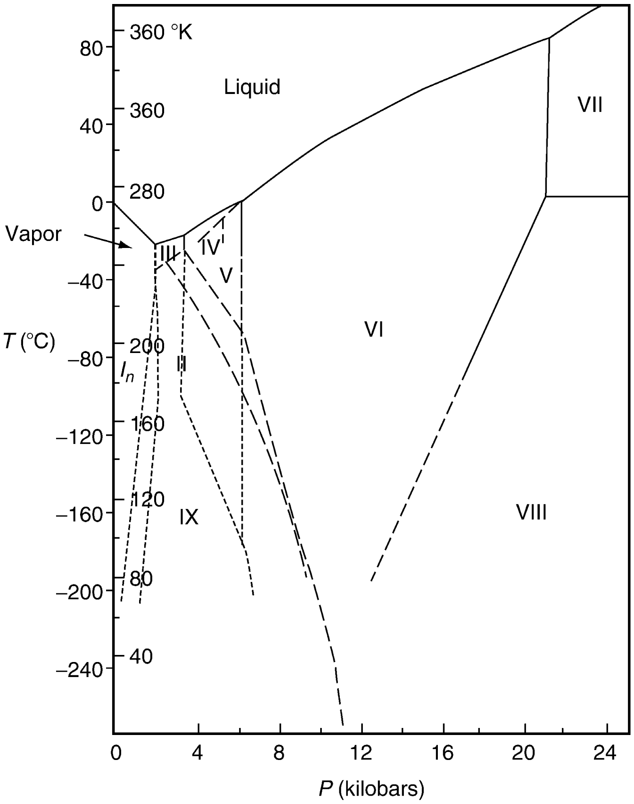


Figure M2 Phase relations in the one component system H_2O as a function of temperature (*T*) and pressure (*P*). The polymorphs of ice are indicated by *Roman numerals* (Mishima et al., 1984).

The available salts in hot, arid regions are principally carbonates, sulfates and halides of Ca, Mg and Na. Among the commonest are: calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2\ H_2O$), kieserite, hexahydrite and epsomite ($MgSO_4H_2O$, $MgSO_4 \cdot 6\ H_2O$ and $MgSO_4 \cdot 7\ H_2O$ respectively, and thenardite (Na_2SO_4), mirabilite and halite (NaCl). Mixed salts are also found, for example the sodium-magnesium chloro-sulfate d'ansite ($Na_{21}MgCl_3(SO_4)_{10}$). The pressure they exert when they crystallize from solution has been measured by Winkler and Singer (1972). See Table M4.

The term hydration is used here in the sense of IUPAC (1994): the addition of water or of the elements of water (i.e., H and OH) to a molecular entity. Specifically, in the present context, it is the addition of water (called in the older literature) 'water of crystallization' or, more recently 'structural water' to the inorganic solids of the weathering and soil-forming system. The addition of water to a mineral structure exerts a pressure by increasing the molar volume of the solid. In the transformation of thenardite to mirabilite, 10 H_2O is added to the formula unit Na_2SO_4, and the molar volume increases by 315 percent (Table M5).

Swelling and shrinking of clays

Clay minerals with a 2 : 1 type of structure (smectites and vermiculites specifically) have the ability to gain and lose water from interlamellar positions (i.e., between adjacent 2 : 1 sheets). As with the chemical hydration process just discussed this causes volume changes in the solid phases and swelling and shrinking are the well-accepted terms for the physical effects of water gain and water loss respectively. Both mineral groups mentioned are monoclinic, and it is the crystallographic basal dimension (or C) that is affected. In smectites for example the effective basal spacings may more than double (from 10 to 21 Å) as more water is taken up (Deer et al., 1992, p. 370).

In soil science, the shrinking and swelling of clays is most prominent in Vertisols, and in other groups in which vertic horizons have developed. A vertic horizon is produced by the disruption and mixing of soil as clays swell and shrink under seasonal changes of the availability of water. The resulting argillipedoturbation causes cracks, the filling of cracks and the general displacement of soil materials in the horizon affected.

Mechanical weathering due to thermal stresses

Thermal stress is the stress induced in a body by change in temperature. The proximate cause is the need for a solid to expand or contract on heating or cooling. In the case of expansion, if the impulse is restricted (as it would normally be within a rock mass for example) a stress is generated. If the stress exceeds the confining pressure on the rock, it will be relieved by cracking. On a rock outcrop, this can give rise to exfoliation, a phenomenon often explained as the result of thermal shock induced by forest fire.

Table M4 Crystallization pressures of some salts (after Winkler and Singer, 1972)

Salt	Chemical formula	Density (gms cm^{-3})	Molecular weight (gms mole^{-1})	Molar volume (cm^3 mole^{-1})	Crystallization pressure (atm)					
					$C/C_S = 2$		$C/C_S = 10$		$C/C_S = 50$	
					0 °C	50 °C	0 °C	50 °C	0 °C	50 °C
Anhydrite	$CaSO_4$	2.96	136.14	46.00	335	398	1 120	1 325	1 900	2 262
Bischofite	$MgCl_2 \cdot 6\ H_2O$	1.57	203.31	129.50	119	142	397	470	675	803
Dodekahydrate	$MgSO_4 \cdot 12\ H_2O$	1.45	336.00	231.90	67	80	222	264	378	450
Epsomite	$MgSO_4 \cdot 7\ H_2O$	1.68	246.48	147.00	105	125	350	415	595	708
Gypsum	$CaSO_4 \cdot 2\ H_2O$	2.32	127.00	54.80	282	334	938	1 110	1 595	1 900
Halite	NaCl	2.17	58.54	27.85	554	654	1 845	2 190	3 135	3 737
Heptahydrite	$Na_2CO_3 \cdot 7\ H_2O$	1.51	232.10	153.80	100	119	334	365	568	677
Hexahydrite	$MgSO_4 \cdot 6\ H_2O$	1.75	228.00	130.10	118	141	395	469	671	300
Kieserite	$MgSO_4 \cdot H_2O$	2.45	138.39	56.55	272	324	910	1 079	1 543	1 840
Mirabilite	$Na_2SO_4 \cdot 10\ H_2O$	1.46	322.19	220.00	72	83	234	277	397	473
Natron	$Na_2CO_3 \cdot 10\ H_2O$	1.44	286.14	198.70	78	92	259	308	440	524
Tachhydrite	$2\ MgCl_2 \cdot CaCl_2 \cdot 12\ H_2O$	1.66	514.40	309.50	50	59	166	198	282	336
Thenardite	Na_2SO_4	2.68	142.04	53.0	292	345	970	1 150	1 650	1 965
Thermonatrite	$Na_2CO_3 \cdot H_2O$	2.25	124.00	55.0	280	333	935	1 109	1 590	1 891

1 atm = 0.1013 MPa.

Table M5 Molar volume change in hydration reactions (adapted from Erlin and Jana, 2003)

Hydration reactions (reactant product)	Molar volumes of solid phases (cm^3 mole^{-1})	Decrease in reaction volume (%)	Increase in solid volume (%)
$CaSO_4 + 2\ H_2O = CaSO_4 \cdot 2\ H_2O$	45.99	−9.5	61.3
(anhydrite to gypsum)	74.21		
$Na_2SO_4 + 10\ H_2O = Na_2\ SO_4 \cdot 10\ H_2O$	53	−5.6	315.1
(thenardite to mirabilite)	220		
$Na_2CO_3 \cdot H_2O + 9\ H_2O = Na_2CO_3 \cdot 10\ H_2O$	55.11	−8.5	260.5
(thermonatrite to natron)	198.7		
$MgSO_4 \cdot H_2O + 6\ H_2O = MgSO_4 \cdot 7\ H_2O$	56.7	−10.9	158.7
(kieserite to epsomite)	146.71		

In a loose material such as soil, where individual components are free to expand and contract essentially without restriction, thermal stresses are considered to play a negligible role. There is however, a significant effect of temperature change that relates back to phase changes.

In saline soils for example, with a surface efflorescence of salts, diurnal temperature fluctuations can cause repeated hydration-dehydration events – hydration under cool, humid conditions, dehydration at hotter, drier periods of the day. Transformations between thenardite and mirabilite could be induced in this way, and have been suggested as a reason for the typical fluffy morphology of the salt layer of the so-called 'puffed Solonchaks' (FAO, 2001).

Effects of erosion

Erosion involves the mobilization of landscape materials by the action of wind, water and ice, and the lowering of the topography of a region accompanied by the deposition of materials elsewhere as loose sediment. Mobilization inevitably involves attrition and the mechanical breakup of materials. In both the lowering, and wearing down event, and the subsequent depositional phase, the soil mantle is radically affected.

Obvious results are that soils on easily eroded hillslopes tend to be youthful, as indeed do those at the bottom of the slope, where they are constantly buried under colluvium. The downslope transfer of materials also plays the important role of producing accumulations of the most easily mobilized particles, namely the clays, in depressions, thereby enhancing the possibility of formation of Vertisols or, when drainage is particularly diminished, of Gleysols.

Of great importance pedologically, are the extensive deposits of loess produced by the wind erosion of glacial materials and upon which Chernozems and Kastanozems are such a feature. The great grasslands (and now croplands) of the northern hemisphere are the direct result.

Organisms, including us, are an additional factor. On the whole a vegetational cover is a hindrance to erosion of the soil cover, though root wedging can force apart and loosen soil, so that in tectonically active zones, a minor tremor may cause mass movements and even catastrophic landslides.

Probably the most significant human activity in this context has been to encourage deforestation – by fire since the time of Homo erectus, and by expropriation of forest soils for agricultural use over the last 10 000 years.

Over the very long term, erosion of a region may result in the lowering of a landscape on the order of 10^3 meters. Thus a 'load' is removed from underlying rocks and it is possible that this relieves 'residual stress' in a rock body and gives rise to exfoliation. It is debatable, however, whether residual stress actually exists in rocks (Yatsu, 1984).

Eiju Yatsu

Bibliography

Bridgeman, P.W., 1912. Water, in the liquid and five solid forms, under pressure. *Proc. Am. Acad. Arts and Sci.* **47**: 439–558.

Deer, W.A., Howie, R.A., and Zussman, J., 1992. *An Introduction to the Rock Forming Minerals.* London: Longman, 696 pp.

Erlin, B., and Jana, D., 2003. Forces of hydration that can cause havoc in concrete. *Concrete Int.* **25**: 51–57.

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

IUPAC, 1994. Recommendations on Organic and Biochemical Nomenclature, Symbols and Terminology. Accessed at http://www.chem.qmul.ac.uk/iupac.

Mishima, O., Calvert, L.D., and Whalley, E., 1984. 'Melting Ice' I at 77 K and 10 kbar: a new method for making amorphous solids. *Nature* **310**: 393–395.

Washburn, A.L., 1979. *Geocryology.* London: Edward Arnold, 406 pp.

Winkler, E.M., and Singer, P.C., 1972. Crystallization pressure of salts in stone and concrete. *Bull. Geol. Soc. Amer.* **83**: 3509–3513.

Yatsu, E., 1988. *The Nature of Weathering.* Tokyo: Sozosha, 624 pp.

Cross-references

Erosion
Ice Erosion
Water Erosion
Wind Erosion

MELANIZATION

The development of a dark, usually brownish color in a soil as a consequence of the incorporation of organic matter. A significant soil-forming process in the formation of mollic surface horizons in soils of the grasslands: Chernozems, Kastanozems, and Phaeozems; and of umbric surface horizons, for example in Umbrisols.

Bibliography

Bockheim, J.G., and Gennadiyev, A.N., 2000. The role of soil-forming processes in the definition of taxa in Soil Taxonomy and the World Soil Reference Base. *Geoderma.* **95**: 53–72.

METAL COMPLEXING

See *Humic Substances*.

METAMORPHIC

The family of rocks that have been transformed from their original condition, by being subjected to a change in the physico-chemical conditions of their environment. All transformations short of melting are included in metamorphism (for example, dehydration, decarbonation, new mineral formation, and recrystallization). Ultrametamorphism (also called anatexis) marks the beginning of melting, and the transition into the igneous realm.Metamorphosed soils are not unknown, a typical occurrence being beneath lava flows where temperatures in excess of 300 °C may persist long enough to dehydrate hydroxide and clay minerals at least partially (see Figure T7, and Chesworth et al., 1985).

Bibliography

Chesworth, W., Dejou, J., de Kimpe, C., Macias Vasquez, F., Cantagrel, J-M., Larroque, P., Garcia Paz, C., Rodeja Garcia, E., and Quantin, P., 1985. Etude de palèosols rouges developpès sur les basaltes Miocenes du Massif Central francais. Cahiers O.R.S.T.O.M., sèr. Pedologie. **20**: 189–208.

MICROBIAL ECOLOGY AND CLAY MINERALS

See *Soil Microbiology*.

MICROHABITATS

Soil, the most complicated biomaterial on the planet, is a system in which minerals, fluids and organisms interact, with much feedback between the component parts, at scales ranging from the molecular to the planetary. At the smallest scale microorganisms survive, reproduce and move within the soil's pore space. Therefore, the size, shape and distribution of this space exerts a major influence over the dynamics of these soil organisms. However, since a large class of microorganisms are essentially aquatic and live in water films on the surface of soil particles, it is the interaction between soil structure and moisture which exerts the greatest influence. (Young and Crawford, 2004).

Soil pore space

Although one gram of soil may contain 10^9 bacteria and 10^3 m of fungal hyphae, it has been estimated that between 0.17% of soil organic matter surfaces, and 0.02% of soil mineral surfaces are occupied by soil microorganisms (Hissett et al., 1970). Other estimates suggest that active microbes cover less than 1×10^{-5}% of the total surface area Young and Crawford (2004). Yet, an active plant root exploring an aggregate would confound these figures since the vast majority of microbial activity would occur within the rhizosphere. However, movement within and to the rhizosphere would be dominated by the soil structure (Griffiths et al., 1991).

Bacteria, protozoa, and nematodes are all restricted to the extent by which they can move in the soil by their body sizes. While pores of the same diameter as the bacteria (e.g., 0.75 μm) are accessible to them, most bacteria and bacterial colonies are found in pores three times their diameter. This 3 : 1 ratio has been found to be quite consistent (Kilbertus, 1980), although it is unclear as to why. Protozoa are larger than bacteria, however their plastic morphology allows them to access relatively small pores. The smallest flagellates and amoebae can access pores around 2 μm in diameter; ciliates can move into pores approximately of 10 μm diameter and above, and although it has been shown that by eliminating pores greater than 30 μm the ciliate population was reduced by two orders of magnitude (Corteaux, 1985). Pores less than 20 μm drastically limit nematode movement. In bulk soil, fungi are typically restricted to larger pores between aggregates (Forster, 1988).

Van Veen and Kuikman (1990) estimate that over 90% of the pore space in a loamy soil is in structure smaller than 1 μm. While other estimates suggest that this number may be nearer than 60% (Rovira and Greacen, 1957). It is clear that the major proportion of soil pore space is inaccessible to soil microorganisms, unless they use alternative foraging strategies that overcome the limitations imposed on them by their body size. Inaccessible pore space may then contain organic matter, which is physically protected from microbial decomposition. When the soil is physically disturbed (e.g., by ploughing) a proportion of the previously protected organic matter may become accessible to microbes and be decomposed (Powlson, 1980). Further, the addition of clay to soil has been shown to increase the survival rate of bacteria by creating protected habitats for the bacteria against predating protozoa (Heijnen and Van Veen, 1991; Van Elas et al., 1991). Thus, it is clear that there are physically inaccessible pores within soil, which protect bacteria from predation by protozoa, and organic matter from decomposition by bacteria.

Estimation of pore sizes in soil is not easy although it is vital since when pores of certain diameters drain they may become inaccessible to microbes. Direct quantification of pore size distribution can be achieved by using soil thin-sections and image analyzers (Darbyshire et al., 1989). However, the preparation of thin-sections of soil by adding acetone to replace water, and then impregnating with resin may alter the structure through displacement and or shrinkage of soil. Thus, to some extent the observed structure in a soil thin-section may partly be an artifact of its production. Indirect estimation of pore sizes and whether they are saturated or unsaturated with water can be found from the soil water release curve. In soil the diameter of pores, d is related to the applied suction by the equation

$$d = \frac{4\ddot{a}}{\tilde{n}gh} \tag{1}$$

where, $\ddot{a}$ is the surface tension, $\tilde{n}$ is the density of water, h is the soil water suction, and g is the acceleration due to gravity. This technique although used widely (Rutherford and Juma, 1992; Heijnen and van Veen, 1991) is recognized to be inaccurate primarily because the main assumption is that all pores are spherical. In essence d relates to the diameter of the largest water filled pore neck. As Reeve and Carter (1991) point out "*… If a void of 200 μm diameter has a neck exit of only 30 μm, water in the void will be released only when the suction exceeds 10 kPa.*" Further, in a shrinking soil as water drains, pores may increase in diameter through shrinkage and new cracks may propagate. Therefore, estimation of pore size distribution using soil moisture release curves gives, at best, only a general indication of soil pores.

Moisture retention

The extent to which pores are accessible to microbes depends not only on the physical size of pores but also on their water status. As the soil dries, matric potential decreases and the thickness of the water films on the surface of soil particles decreases. It is this thickness in relation to microbial size, which controls speed of movement of specific motile microbes (Wallace, 1958). Figure M3 illustrates the observed relation between water-film thickness and nematode movement. By altering the water-film thickness on an agar plate Wallace (1958) observed the effect this change had on the speed and direction of movement of nematodes. The greatest nematode speed was found for a thickness of 2.5 μm. At this level the water-film covered approximately a quarter of the nematode's body. For comparison, the nematode's body was just completely covered by a water-film of 10–20 μm. The rate of movement of the nematode within water of a film thickness of 2.5 μm is greatest because at this point lateral movement of the nematode is minimized and forward movement is maximized.

In general, as soil matric potential decreases (i.e., as soil dries) the numbers and activities of bacteria, protozoa, nematodes and fungi decline (Postma and Van Veen, 1990; Douds and Schenck, 1991; Rattray et al., 1992). Clearly, the amount

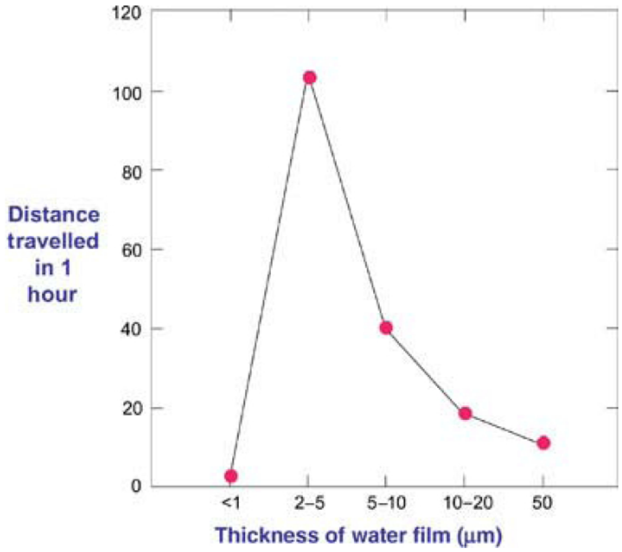


Figure M3 Relation between water-film thickness and nematode movement.

of oxygen within the soil and water films also affects microbial activity: at high oxygen levels, aerobic systems operate; at low oxygen levels, anaerobic systems operate.

However, assessing the aerobic condition of the soil presents difficulties due to the heterogeneous distribution of water and/or oxygen within single aggregates. Even in well-aerated soils isolated anaerobic volumes may prevail (Currie, 1961). Such situations may exist due to isolated pockets of high-density soil with aggregates (i.e., low pore diameters), which hold water at relatively high tensions. Thus, the average respiration rates calculated for a single aggregate may be many times different than local respiration rates from within isolated volumes of an aggregate (Rappoldt, 1992).

Measuring the diffusivity of oxygen at such small scales (μm) is clearly problematic. Although oxygen electrodes with a 10 μm diameter tip have been developed to operate on a millimeter scale (Rappoldt, 1992). However, all such methods are destructive and may alter the soil/aggregate structure when pushed into the soil, thus altering the diffusivity reading.

Transport in soil

Since the development of genetically engineered microorganisms, more attention has been paid to the transport of microbes in soil, with particular reference to residence times and the ultimate fate/position of introduced microbes (genetically engineered or otherwise). Soil structure plays an obvious role in influencing transport, both acting as pathways through soil to water tables and as buffers regulating microbial flow through preferential absorbency onto specific soil particles.

Clearly water plays a major role in microbial transport through soil. Any rain or irrigation event, which creates a downward flow of water within the soil profile, will effectively mobilize microbes. The greater movement of bacteria in coarse sand, compared to fine sand, has been attributed to the greater hydraulic conductivity of the former size fraction (Tan et al., 1991). Worrall and Roughly (1991) found that for sand and clay loam soils, vertical movement of bacteria was greater when both soils were initially saturated as compared to initially dry samples. In general the downward movement of microbes is directly related to the amount of water applied (Hambi, 1971). The rate of microbial transport is also dependent on the type of adsorption sites on the soil and the predilection of bacteria to being absorbed onto soil. The soil microenvironment is composed of highly negatively charged clay and humic particles. Generally microorganisms carry a net negative charge and therefore can be repulsed by clay surfaces. However, the ability of microbes to produce mucilage means that they can overcome like-charged problems and become strongly attached to the particle surface (Burns, 1990). Soils with a high clay and organic matter content have the greatest potential to adsorb microbes, while sandy soils with low absorbency capacities and surface areas have the least potential to adsorb bacteria. Where sand grains are covered in a skin or clay of silt the adsorption potential increases. There is a significant variation in degrees of adsorption of different bacteria on soils. Marshall (1968) found that rhizobial cells containing carboxyl-type surfaces were adsorbed to a greater degree onto sodium-saturated montmorillonite or illite than were similar cells containing amino-carboxyl surfaces. Clearly microbes with a high specificity of adsorption would be less likely to be transported within soil.

Structural stability of soil also influences the transport of microbes within the soil profile. Although microbes may be securely attached/adsorbed onto particulate surfaces and be resistant to movement by percolating water, the particulates themselves may become dislodged and be translocated to depth.

Heterogeneity

Soil structural heterogeneity is an underpinning framework for root-soil research.

It is widely recognized that the structure of soil is complex containing a vast array of shapes and sizes over a wide range of scales (nanometers to kilometers). In spite of this, a large portion of the research on the interactions of soil structure and microbial dynamics either uses synthetic homogeneous soil or utilizes equations which have inherent assumptions of homogeneity. For instance, the widely used calculation of pore sizes from moisture retention curves rests entirely on the assumption of spherical pores, which drain into larger pores. This is clearly not the case as can be observed in any soil thin section. Further, pore tortuosity and connectivity, which strongly influence microbial movement, are rarely accounted for. Hattori (1988) recognized three main types of pores: closed; bottle-type; and tubular open-ended pores. However, there are innumerable complex pore shapes which all play different roles in affecting microbial transport, none of which have been adequately quantified and related to microbial dynamics. The presence of such complex pore pathways means that when water drains from the soil, isolated reservoirs of water are often left behind. The microbial activity in such pools of water would clearly be different from the immediately surrounding, drier soil.

Such heterogeneous structure is an everyday occurrence in soils, and the greatest challenge facing the scientist is how to connect such heterogeneity with microbial dynamics in a quantitative manner. The root of the problem rests on how to quantify the complex nature of the physical characteristics of the microhabitats in the soil. The semi-quantitative and qualitative estimates of soil structures as crumb-like, or the arbitrary division of soil into macro- or microstructures, offer no clear path to a mechanistic link with specific functions or activities of microbes in soil. However, the recent observation that soils exhibit fractal properties (Young and Crawford, 1991, 1992; Bartoli et al., 1991) suggests that a quantitative link between structure and microbial dynamics is possible.

The value of fractals in interpreting quantitative links can be shown when we consider protozoan predation of bacteria. The main question related to predation dynamics is how much habitable pore space is available for bacteria and protozoa? The central feature of a large class of fractal objects is self-similarity. Consider an irregular tortuous pore pathway. If the pore pathway is fractal in this way then any magnified portion of the total pore contains structure, which looks similar to the whole pore pathway of which it is part.

Since magnification of a portion of the pore revealed additional structure, the implication is that the measured length is sensitive to the resolution of measurement. Because of this, the available habitat space of microbial species is a function of body size and increases for smaller species. The rate of increase of habitat with body size is characterized by the fractal (Hausdorff) dimension, D, and this can be determined by measuring the length of a pore pathway or line over a range of measurement scales.

The most common method used for this purpose is known as the 'box counting method', which computes the length of a line by covering it with square boxes of side *r*. For a given range of value of *r*, the number of boxes, *N*, required to totally cover the line is determined. For a fractal curve it can be shown (Mandelbrot, 1983) that *N* varies with *r* according to

$$N(r) = \frac{k}{rD} \tag{2}$$

where *k* is the constant of proportionality and *D* is the fractal dimension. A log-log plot of *N* versus *r* yields a line whose negative slope is the dimension *D*. Values of *D* close to the Euclidean value of 1 indicate that the line is relatively smooth and the estimate of the length is insensitive to ruler size. As the line becomes more tortuous *D* increases. Hence *D* is a quantitative measure of the tortuosity or a line of pore profile. It is clear that the roughness/tortuosity of any line/path may be quantified using fractals. Now, knowing the tortuosity or ruggedness of the line we can then calculate predation, the fraction *F* of total surface available to bacterial which is inaccessible to protozoan predation *F*. Crawford et al. (1992) show that

$$F = 1 - \left(\frac{r_1}{r_2}\right)^{D-2} \tag{3}$$

where r_1, and r_2 relate to the radius of bacteria and protozoa respectively. Assuming $r_1 = 1$ μm, $r_2 = 10$ μm, and $D = 2.36$ (Young and Crawford, 1992), it is shown that over 60% of the potential habitable area of the bacteria is inaccessible to protozoan predation. Indeed this number is probably an underestimate because some regions of pore space may be inaccessible to protozoa because of pore neck effects. Clearly soil structure has a profound impact on microbial population dynamics.

Sustainability

Sustainable ecological practice is the goal of all applied soil scientists, and the manifold complexity of soils at all scales requires an integrated approach to soil if the goal is to be achieved (Young and Crawford, 2004).

Iain M. Young

Bibliography

Bartoli, F., Philippy, R., Dorisse, M., Niquet, S., and Dubuit, M., 1991. Structure and self-similarity in silty and sandy soils: the fractal approach. *J. Soil Sci.* **42**: 167–186.

Burns, R.G., 1990. Microorganisms, enzymes and soil colloid surfaces, Chapter 12. In De Boodt et al., eds., *Soil Colloids and Their Associations in Aggregates* New York: Plenum Press, pp. 337–361.

Couteaux, M.M., 1985. Relation entre la densité apparente d'un trumus et l'aptitude a la croissance des ses Ciliés. *Pedobiologia* **28**: 289–303.

Currie, J.A., 1961. Gaseous diffusion in aeration of aggregated soils. *Soil Sci.* **92**: 40–45.

Derbyshire, J.F., Griffiths, B.S., Davidson, M.S., and McHardy, W.J., 1989. Ciliate distribution amongst soil aggregates. *Rev. Ecol. Biol. Soil* **26**: 47–56.

Douds, D.D., and Shenck, N.C., 1991. Germination and hyphal growth of VAM fungi during and after storage in soil at five matric potentials. *Soil Biol. Biochem.* **23**: 177–183.

van Elsas, J.D., van Overbeak, L.S., Feldmann, A.M., Dullemouns, A.M., and de Leeuw, O., 1991. Survival of genetically engineered Pseudomonas fluorescens in soil competition with the parent strain. *FEMS Microbiol. Ecol.* **85**: 53–64.

Forster, R.C., 1988. Microenvironments of soil microorganisms. *Biol., Fertil., Soils* **6**: 189–203.

Griffiths, B.S., Young, I.M., and Boag, B., 1991. Nematodes associated with the rhizosphere of barley (*Hordum vulgare*). *Pedobiologia* **35**: 265–272.

Hambi, Y.A., 1971. Soil water tension and the movement of rhizobia. *Soil Biol. and Biochem.* **3**: 121–126.

Heijnen, C.E., and van Veen, J.A., 1991. A determination of protective microhabitats for bacteria introduced into soil. *Fems Micro. Ecol.* **85**: 73–80.

Hissett, R., and Gray, T.R.G., 1970. Microsites and time changes in soil microbe ecology. In Anderson, and MacFayden, eds., *The Role of Terrestrial and Aquatic Organisms in Decomposition Processes.* Oxford: Blackwell, pp. 23–29.

Kilbertus, G., 1980. Etude des microhabitats contenus dans les agrégats du sol: Leur relation avec la biomasse bactérienne et la taille des procaryotes présents. *Rev., Ecol., Biol. Soil.* **17**: 543–557.

Mandelbrot, B.B., 1983. *The Fractal Geometry in Nature.* New York: Freeman.

Marshall, K.C., 1968. Interaction between colloidal montmorillorite and cells of Rhizobium species with different ionogenic surfaces. *Biochim., Biophys., Acta* **156**: 179–186.

Postma, J., and van Veen, 1990. Habitable pore space and survival of *Rhizobium leguminosarum* biovar Trifolii introduced into soil. *Microb. Ecol.* **19**: 149–162.

Powlson, D.S., 1980. The effects of grinding on microbial and non-microbial organic matter in soil. *J. Soil Sci.* **31**: 77–85.

Rappoldt, C., 1992. Diffusion in aggregated soil. Doctoral thesis, Wagengingen Agricultural University, Wageningen, The Netherlands.

Rattray, E.A.S., Prosser, J.I., Glover, L.A., and Killham, K., 1992. Matric potential in relation to survival and activity of a genetically modified microbial inoculum in soil. *Soil Biol., Biochem.* **24**: 421: –425.

Reeve, M.J., and Carter, A.D., 1991. Water release characteristic. In Smith, and Mullins eds., *Soil Analysis, Physical Methods.* New York: Marcel Dekker, pp. 111–160.

Rovira, A.D., and Greacen, E.L., 1957. The effect of aggregate disruption on the activity of microorganisms in the soil. *Aust., J., Agr., Res.* **8**: 659–673.

Rutherford, P.M., and Juma, N.G., 1992. Influence of texture on habitable pore space and bacterial-protozoan populations in soil. *Biol. Fertil. Soils* **12**: 221–227.

Tan, Y., Bond, W.J., Rovira, A.D., Brisbane, P.G., and Griffin, D.M., 1991. Movement through soil of a biological control agent, *Pseudomonas fluorescens*. *Soil Biol., Biochem.* **23**: 821–825.

Wallace, H.R., 1958. Movement of eelworms. *Anns., Appl. Biol.* **46**: 74–85.

Worrall, V., and Roughley, R.J., 1991. Vertical movement of *Rhizobium leguminosarum* bv *Trifolii* in soil as influenced by soil water potential and water flow. *Soil Bio. Biochem.* **23**: 485–486.

Young, I.M., and Crawford, J.W., 1991. The fractal structure of soil aggregates: its measurement and interpretation. *J. Soil Sci.* **42**: 187–192.

Young, I.M., and Crawford, J.W., 1992. The analysis of fracture profiles of soil using fractal geometry. *Aust. J. Soil Res.* **30**: 291–295.

Young, I.M., and Crawford, J.W., 2004. Interactions and self-organisation in the soil–microbe complex. *Science* **304**: 1634–1637.

Cross-references

Compaction
Conductivity, Hydraulic
Micromorphology
Microstructure, Engineering Aspects
Structure
Water Content and Retention

MICROMETEOROLOGY

Introduction

Micrometeorology is concerned with the climate close to the land surface. The central problem of micrometeorological research since its genesis has been the measurement of scalar fluxes of mass and energy to and from the Earth's surface. Pioneers in micrometeorology such as C. W. Thornthwaite, O. G. Sutton and F. Pasquill had a great interest in measuring water vapor flux as a means of determining evapotranspiration from land, and thereby answering very practical questions such as how much irrigation water a crop required. Later researchers such as J. L. Monteith became interested in carbon dioxide fluxes in order to quantify photosynthetic activity and plant productivity. Currently much activity is directed at other greenhouse gas fluxes, such as methane from bogs and nitrous oxide from cropland. A sampling of other important historical and current micrometeorological questions includes ammonia losses from manure application to address nitrogen loss and environmental pollution, heavy metal emissions such as mercury from natural and anthropogenic sources, and energy budgets and temperature profiles for crop growth modeling. In all these research programs, the requisite measurement is a vertical flux of mass or heat above a surface.

This article will discuss the development of micrometeorological flux measurement theory, which allows micrometeorologists to translate various atmospheric measurements into estimates of trace gas flux density. It will begin with a survey of the origins of turbulent transport theory and then discuss application of those results to micrometeorological flux measurements. Following that it will review the practice of trace gas flux measurement, including instrumentation and site requirements. All these techniques are used for monitoring gas fluxes to and from soil, and apply equally well to measurements over a vegetated surface.

Development of micrometeorological theory

The importance of turbulence in fluid mechanics has been recognized since the middle of the nineteenth century. Stokes, in 1857, suggested that the failure of the basic equations of fluid motion to correctly predict the resistance to flow of a body moving above a certain speed was due to the eddy motions that occur in that situation. Boussinesq in 1877 and 1896 proposed that this effect could be described by a 'mixing coefficient' analogous to the viscosity of Newton's Law of Friction. This became known as the 'apparent', 'virtual' or 'eddy' viscosity. Later, Reynolds (1895) derived equations showing that turbulence was responsible for momentum transport in fluids. These investigations formed the foundations of much of our knowledge of turbulent motions in fluids, but up to this point only dealt with the problem of momentum transfer and were not applied to meteorological questions. Earlier, Reynolds had also suggested that turbulence transported heat in the same fashion as momentum. This suggestion is now known as the 'Reynolds analogy' and was later extended to other scalar quantities.

The first investigation of turbulent scalar transport in the atmosphere is due to Taylor (1915), who not only derived an equation of turbulent transport analogous to the classic heat equation, but also was able to calculate approximate values of what he termed the 'eddy conductivity' of the atmosphere. Taylor considered a vertical gradient of mean temperature with no horizontal gradient. He then imagined turbulent eddies moving up and down through a horizontal plane while retaining the temperature of their point of origin for some distance d before mixing with their new surroundings. In this way he derived the equation

$$\frac{\partial \theta}{\partial t} = \frac{vd}{2}\frac{\partial^2 \theta}{\partial z^2} \tag{1}$$

where θ is temperature, t is time, v is a velocity scale, and z is the vertical co-ordinate. Equation (1), Taylor noted, is directly analogous to Fourier's heat equation in a solid if $\frac{1}{2}vd = \kappa/(\rho c_P)$, where ρ is the density of air and c_p is the specific heat of air. He called the conductivity κ the 'eddy conductivity' of the atmosphere. We shall refer in this article to the 'eddy diffusivity' $K = ½vd$. Richardson (1920a) cites Taylor as originating the K notation to which the eddy diffusivity formulation owes its current name of *K-theory*. K-theory is most often expressed analogously to Fick's Law as

$$F = -K\frac{\partial c}{\partial z} \tag{2}$$

where c is the density of the scalar of interest.

Taylor's eddy diffusivity is related to molecular diffusivity by being composed of a length scale d and a velocity scale v, analogous to the mean free path and the molecular velocity, respectively. The length scale represents the mean distance an eddy travels before mixing with the surrounding air, and the velocity scale represents the mean velocity of the turbulent eddies in the direction of the mixing. Taylor (1935) admitted that the notion of eddies traveling at some mean speed for some mean distance before completely mixing lacked physical rigor. However, the idea has been very powerful and useful.

Independently of Taylor, Prandtl in 1925 developed the idea of *Mischungsweg*, commonly known in English as mixing-length theory. Similarly to Taylor, he considered a mean profile in the vertical and eddies moving some distance z up and down, thereby carrying the concentration difference Δc between the two levels. Prandtl was concerned with momentum transfer $\overline{u'w'}$, and derived the equation

$$\overline{u'w'} = l^2\left(\frac{\partial \overline{u}}{\partial z}\right)\left|\frac{\partial \overline{u}}{\partial z}\right| \tag{3}$$

where $\overline{u}$ is the mean horizontal wind speed and the 'mixing-length' l is a unique property of the intensity of turbulent mixing. This allows an eddy viscosity to be defined as

$$K_{\mathrm{M}} = l^2\frac{\partial \overline{u}}{\partial z} \tag{4}$$

Schmidt in 1917 also made the analogy to molecular diffusion by proposing *Austausch-Koeffizienten*, or ‘exchange coefficients’. This was very similar to Boussineq’s earlier proposal, only now, following Reynold’s analogy, these were meant to describe scalar transfer as well as momentum transfer. Richardson (1920a) cites observational evidence that the eddy viscosity and eddy conductivity are equal, as proposed by Taylor (1915). This was later shown false, in part due to Richardson’s (1920b) work.

The work discussed here, when applied to momentum transfer, led to the development of the *logarithmic profile* for wind speed. This is usually expressed as

$$u(z) = \frac{u_*}{k} \log\left(\frac{z}{z_0}\right) \tag{5}$$

for a bare surface, where u_* is the friction velocity, k is von Kármán’s constant (normally taken as 0.4), z is height above the surface and z_0 is the roughness length, a measure of the roughness of the surface. Roughness length is sometimes parameterized as 0.1 h, where h is the height of the surface roughness elements. This log-profile, as it is called, shows that wind speed should be a linear function of $\log(z)$. This is only true under conditions of neutral stability. Stability, discussed in more detail below, is a measure of the thermal stratification of the atmosphere, where neutral implies no stratification, unstable is when rising air finds itself warmer than the environment, and stable describes the situation of increasing temperature with height, effectively suppressing turbulence. The log-profile is a key concept in all fields relating to fluid flow, however it is not the only possible description of the atmospheric wind speed profile. Power-law relationships can provide equally valid descriptions of the wind profile, and were used extensively by John Philip throughout his career.

The next major advance in atmospheric flux theory was due to Richardson (1920b) who considered what effects thermal stratification would have upon turbulence. Previous work, geared toward engineering flows and wind tunnel studies, had focused on situations with neutral stability. Richardson showed that heat input into the system, by mechanisms such as solar heating of the surface, would provide energy for the generation of turbulent motions. He derived the ratio

$$R_i = \frac{\mathrm{g}(\partial\theta/\partial z)}{\theta(\partial\overline{u}/\partial z)^2} \tag{6}$$

where g is the acceleration of gravity. Equation (6) expresses the ratio of kinetic energy production from buoyant and mechanical forces, and is therefore equal to 0 in a neutral environment and is positive for stable and negative for unstable conditions. This Richardson number has been found to be profoundly useful, and most formulations of stability effects on turbulent transport have made use of it.

The obvious application of the preceding work is to measure the gradient of, say, water vapor along with other meteorological parameters such as wind speed, and use this information to calculate an eddy diffusivity and a flux. To the best of the author’s knowledge, the first attempt to do this in a recognizably micrometeorological fashion was by Thornthwaite and Holzman (1939). Based on work by Rossby and von Kármán, these authors derived a practical mixing-length equation and made measurements of humidity at several heights using hair hygrothermographs in instrument shelters suspended between masts with a pulley system to raise and lower the shelters. Measurements were conducted over a mowed hay field. Their results clearly illustrated the diurnal cycle of evapotranspiration as well as monthly patterns related to precipitation. Though aware of the need for stability corrections, Thornthwaite and Holzman were at the time unaware of any suitable method of doing so.

Another noteworthy attempt at micrometeorological evapotranspiration measurements was a very intensive, lengthy and careful experiment conducted by Pasquill (1949). His was the first experiment, which would be readily recognized by a micrometeorologist of today; he used cup anemometers, wet- and dry-bulb thermocouples, and thermocouples in the soil, all logarithmically spaced. In addition, he used a weighing lysimeter system as a control for his micrometeorological evaporation estimates. He also examined stability and showed clearly the bent logarithmic profiles caused by non-neutral conditions. Further, he derived several empirical equations to correct his measurements for stability, foreshadowing important developments in the coming decades.

As an aside, Penman published equations in 1948 combining an energy budget with a sink strength equation. (Note: The sink strength equation was originated by Dalton and is of the form $E = (e_\mathrm{a} - e_\mathrm{s})f(\overline{u})$, where E is evaporation rate, e_a and e_s are the vapor pressure of the air and surface, and $f(\overline{u})$ is some function of wind speed). This model has been used extensively in evapotranspiration and ecophysiological studies. We will not, however, discuss it further here, as it is strictly limited to evapotranspiration and not applicable to the general scalar flux problem.

The problem of stability was being tackled concurrently with Pasquill’s work by Obukhov (1946). In his famous paper he derived the Obukhov length

$$L_\circ = \frac{-\theta u_*^3}{kg\overline{\omega'\theta'}} \tag{7}$$

where $\overline{\omega'\theta'}$ is the kinematic surface sensible heat flux. The Obukhov length is typically thought to define the approximate height of the sub-layer of dynamic turbulence, the layer wherein mechanical production of turbulence dominates. Using this result, and further similarity analysis, he derived expressions for stability corrections to the mixing-length equations based on the Richardson number. This was of pivotal importance in micrometeorology, but experimental verification and determination of the empirical constants had to wait more than two decades.

The story continues with the work of Monin and Obukhov (1954). Based on systematic dimensional analysis, they derived a number of dimensionless groups for the important variables of interest in the lower atmosphere. These were considered to be of great value in that they could account for the fluxes of momentum, energy and mass in a variety of stability and roughness situations. A number of experiments were conducted in the late 1960s and 1970s to determine the empirical constants of Monin-Obukhov similarity theory. A number of investigators contributed to this work, including Businger et al. (1971), Wyngaard et al. (1971) and Dyer (1974). Their analyses of the experimental data have formed the basis for most aerodynamic flux measurements in the last three decades. The equations developed by these many workers will be discussed in more detail below.

Following Reynolds’ analysis of the eddy viscosity, it had long been recognized that similar methods could be applied to scalars. Reynolds’ analysis proceeded by decomposing each variable into a mean and a fluctuating component, e.g., $x(t) = \bar{x} + x'$, where an overbar indicates a time-average and a prime indicates deviations from the mean. The instantaneous scalar flux is

$$F(t) = \rho wc \tag{8}$$

where w is vertical wind speed. By applying the decomposition and multiplying through, one arrives at

$$F(t) = \rho(\overline{w}\overline{c} + \overline{w}c' + w'\overline{c} + w'c') \tag{9}$$

The flux over some period of time is the average of this equation

$$\overline{F} = \rho(\overline{w}\overline{c} + \overline{w'c'}) \tag{10}$$

where, by definition, the mean of a fluctuating component is 0. Note that we have ignored the possibility of a turbulent component to ρ; this assumption is well supported by data. Finally, we note that, by incompressibility, we expect the vertical wind to average to 0 over space, and we postulate that it should average to 0 over time at a point. (Note: This assumption has been called into question, especially in recent literature. However, we lack a single agreed-upon means of estimating this term.) This leaves only the second term and thus the covariance of vertical wind speed and scalar concentration is seen to be a direct measure of turbulent flux. Though recognized, this knowledge could not be properly utilized until sufficient advances in instrumentation had been made. The first published measurements of the eddy flux are due to Swinbank (1951), who used fine wire thermocouples (wet- and dry-bulb) and an arrangement of hot-wire anemometers to record the eddy fluxes of heat and water vapor. The field of eddy correlation measurements grew slowly at first, but with the advent of the sonic anemometer in the 1950s and the development of fast-response infrared gas analyzers, eddy correlation became the standard technique for many flux measurements. Currently eddy covariance measurements of CO_2 and H_2O fluxes are made on over 140 permanent FLUXNET towers (Baldocchi et al., 2001), as well as in countless other short- and long-term experiments.

To summarize, a theoretical framework is required for one to estimate a surface flux density from atmospheric measurements. Our understanding of turbulent transport, based on the early work of Reynolds, led to the development of the eddy covariance technique. However, practical application of eddy covariance required the development of sophisticated electronic technology. In the meantime, relationships between source strength and vertical gradients were developed. In the case of neutral stability, this theory can be readily applied to a gas flux measurement. In the real atmosphere, however, this is a rare occurence. The development of Monin-Obukhov similarity theory, and the subsequent empirical determination of their functions, have enabled flux-gradient techniques to be applied successfully to gas flux measurement.

Gas flux measurement practice

Eddy covariance

As the most prevalent technique in the literature, we first consider current application of the eddy covariance technique. As noted above, it relies on high-frequency measurements of the vertical wind speed and the scalar of interest. Though sensitive propeller anemometers have been used for eddy covariance measurements, currently the great majority uses ultra-sonic anemometers. These devices measure one, two or three components of the wind vector by measuring the travel time of sound waves between two piezo-electric transducers. The number of pairs of arms determines the number of wind components that are resolved. Operating frequencies of up to about 60 Hz are possible with this instrumentation, typically in agricultural applications data is collected at ~10 Hz, while over forests 1 Hz measurements are usually sufficient.

For measurement of a gas flux, such as water vapor or carbon dioxide, a high-frequency concentration measurement is also required. Two classes of gas analyzer can be employed for the task: open- and closed-path gas analyzers. An open-path analyzer normally uses infrared absorption spectroscopy with the sample path open to the atmosphere at the point of measurement. A closed-path analyzer requires a pump to draw air from the sampling location through the analyzer. The most common instruments of this type also use infrared absorption to determine concentration because this technique allows for the continuous, high-frequency measurements necessary.

Historically, eddy covariance systems were typically controlled by a datalogger, which would monitor the signals from the anemometer and gas analyzer and compute time-averaged values of means, variances and covariances at a specified interval, often a half-hour or an hour. With the advent of inexpensive computer storage, it has become common practice to save all high-frequency measurements, which are then later analyzed.

Eddy covariance measurements are subject to a number of known instrument errors. Fluctuating temperatures create fluctuations in air density, which can lead to errors in gas concentration. Similarly, fluctuations in water vapor concentration create density fluctuations in trace gas concentrations. This problem was analyzed by Webb et al. (1980) who derived equations to correct for this error. Currently, many practitioners instead convert high-frequency concentration measurements to units on a dry-air, constant temperature basis, which avoids the problem. Averaging across the length of the ultrasonic path, sensor separation and sampling time of the measurement all produce spectral errors, so-called because they vary in relation to the frequency of motion. These can range from very minor corrections to systematic flux underestimates of 10–20%. The most commonly cited corrections for these errors are those of Moore (1986), though papers re-analyzing these types of errors continue to appear in the literature annually. Various errors relating to distortion of the wind flow by the instruments are inherent in the measurement, but have been reduced by careful design of the sensor housing.

A much more difficult problem with eddy covariance measurements is known as the energy budget closure problem. Though there is still some debate whether or not this problem really exists, largely it has become accepted as fact (Wilson et al., 2003). Over a simple surface, the net radiation less the soil heat flux is the total available energy. This energy will either warm the air (sensible heat flux) or evaporate water (latent heat flux). Both of these fluxes are measured by eddy covariance, but normally sum up to only ~80% of the independently measured available energy. This problem has spurred much work toward a better understanding of eddy covariance, and is still an active topic of research.

Flux-gradient method

Probably the next most common gas flux measurement technique is the flux-gradient method. As discussed above, this method relies on the measurement of a concentration difference between two heights, along with aerodynamic parameters to calculate an eddy diffusivity. Typical equations are presented to illustrate the method.

The integrated (finite-difference) form of Equation (2) with stability corrections from Monin-Obukhov similarity theory is

$$Flux = \frac{-u_* k \Delta c}{\ln\left(\frac{z_u - d}{z_l - d}\right) - \Psi_{hu} + \Psi_{hl}} \tag{11}$$

where z_u and z_l are the upper and lower measurement heights, respectively, Δc is the concentration difference between z_u and z_l, d is the displacement height (for work over plant canopies) and Ψ_{hl} is the diabatic correction function for the upper and lower intakes.

Under stable conditions, Ψ_h is given by (Hicks, 1976)

$$\Psi_h = -5\frac{z - d}{L_\circ}. \tag{12}$$

In unstable conditions, Ψ_h is given by (Paulson, 1970)

$$\Psi_h = 2\ln\left(\frac{1 + x^2}{2}\right) \tag{13}$$

where x is:

$$x = \left[1 - \frac{16(z - d)}{L_\circ}\right]^{0.25} \tag{14}$$

Other forms of the Monin-Obukhov diabatic corrections have been proposed; all are roughly equivalent.

As with eddy covariance, a key component of the measurement system is a gas analyzer. With eddy covariance, the most important factors are frequency response and resolution. For a flux-gradient measurement, one requires a time-averaged concentration difference, so response time is less important than the ability to accurately resolve differences. Thus, applications of this method normally employ a single analyzer with switching valves to bring air samples from different heights. Note that it is also possible to bring in air from different sites, allowing for multiple-plot experiments.

Measurements of u_* can be obtained either from a profile of horizontal wind speed or from sonic anemometer measurements of $\overline{u'w'}$, as $u_* = \sqrt{(-\overline{u'w'})}$. Sensitive cup anemometers are most often used when the former approach is taken. When a sonic is used, it is also able to provide measurements of the heat flux for computing the diabatic corrections; otherwise this parameter must be estimated from radiation measurements, often as some fraction of the net radiation.

Fetch and footprints

Both eddy covariance and flux-gradient techniques provide non-invasive, non-destructive, spatially-averaged estimates of gas flux density. Micrometeorological methods are argued to be the best means of estimating surface exchange for just that reason. However, this also forces the requirement that the upwind surface be both large and homogeneous. For both eddy covariance and flux-gradient measurements, the standard rule of thumb for *fetch* is 100 : 1. This means that one would like the upwind surface to be homogeneous and flat for a distance at least 100 times the instrument height. This generally works well, though LeClerc and Thurtell (1990) showed that, under certain conditions, it might be insufficient.

Schmid (2002) credits Pasquill's 1972 work on *effective fetch* as the first paper examining footprints. Schuepp et al. (1990) coined the term *flux footprint*, which is the area contributing most of the measured scalar flux to the measurement. It will vary with wind speed, direction and turbulence levels. Ideally, one would like a situation where all likely footprints are contained within a homogeneous area, however this is not always possible. Under these circumstances, one is faced with either discarding data when the footprint was inappropriate, or trying to model the footprint to estimate a spatial distribution of sources. Schmid (2002) provides a thorough review of footprint modeling.

Other techniques

Though most micrometeorological measurements in the literature are flux-gradient or eddy covariance, several other techniques are also used. These include the Bowen-ratio method and mass-balance approaches.

The Bowen ratio (Bowen, 1926) is

$$\beta = \frac{H}{\lambda E} \tag{15}$$

where H is the sensible heat flux density and λE the latent heat flux density. Because the net radiation less the soil heat flux G must equal $H + \lambda E$ (as discussed above), evaporation can be measured as

$$\lambda E = \frac{R_n - G}{1 + \beta} \tag{16}$$

From flux-gradient theory, one can see that the Bowen ratio can be expressed as

$$\beta = \frac{-\rho c_p K \frac{dT}{dz}}{-\rho \lambda K \frac{dr}{dz}} \tag{17}$$

where λ is the latent heat of fusion for water, r is the mixing ratio (mass of water per mass of air), and, since K cancels, we need not include stability effects. In other words, the Bowen ratio can be determined from measurements of the gradients of temperature and humidity, allowing heat and vapor fluxes to then be estimated with only the addition of net radiation and soil heat flux. Further, other gas fluxes can be computed from their gradients since, having determined the evaporative flux; one can back out the eddy diffusivity. Thus Bowen ratio flux measurements require simpler instrumentation than do eddy covariance measurements, and do not require empirical corrections, as do flux-gradient measurements. However, the technique breaks down as $\beta \rightarrow -1$ and it is quite sensitive to errors in the gradient measurements, making its application technically demanding despite its theoretical simplicity.

For work from smaller sources, such as manure storage pits, micrometeorologists sometimes use a mass-balance approach referred to as the *integrated horizontal flux*. In this technique, a profile of wind speed and gas concentration is measured upwind of the source and downwind, and the flux calculated as

$$F = \frac{1}{L}\int_0^{z_p} \overline{\bar{u}(c_d - c_u)}dz \tag{18}$$

where z_p is the top of the emission plume, L is the distance between up- and downwind measurement towers and c_u and c_d are the up- and downwind concentrations, respectively. For more details of this method, see Denmead (1995).

Recently, some workers have also tried a large-scale mass-balance approach using the atmospheric boundary layer as a sort of chamber. During the day time, the convective boundary layer can grow to 1–2 km, while at nighttime a stable boundary on the order of 100 m often forms. Use of this method necessitates tethered balloons or aircraft to obtain concentration measurements throughout the boundary layer. Regionally averaged fluxes are then estimated from the changing concentrations in the layer. Again, this technique is discussed in more depth by Denmead (1995).

Summary and the future

This article has illustrated the rich theoretical history that allows micrometeorologists to estimate gas exchange between the surface and the atmosphere. It has also indicated how the theory is practically applied to make flux measurements. Though it is still common practice to search for homogeneous sites with good fetch, increasingly researchers are attempting to adapt these techniques to complex terrain. Much of this work currently relates to footprint analysis, but we can also expect to see more measurements of horizontal advection (Staebler and Fitzjarrald, 2004) as well as increasing use of new techniques such as backwards Lagrangian analysis (Flesch et al., 1995).

Jon Warland

Bibliography

Baldocchi, D., Falge, E., Gu, L., Olson, R., Hollinger, D., Running, S., Anthoni, P., Bernhofer, C., et al., 2001. FLUXNET: a new tool to study the temporal and spatial variability of ecosystem-scale carbon dioxide, water vapor, and energy flux densities. *Bull. Am. Meteor. Soc.* **82**: 2415–2434.

Bowen, I.S., 1926. The ratio of heat losses by conduction and by evaporation from any water surface. *Phys. Rev.* **25**: 779–787.

Businger, J.A., Wyngaard, J.C., Izumi, Y., and Bradley, E.F., 1971. Flux–profile relationships in the atmospheric surface layer. *J. Atm. Sci.* **28**: 181–189.

Demead, O.T., 1995. Novel meteorological methods for measuring trace gas fluxes. *Phil. Trans. R. Soc. Lond. A* **351**: 383–396.

Dyer, A.J., 1974. A review of flux-profile relationships. *Boundary-Layer Meteor.* **7**: 363–372.

Flesch, T., Wilson, J., and Yee, E., 1995. Backward-time Lagrangian stochastic dispersion models, and their application to estimate gaseous emissions. *J. Appl. Meteor.* **34**: 1320–1332.

Hicks, B.B., 1976. Wind profile relationships from the 'Wangara' experiment. *Q. J. R. Meteor. Soc.* **102**: 535–551.

Leclerc, M., and Thurtell, G., 1990. Footprint prediction of scalar fluxes using a Markovian analysis. *Boundary-Layer Meteor.* **52**: 247–258.

Monin, A.S., and Obukhov, A.M., 1954. Basic laws of turbulent mixing in the ground layer of the atmosphere. *Tr. Geofiz. Instit. Akad. Nauk, SSSR* **24**: 163–187.

Moore, C.J., 1986. Frequency response corrections for eddy correlation systems. *Boundary-Layer Meteor.* **37**: 17–35.

Obukhov, A., 1946. Turbulence in an atmosphere with non-uniform temperature. *Trudy Inst. Teoret. Geofiz: AN–S.S.S.R., No 1 (English Translation* (1971), *Boundary-Layer Meteorol.,* **2**: 7–29).

Pasquill, F., 1949. Some estimates of the amount and diurnal variation of evaporation from a clayland pasture in fair weather spring. *Q. J. R. Meteor. Soc.* **75**: 249–256.

Paulson, C.A., 1970. The mathematical representation of wind speed and temperature profiles in the unstable atmospheric surface layer. *J. Appl. Meteorol.* **9**: 857–861.

Reynolds, O., 1895. On the dynamical theory of incompressible viscous fluids and the determination of the criterion. *Phil. Trans. R. Soc. Lond. A* **186**: 123–164.

Richardson, L.F., 1920a. Some measurements of atmospheric turbulence. *Phil. Trans. R. Soc. Lond. A* **221**: 1–28.

Richardson, L.F., 1920b. The supply of energy from and to atmospheric eddies. *Proc. R. Soc. Lond. A* **97**: 354–373.

Schmid, H.P., 2002. Footprint modeling for vegetation atmosphere exchange studies: a review and perspective. *Agric. For. Meteor.* **113**: 159–183.

Schuepp, P.H., Leclerc, M.Y., MacPherson, J.I., and Desjardins, R.L., 1990. Footprint prediction of scalar fluxes from analytical solutions of the diffusion equation. *Boundary-Layer Meteor.* **50**: 355–373.

Staebler, R.M., and Fitzjarrald, D.R., 2004. Observing subcanopy CO advection. *Agric. For. Meteor.* **122**: 139–156.

Swinbank, W.C., 1951. The measurement of vertical transfer of heat and water vapor by eddies in the lower atmosphere. *J. Meteorol.* **8**: 135–145.

Taylor, G.I., 1915. Eddy motions in the atmosphere. *Phil. Trans. R. Soc. Lond. A* **215**: 1–26.

Taylor, G.I., 1935. Statistical theory of turbulence. Parts I–IV. *Proc. R. Soc. Lond. A* **151**: 421–478.

Thornthwaite, C., and Holzman, B., 1939. The determination of evaporation from land and water surfaces. *Monthly Weather Rev.* **67**: 4–11.

Webb, E.K., Pearman, G.I., and Leuning, R., 1980. Correction of flux measurements for density effects due to heat and water vapour transfer. *Q. J. R. Meteor. Soc.* **106**: 85–100.

Wilson, K., Goldstein, A., Falge, E., Aubinet, M., Baldocchi, D., Berbigier, P., Bernhofer, C., Ceulemans R., et al., 2003. Energy balance closure at FLUXNET sites. *Agric. For. Meteor.* **113**: 223–243.

Wyngaard, J.C., Coté, O.R., and Izumi, Y., 1971. Local free convection, similarity, and the budgets of shear stress and heat flux. *J. Atm. Sci.* **28**: 1171–1182.

MICROMORPHOLOGY

Definition and history

Micropedology is a method of studying undisturbed soil- and regolith samples with the aid of microscopic and ultramicroscopic techniques in order to identify the different constituents and to determine their mutual relations, in space and time, as far as the latter is possible. This means that the investigations should be carried out on undisturbed (and mostly naturally oriented) soil samples, in contrast to the other analytical methods used in soil science (e.g., mineralogical, chemical and physical analyses) requiring mostly a mixing, crushing, solubilization or fractionation of the samples.

The term micromorphology was originally used to refer to that field of micropedology dealing with fabric analysis only, but soon both were used as synonyms. Micromorphology, as a general term, comprises both the qualitative and the quantitative analysis of the soil; the latter is commonly referred to as micromorphometry.

The publication of W. L. Kubiëna's "*Micropedology*" (1938) is considered as the official birth of this discipline. It contains the basic philosophy, some techniques (among others on the preparation of thin sections of unconsolidated materials) and a first terminology to describe soil microfabrics in a morphoanalytical way, i.e., by giving an enumeration of the morphologically distinguishable units present. The basic fabric types described by Kubiëna were the basis for the later classifications of related distributions patterns by Brewer (1964) and Stoops and Jongerius (1975). The first technical basis for the consolidation of friable materials, necessary for preparing thin sections, was laid by Ross (1924).

Systematic studies of soils from Central Europe and Spain inspired Kubiëna to a new, morphogenetic approach on soil fabric, which he published first in "*Entwicklungslehre des Bodens*" (1948) and later rephrased in "*The Soils of Europe*" (1956). In this system the microscopic observation of soil materials (mainly in thin sections) leads directly towards the classification of the soil and its genetic interpretation. A same terminology therefore is used for both the type of microfabric and the type of soil or humus (e.g., Braunlehm, Braunerde, Mor).

This system, extended later with a few soil/fabric types from the semi-humid and humid tropics (e.g., Roterde, lateritic Roterde) was in general use till the end of the sixties. Main problems were caused by the fact that it could be used only for describing soil fabrics recognized and described as such by Kubiëna, and that it implied an implicit agreement of the scientist with the genetic considerations of Kubiëna on these materials (Kubiëna, 1970). The system moreover considers only soil *sensu stricto,* not the other regolith material.

Early in the sixties R. Brewer and J. Sleeman from CSIRO, Australia, published several papers on a new, morphoanalytical approach towards soil fabrics. They resulted in Brewer's "*Fabric and Mineral Analysis of Soils*" (1964 and 1976). This was the first system fit for a systematic analysis and description of any soil or regolith material; the terminology consists for a large part of new coined words. By applying systematically this description technique to a large variety of soils from all over the world, micromorphologists gained a better insight in soil fabric in general, which in turn draw the attention to some weaker points in the system, giving rise to a common effort of a working group of the International Society of Soil Science to develop a new, more comprehensive system, published by Bullock et al. (1985), recently adapted and completed by Stoops (2003). Other important contributions to methodology of thin section analysis, not proposing a specific terminology, are the works of Altemüller (1974) and FitzPatrick (1984 and 1993). Also the fundamental contributions of Babel (e.g., 1975) to the micromorphology of organic soil components have to be mentioned. In the Soviet Union micromorphological research developed in several institutes, partially based on a long tradition in sediment petrography from which many terms (e.g., scaly and fibrous microtextures) were borrowed (Parfenova and Yarilova, 1962; Dobrovolski, 1983).

Apart from the morphogenetic approach of Kubiëna (1948 and 1956) all above mentioned systems are dealing with the individual description of the lowest level of organization, that of the basic constituents. Only in few cases these individual features are diagnostic for a given material or pedogenic process; in general a combination of features is necessary for a diagnosis. In order to make descriptions less lengthy and easier to compare, several authors proposed morphosynthetic systems, allowing describing these characteristic combinations in a few terms. Tentatives published by Brewer and Sleeman (1988), Stoops (1994) and Gerasimova (1994 and 2003) got hitherto little attention.

Whereas micromorphology was during the first two decades of its existence mainly used in studies on soil genesis and classification, on a qualitative basis, more and more need was felt for quantitative data. This tendency was first illustrated in Kubiëna's "*Die mikromorphometrische Bodenanalyse*" (1967). With the introduction of electro-optical equipment end of the sixties, more emphasis was given to the quantification of pores and their distribution in the frame of studies on soil structure, permeability, compaction, crust formation etc. At present, image analysis is becoming a major technique in micromorphology.

End of the sixties new powerful tools were developed and became commercially available, opening new possibilities for micromorphology: the scanning electron microscope (S.E.M.) and different types of microprobes. S.E.M. gave the possibility to study in great detail and in three dimensions the finest fabric components (e.g., mineral neoformations, alterations); the microprobe opened hitherto unexpected possibilities to determine chemical composition of fabric units (Bisdom, 1981), stimulating for instance the application of micromorphology in the field of soil pollution studies.

International Working Meetings on Soil Micromorphology are organized every four years since end of the fifties. Their transactions are a main source of micromorphological information. An annotated bibliography of micromorphology covering the period 1968–1986 was prepared by Miedema and Mermut (1990).

Micromorphological research has to follow three subsequent steps: (*i*) sampling and sample preparation, (*ii*) fabric analysis and (*iii*) interpretation. They will be discussed systematically below.

Sampling and sample preparation

Because of the very nature of micromorphology, undisturbed and oriented samples are needed. This requires specific sampling techniques and precautions. Non-coherent soils are mostly sampled with the help of "Kubiëna boxes", i.e., metal boxes with two loose covers and a body that can be opened, so that samples easily can be removed in the laboratory without disturbance (Figure M4). Pressing the box in a vertical or horizontal section of the profile does sampling. In many cases it is important to preserve the original moisture content during transport, in order to prevent formation of shrinkage cracks, dehydration of colloids or hydration of hygroscopic salts, e.g., by wrapping the boxes in plastic sheets. In case of very loose or brittle materials, the samples have to be pre-impregnated in the field, before transport, with a colorless varnish, such as cellulose acetate solution in acetone (Murphy, 1986).

For the preparation of thin sections, soil materials have to be made coherent by impregnation with a cold setting resin (Murphy, 1986) such as polystyrene, as first recommended by Altemüller (1962) or epoxy. Since these resins are not compatible with water, the latter should be removed. Because air-drying results mostly in the formation of shrinkage cracks and transformation of amorphous organic components, replacement

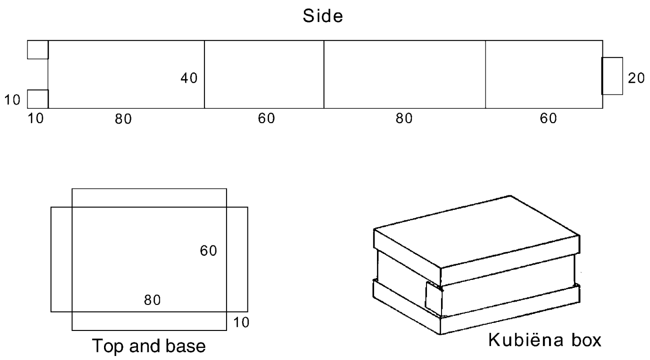


Figure M4 Kubiëna box.

of the water by acetone (Miedema et al., 1974; FitzPatrick, 1984; Chartres et al., 1989) is recommended. This can happen by immersing the sample in acetone, and replacing the latter daily, until all water is removed, or by the vapor phase method, in which the moist samples are put in a hermetically closed container over an acetone/water solution, which is every day replaced by a more concentrated solution, finally by pure acetone, until all water is removed (the first day a 2% acetone/water solution is used, which is doubled every day).

After impregnation with, and hardening of the resin, a slab is sawn from the block, grounded and lapped at one side, mounted on an object glass (1 mm thick), thinned by lapping until a maximum thickness of 20–30 μm, and covered by a cover glass (0.17 mm thick). During all these treatments only oil should be used as lubricating and cleaning agent instead of water, in order to prevent swelling of clays and dissolution of salts. Sizes of the thin sections range between 28 × 48 mm (petrographic size) and 120 × 180 mm (mammoth size), depending upon the type of research: the study of microstructure for instance requires large thin sections; detailed mineralogical identifications are easier to do on petrographic size sections. Preparation of thin sections of a sufficient large size and good quality has been, and still often is, one of the problems hindering a more general use of micromorphological techniques.

For S.E.M., undisturbed and dry micro samples are mounted with special glue on stubs and covered with a conductive coating (e.g., C, Au or Pd). Microprobe analyses require highly polished surfaces (e.g., specially polished, uncovered thin sections) and a conductive coating, preferentially of C.

Observation techniques

Soil thin sections are mostly studied with the help of an optical polarizing microscope (petrographic microscope), using transmitted light. In some cases circular polarized light is used, especially to study the fabric of the fine material (Pape, 1974) or to enhance the image of the porosity (Ruark et al., 1982). Identification of opaque materials (e.g., charcoal, pyrite, Mn-oxyhydrates) requires the help of oblique incident or dark ground incident light (Stoops, 2003). Phase contrast microscopy has been used by Altemüller (1964) on very thin (10 μm) thin sections to study the composition of the colloidal fraction of the soil.

UV or blue light fluorescence microscopy is an important tool for the study of organic matter, Al-colloids and some other mineral components (Babel, 1972; Altemüller and Van Vliet, 1990). Fresh organic matter can be stained with fluorochromes and studied with fluorescence techniques (Altemüller and Van Vliet, 1990; Tippkötter, 1990). More recently, cathodoluminescence has been used (on uncovered thin sections) to distinguish calcite grains and nodules of different origins.

Selective extraction of amorphous and free iron (Arocena et al., 1989; Curmi et al., 1994) on uncovered thin section proved to be of great help both in the study of iron components in soils and of the fabric of the groundmass, no longer masked by iron; staining tests for carbonates, feldspars and clays are used in some cases. For more details on optical methods the reader is referred to Drees and Ransom (1994), FitzPatrick (1993), and Stoops (2003).

Fabric analysis: concepts and terminology

In the following paragraphs the concepts of fabric analysis and terminology as proposed by Bullock et al. (1985) and completed by Stoops (2003) are explained. Corresponding terms according to Brewer (1964) or to Russian authors are indicated in italic. It should be realized however that they are not synonyms, as the basic concepts are different.

The most crucial part of micromorphological research is the detailed analysis of the fabric. Soil fabric *"deals with the total organization of a soil, expressed by the spatial arrangement of the soil constituents (solid, liquid, gaseous), their shape, size and frequency, considered from a configurational, functional and genetic viewpoint"* (Bullock et al., 1985).

A special type of soil fabric is microstructure. It *"is concerned with the size, shape and arrangement of primary particles and voids in both aggregated and non-aggregated material, and the size, shape and arrangement of any aggregates present"* (Bullock et al., 1985). Analysis of microstructure is still mainly an extension of that of the structure in the field, but performed at higher magnification. The same types of aggregates or peds as described in the field are recognized in thin sections giving rise to several pedal microstructures such as granular, (sub)angular blocky, crumb, lenticular, etc. In apedal soil materials the type of voids present determines the microstructure: channels (Figure M9), chambers, (spherical) vesicles, (irregular) vughs or planar voids (Figure M5). Efforts have been made to determine microstructure on the basis of parameters obtained by image analysis (e.g., Jongerius et al., 1972; Mermut and Norton, 1992), but till now without satisfying result.

The study of the fabric of the solid material was strongly influenced by concepts of (sediment) petrography. Fabric analyses require first the recognition of units, which can be distinguished on basis of composition, relative size, shape, etc., followed by a study of their mutual arrangement.

A first important step in all descriptive systems is to make a distinction between *coarse material* and *fine material* or *micromass* (Stoops and Jongerius, 1975; Bullock et al., 1985; Stoops, 2003), respectively called *skeleton grains* and *plasma* by Kubiëna (1938) and Brewer (1964), or *F (framework)-members* and *F-matrix* by Brewer and Sleeman (1988). The limit between *skeleton grains* and *plasma* is generally situated at about 2 μm. Sometimes additional criteria are added (e.g., for Brewer, 1964, *skeleton grains* represent the stable material, *plasma* the colloidal and/or soluble material). The limit between coarse and fine material *sensu* Stoops and Jongerius (1975) is not fixed

The *relative distribution* of these coarser and finer constituents (c/f) is often characteristic for given soil materials. Five basic patterns of c/f-related distributions are recognized by Stoops and Jongerius (1975) and additional subdivisions proposed by Stoops (2003): (1) *monic* (only one size group is present, either the coarser one (coarse monic), e.g., in pure sand, or the finer one (fine monic), e.g., in pure clay; (2) *chitonic* (fine material forms coatings around coarser material, e.g., in sandy spodic or argillic horizons); (3) *gefuric* (fine material forms concave or convex bridges between coarser grains, e.g., in some cambic horizons); (4) *enaulic* (fine material occurs as micro aggregates between coarser components, e.g., in loose spodic horizons) (5) *porphyric* (coarser grains are embedded in a dense mass of fine material, e.g., in Vertisols) (Figure M6). Depending upon the relative distance between the coarser grains following types of enaulic and porphyric are recognized: close (coarse grains are in touch), single spaced (spacing between coarser grains less than their mean diameter), double spaced (spacing intermediate between once and twice the mean diameters) and open (spacing larger than twice the diameter). Further subtypes of enaulic are determined by the size relation between the coarser grains and the aggregates of fine material (Figure M7). Correlations with other systems are given in Table M6.

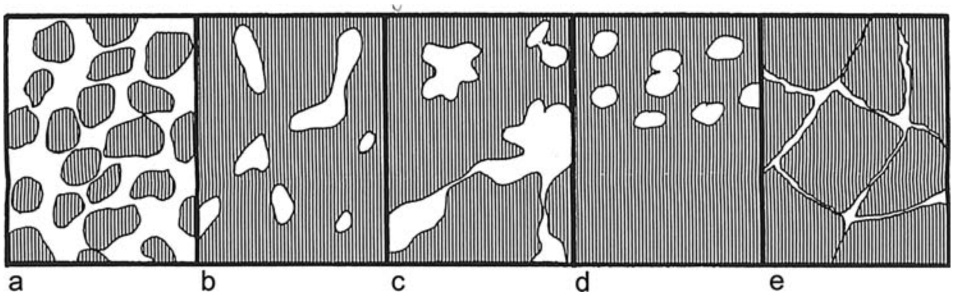


Figure M5 Some types of microstructures and voids: (**a**) granular microstructure with packing voids, (**b**) channel microstructure, (**c**) vughy microstructure with irregular smooth vughs, (**d**) vesicular microstructure, (**e**) angular blocky microstructure with accommodating planes.

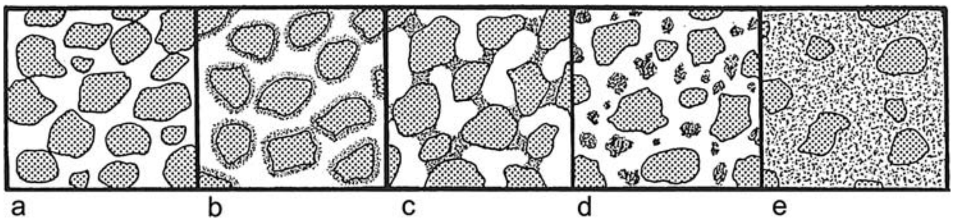


Figure M6 C/f-related distribution patterns: (**a**) monic, (**b**) chitonic, (**c**) gefuric, (**d**) enaulic, (**e**) porphyric.

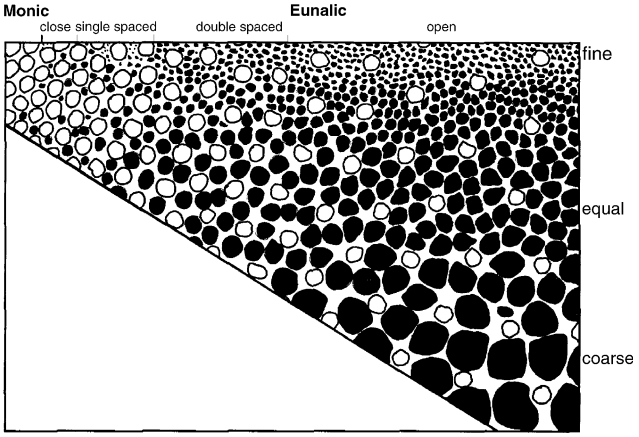


Figure M7 Gradual transition from coarse monic (*left*) c/f-related distribution pattern over single and double spaced enaulic to open enaulic. From top to bottom transition from fine over equal to coarse enaulic.

Soil material can be split up in a more or less undifferentiated *groundmass* or matrix and in distinct *pedofeatures* (respectively *s-matrix* and *pedological features* sensu Brewer, 1964). Pedofeatures are larger than 20 µm and can be distinguished from the groundmass on basis of difference in composition or internal arrangement.

Fabric analysis of the groundmass comprises the description of (*i*) nature, shape, size, degree and type of weathering (Delvigne, 1998) of the coarse material (Figure M9b), (*ii*) characteristics of the fine material or micromass, such as color, limpidity and interference colors, if any and (*iii*) the c/f-related distribution pattern. Randomly oriented clay sized phyllosilicates do not show interference colors in thin sections, because superposition of many randomly arranged particles gives rise to a statistical isotropy. Phyllosilicate clay particles occur however practically always as small (about 20 µm) aggregates (called domains). Because of this parallel orientation the domains behave as small single anisotropic crystals – called *pseudocrystals* by the Russian micromorphologists (Dobrovolski, 1983) – and display therefore interference colors in thin sections.

Patterns of these interference colors determine the (*birefringence*)-fabric (partially equivalent to Brewer's (1964) *plasmic fabric* and the Russian *microtexture*). An *undifferentiated b-fabric* (i.e., no interference colors visible; *isotic* according to Brewer, 1964) points to the presence of amorphous clays (e.g. allophane in Andosols) or to high amounts of organic colloids (in many humic horizons) or sesquioxides (oxic horizons) in the clay fraction, masking the interference colors. Parallel arrangement of the clay domains in the micromass is realized by (shear) stress, e.g., in Vertisols. This becomes visible in thin sections as elongated patterns of interference colors (*striated b-fabrics*, partially corresponding to the *sepic plasmic fabrics* according to Brewer (1964), or *fibrous microtextures* according to the Russian micromorphologists), e.g., *porostriated b-fabric* along fissures (slickensides in Vertisols), *granostriated b-fabric* around grains (Figures M9d and M9f), etc. Less developed random patterns of short (20–50 µm) domains are called *speckled b-fabrics* (partially the *asepic plasmic fabric sensu* Brewer (1964) or *scaly microtextures* according to the Russian micromorphologists). When the micromass contains numerous crystallites (e.g., of calcite) or mineral splitters (e.g., sericite flakes) determining the interference pattern, a *crystallitic b-fabric* (*crystic* according to Brewer, 1964) results (Figure M9f).

Apart from the mineral components, also the organic ones are described. Special attention is given to the degree of fragmentation and humification of plant fragments. A distinction

Table M6 Comparative table of types of related distribution of coarse and fine material

Kubiëna (1938)	Brewer (1964)	Stoops and Jongerius (1975)	Eswaran and Baños (1976)	Brewer and Sleeman (1988)
Elementary fabric	related distribution of plasma and skeleton	c/f related distribution	normal and specific related distribution	fabrics of f-members/f-matrix
bleached sand	granular	monic	granic phyric	granic
intertextic	intertextic	gefuric	intertextic	iunctic
plectoamictic p.p.	agglomeroplasmic	enaulic	congelic p.p.	agglomeric enaulic
chlamydomorphic	–	chitonic	dermatic	chlamlydic
porphyropeptic porphyropectic	porphyroskelic	porphyric	plasmic porphyric	porphyric

Note. The equivalence between the terms is not absolute, as the concepts of coarse/fine, f-members/f-matrix and plasma/skeleton grains are not identical. For Kubiëna (1938), Brewer (1964) and Eswaran and Baños (1976) the limit between coarse and fine is situated at 2 µm, for Stoops and Jongerius (1975) and Brewer and Sleeman (1988) the limit is not fixed.

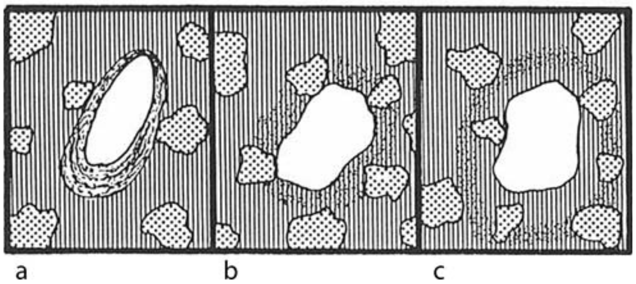


Figure M8 Pedofeatures related to surfaces: (**a**) coating in a, (**b**) hypocoating in the groundmass surrounding a channel, (**c**) quasicoating in the matrix.

is made between *organ residues* (Figure M10a) (containing more than 5 cells belonging to different types of tissue, e.g., root residues), *tissue residues* (containing more than 5 cells of a same type, e.g., paranchymatic residues), *cell residues* (containing less than 5coherent cells) and *fine organic material* (colloidal fraction) (Figure M10a) (Bullock et al., 1985).

Stoops (2003) subdivided *pedofeatures* at the highest level into matrix pedofeatures and intrusive pedofeatures. Whereas *matrix pedofeatures* represent a change in the groundmass by impregnation with a component (Figure M9a), depletion of a component (Figure M9e) or change of the fabric, *intrusive pedofeatures* (Figure M9a) such as clay coatings (Figure M10c) or gypsum crystals (Figure M9c) occur outside the groundmass.

According to their morphology and fabric following types of pedofeatures are distinguished (Bullock et al., 1985):

1. *Coatings*, *hypocoatings* and *quasicoatings* (Figure M8). These are pedofeatures related to surfaces of pores, aggregates or grains. In most cases they can be correlated with Brewer's (1964) *cutans*, *neocutans* and *quasicutans* respectively.

   Coatings are intrusive pedofeatures lining the walls of pores or surrounding grains or aggregates, such as clay coatings in argillic horizons (Figure M10c and M10d), calcite pedents (beards) below pebbles in semi-arid soils, silt cappings on aggregates in frozen soils or due to agriculture (Figure M10b), gibbsite coatings around quartz grains in oxisols. *Hypocoatings* are matrix pedofeatures related to, and immediately adjoining natural surfaces, such as impregnations of cryptocrystalline iron oxihydrates along voids in temporarily wet soils, microcrystalline calcite impregnations around channels (pseudomycelium), calcite depletions around root channels in calcareous soils or groundmass compactions around animal burrows. *Quasicoatings* are also matrix pedofeatures related to surfaces, but at some distance of the latter ones, e.g., cryptocrystalline goethite around channels in hydromorphic soils (cf. the so called Liesegang-rings in geology).
2. *Infillings* consist of materials filling, or partially filling voids, such as excrements filling a channel, illuviated clay filling a fissure, or loose gypsum crystals in a void. A partial equivalent in Brewer (1964) are the *pedotubules;* but these are restricted to infillings of channels or chambers with soil material, mainly of biological origin, with exclusion of pure plasma (clay or soluble material). Also some of his *crystallaria* cover the concept of infillings.
3. *Crystals* and *crystal intergrowths* are intrusive pedofeatures consisting of single crystals, or intergrowths of crystals, larger than 20 µm, euhedral or subhedral in shape and embedded in the groundmass. They correspond to Kubiëna's (1938) and Brewer's (1964) *intercalary crystals.* It are mainly crystals of the more soluble fraction of the soil, such as gypsum (Figures M9c and M9d), calcite and goethite, but also more exotic pedogenic minerals such as barite, celestite and vivianite do occur.
4. *Nodules* are three-dimensional bodies occurring in the groundmass, i.e., not related to surfaces or pores. They correspond in general to Brewer's (1964) *glaebules.* According to their internal fabric different types are distinguished, such as *typic nodules* (with an undifferentiated internal fabric) (Figures M9c and M9d), *concentric nodules* (*concretions* according to Brewer, 1964), *nucleic nodules* (with a foreign core). Nodules may be intrusive pedofeatures (e.g., pure calcite nodules in Vertisols) or may be matrix pedofeatures, i.e., corresponding to zones of groundmass more or less strongly impregnated with or depleted of one or other component, such as iron oxyhydrates (rusty flecks) in hydromorphic soils or microcrystalline calcite (in arid soils). Pure nodules have sharp boundaries, whereas impregnative ones may have diffuse boundaries when formed in situ, or sharp ones when transported. Nodules formed in situ and not disturbed are said to be *orthic*, but when they were subject to translocations they are *disorthic*; inherited nodules are called *anorthic* (Wieder and Yaalon, 1974).
5. *Intercalations* are elongated, undulating pedofeatures not associated with pores or surfaces, embedded in the groundmass. They are mainly related to differences in texture, but little is known about their genesis. There is no equivalent in Brewer's (1964) terminology.

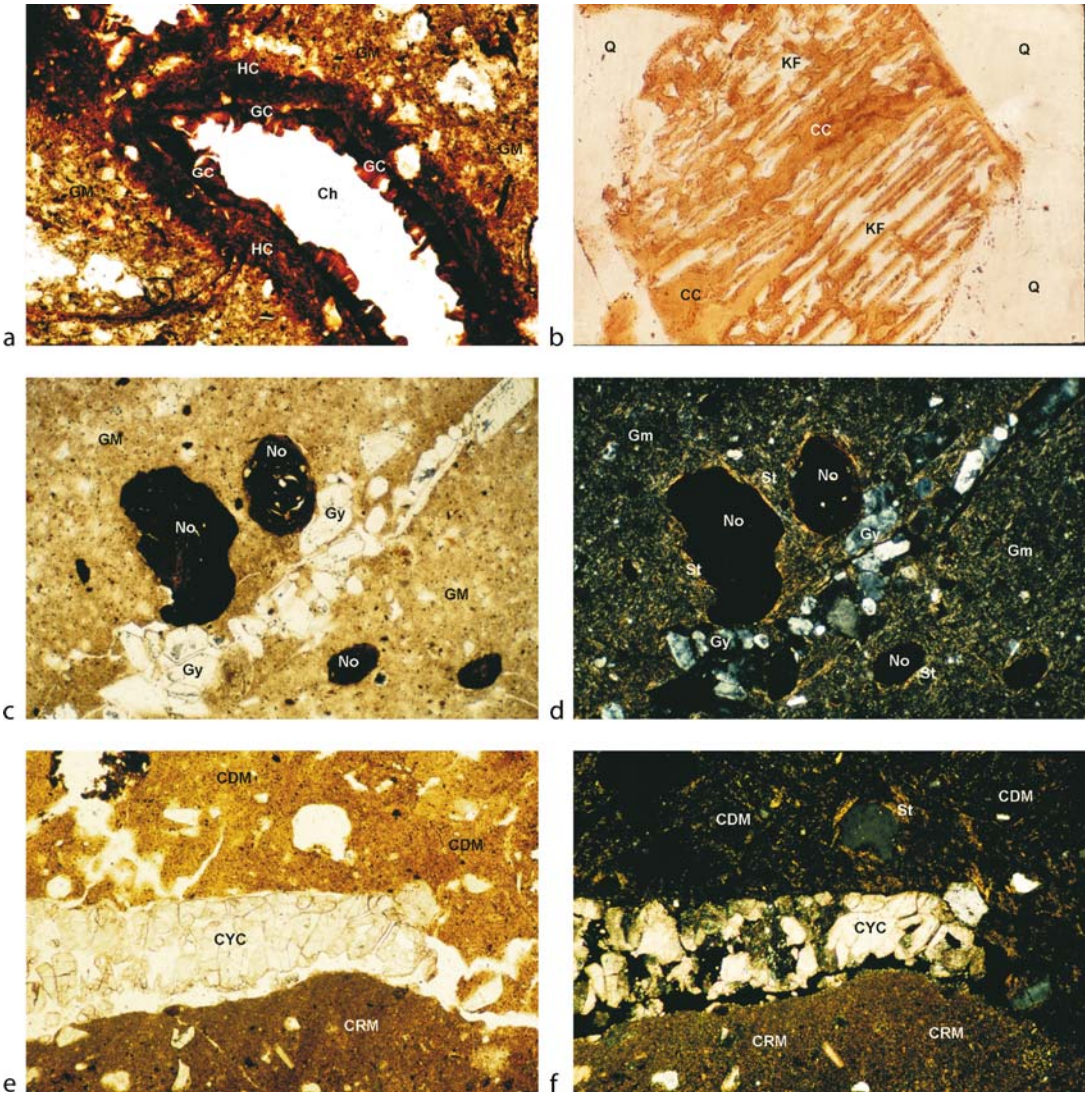


Figure M9 (**a**) Hypocoating (*HC*) of iron hydroxide in groundmass (*GM*) around channel *Ch* (impregnative pedofeature), and goethite coating (*GC*) covering the walls of the channel (intrusive pedofeature) Plain light. (**b**) Weathering of perthite (intergrowth of lamellae of Na- and K-feldspar) in granite. The Na-feldspar is completely weathered and replaced by illuviated yellowish clay (*CC*), only the K-feldspar lamellae are still intact (*KF*). The grain is surrounded by quartz (*Q*). (**c**) Grayish groundmass (*GM*) of a clayey soil with nodules of Fe and Mn hydroxide (*No*), and gypsum crystals (*Gy*) infilling a former void. Plain light. (**d**) Same as (**c**), but crossed polarizers. Note striations (*St*) around nodules, due to orientation of clay particles (granostriated b-fabric). (**e**) Quera. Cytomorphic calcite (*CYC*) in root channel. The groundmass below is rich in fine calcite (*CRM*), the part above the channel has been calcite depleted (*CDM*). Plain light. (**f**) Same as (**e**) but crossed polarizers. Notice striations (*St*) around quartz grain (granostriated b-fabric) due to clay orientation (*CDM*), and interference colors of fine calcite throughout CRM (crystallitic b-fabric).

6. *Excrements* of the soil mesofauna are common in many soils, especially in the surface horizons. They can be purely organic, or mixed organic and mineral. They are subdivided according to their external shape (Figures 10a, 10c and 10d). Aging gives rise to disintegration or coalescence. Excrements correspond to Brewer's (1964) *fecal pellets*.
7. *Compound and complex pedofeatures:* Compound pedofeatures are those that consist of a mixture of two or more pedofeatures, for instance superposed coatings of clay and goethite, or impregnative iron nodules containing clay coatings. Complex pedofeatures (Stoops, 2003) are specific associations of pedofeatures with a diagnostic genetic relationship, such as cytomorphic calcite crystals in root channels, surrounded by calcite depletion hypocoatings (Figures M9e and M9f) in Mediterranean (*queras*, as defined by Herrero and Porta, 1987).

Quantitative analyses

The fundament of the quantitative analysis of thin sections is the Law of Delesse which states that proportions of areas measured on a surface correspond to the proportions of volumes of the three dimensional body.

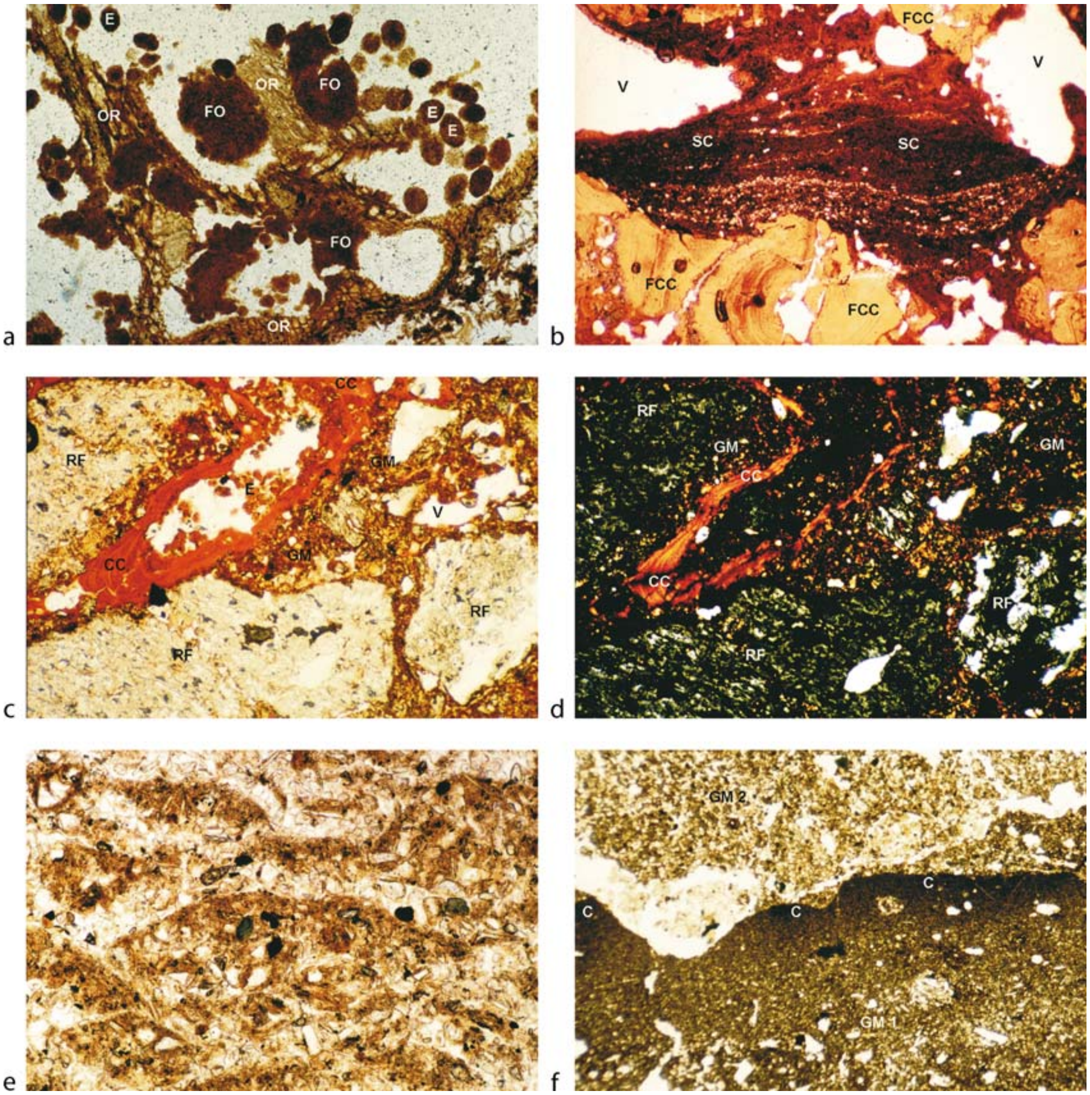


Figure M10 (**a**) Organ residues (*OR*) with large excrements of fine organic material (*FO*) and smaller excrements (*E*) (plain light). (**b**) Horizontal coating of clay and silt (*SC*), partially filling a void (*V*), in material consisting almost only of fragments of clay coatings (*FCC*) in clay with flint deposit (plain light). (**c**) Close packing of rock fragments (*RF*), interstitial groundmass (*GM*) and orange illuvial clay coating (*CC*), some excrements (*E*) and voids (*V*) (plain light). (**d**) Same as (**c**), but between crossed polarizers. Note interference colors of the clay coating. (**e**) Lenticular microstructure. In each aggregate the fine material is concentrated on top, whereas the lower part is depleted of clay. Microstructure formed as a result of repeated cycles of freezing and thawing (plain light). (**f**) Buried surface crust. GM1: groundmass of the old loess; C crust showing fining up, GM2: groundmass of the younger loess (plain light). Note depressions in crust due to local erosion.

A distinction has to be made between the quantitative analyses of the solid material (groundmass and pedofeatures) and that of the porosity (voids).

For the quantification of the solid components the classical petrographic techniques of point counting (Eswaran, 1968) and line counting are still the most popular and in most cases the only that can be used. The aim is to quantify indirectly pedogenic processes. Not all fabric elements or units can be quantified: the area of matrix pedofeatures does not yield any information that can be interpreted in an unequivocal way (Stoops, 1978). Therefore pure fabric units, such as inherited or pedogenic minerals or clay illuviation features are the most commonly quantified. The aim of such studies is for instance the quantification of clay illuviation processes (Ducloux, 1973; Miedema and Slager, 1972), of ratios of inherited to pedogenic carbonates or sulfates, the relative increase or decrease of weatherable and stable minerals through a profile. Quantification of orientations (especially of phyllosilicates) can be used to determine pedoplasmation processes.

Image analysis is becoming more and more important (Mermut and Norton, 1992; Moran, 1994) in analyzing quantitatively soil fabric, especially microstructures and porosity. In this way not only pore volumes, but also their shapes and orientations can be determined quantitatively. For quantitative studies of porosity, a fluorescent dye is often added to the resin: observed under UV-light pores will appear as bright features. Comparison of micromorphometric data with results of physical analyses yields good results. Comparing data of different authors however remains difficult, as no agreement exists on standardization of methodology and parameters to be used.

Interpretation and applications

Introduction

Interpretation of micromorphological descriptions is partially based on deduction, partially on comparison with known materials and for a small extend on results of experiments. Advantage is taken particularly of the potentiality to deduce from spatial relationships chronological or genetic ones, for instance to conclude in which order pedogenic features were formed (e.g., yellowish clay coatings on pores traversing red mottles indicate that the illuviation postdates hydromorphism), and which processes are still active.

Applications in pedogenesis

Coatings, hypocoatings, quasicoatings and infillings are practically always the result of in situ formation (pedogenic in soil materials). The juxtaposition of (hypo)coatings gives a relative chronology. Nodules can be pedogenic or inherited from the parent material or from older soils (orthic versus anorthic).

Combination of fabric analysis and determination of the nature of the constituents enables a micromorphologist in most cases to determine the origin of the parent material, or to distinguish between clay accumulations formed by in situ weathering or by illuviation. From a genetic point of view the possibility of determining for each feature its position in a sequence of events (chronology), as mentioned earlier, is of uttermost importance.

The transformation of saprolite to a soil material, called pedoplasmation (Flach et al., 1968), is another topic that can be studied only by micromorphology, as it concerns in the first place the transformation of fabrics, initially without mineralogical or chemical changes.

Alteration and weathering

Micromorphological methods are more and more used in studies of rock weathering, as they allow to follow the different weathering stages of each component individually, and to estimate their interactions (Delvigne, 1998). Sometimes micromorphology is the only technique to give an exact insight in the material studied: e.g., the parallel arrangement of orthoclase lamellae in thin sections of undisturbed material points to perthites or antiperthites in the original rock, due to a preferential weathering of the albite lamellae (Figure M9b). Grain mounts or XRD would only reveal the presence of K-feldspars.

Soil classification

Soil classifications, except that of Kubiëna (1956) do in general not use micromorphological data as differentiating criteria, although Soil Taxonomy (Soil Survey Staff, 1975) mentions micromorphological characteristics in the description of some diagnostic horizons. Nevertheless this technique may be useful, or even indispensable to recognize some diagnostic features such as clay illuviation (clay coatings versus pressure faces), calcite translocation, in situ weathering, etc. (Douglas and Thompson, 1985). Systematic applications of micromorphology would, without doubt, be of great help to classification, as for instance it would allow to subdivide cambic horizons on a sense full basis.

Paleopedology, Quaternary geology and archeology

Palaeosols are often difficult to identify as many physical and chemical characteristics have changed as a result of overburden, weathering and seepage of solutions. Micromorphological characteristics however are mostly well preserved and allow then the determination of the soil type, the palaeoclimate and environment. In this way micromorphology became an important tool in Global Change studies.

In Quaternary geology and geomorphology the interpretation of buried palaeosols can be carried out by comparing them with present-day soil formations in various climatic zones (Figure 10f). The use of micromorphological indexes (e.g., Magaldi and Tallini, 2000) helps correlating and dating palaeosols. Also for the interpretation of (peri)glacial deposits and deformations a comparison can be made with micromorphological analysis of sediments and deformation features observed in (peri)glacial areas of to day (Dumanski and St. Arnaud, 1966; Harris, 1985; Van Vliet-Lanoë, 1985; van der Meer, 1996). Another source of information is experimental work in combination with thin section analysis. Laboratory experiments made it possible, for example, to identify redeposited loess by splash, rainwash and afterflow processes (Mücher et al., 1981), and to make a distinction between structural modifications by repeated freezing and thawing cycles (Coutard and Mücher, 1985) (Figure M10e).

Applications of micromorphology in archeology are manifold. Apart from those based on the determination of soil genesis and palaeosols, the identification of old living floors, pedoturbations, industrial sites and other traces of human activity is a more and more common practice (Courty et al., 1989; Davidson et al., 1992). More recently micromorphology got also applied in technical geology, soil biology and landscape ecology.

Soil physics, soil degradation

Soil micromorphology is used to study and solve practical problems of soil degradation, water percolation, soil management, etc. One of the most successful applications has been the study of different types of surface crusts (depositional, structural and vesicular crusts) and their formation conditions, both under natural and experimental conditions (Callebaut et al., 1986) (Figure M10f). Problems of soil physics, e.g., the calculation of saturated hydraulic conductivity in heavy soils (Bouma et al., 1979) have been successfully solved using micromorphometric approaches. An increasing attention is given to the evolution of porosity and microstructure under different management practices, where micromorphology and image analyses proved to be sensitive techniques to monitor changes in an early stage. The problem arising in these applications however is the need of a large number of thin sections and measurements to obtain statistically valuable results (Murphy and Banfield, 1978).

Control of analyses

One of the most important applications of micromorphology is to help the interpretation and critical evaluation of results of other analytical techniques. E.g., the knowledge that textural microlaminations are present in a material will influence the sedimentological interpretation of its grain size analyses; when a soil scientist wonders why unstable minerals are present in the silt fraction of an oxisol, the micromorphologist may tell him that they were protected in an iron hydroxide nodule, and liberated during dithionite treatment.

Georges Stoops

Bibliography

Altemüller, H.-J., 1962. Verbesserung der Einbettungs- und Schleiftechnik bei der Herstellung von Bodendünnschliffen mit VESTOPAL. *Zeitschr. PflErnahr. Dung.* **99**: 164–177.

Altemüller, H.-J., 1964. Die Anwendung des Phasenkontrastverfahrens bei der Untersuchung Bodendunnschliffen. In Jongerius, A., ed., *Soil Micromorphology.* Amsterdam: Elsevier, pp. 371–390.

Altemüller, H.-J., 1974. Mikroskopie der Boden mit Hilfe von Dunnschliffen. In Freund, H., ed., *Handbuch der Mikroskopie in der Techniek,* Bd. IV. Frankfurt: Umschau Verlag, pp. 309–367.

Altemüller, H.-J., and Van Vliet-Lanoë, B., 1990. Soil thin section fluorescence microscopy. In Douglas, L.A., ed., *Soil Micromorphology: A Basic and Applied Science.* Amsterdam: Elsevier, pp. 565–579.

Arocena, J., De Geyter, G., Landuydt, C., and Schwertmann, U., 1989. Dissolution of soil iron oxides with ammonium oxalate: comparision between bulk samples and thin sections. *Pedologie* **39**: 275–298.

Babel, U., 1972. Fluoreszenzmikroskopie in der Humusmikroskopie. In Kowalinski, St., ed., *Soil Micromorphology.* Warszava: Polska Akademia Nauk, pp. 111–128.

Babel, U., 1975. Micromorphology of soil organic matter. In Gieseking, J.E., ed., *Soil Components. Vol. I: Organic Components.* New York: Springer Verlag, pp. 369–473.

Bisdom, E.B.A., 1981. Submicroscopic examination of soils. *Adv. Agron.* **36**: 55–96.

Bouma, I., Jongerius, A., and Schoonderbeek, D., 1979. Calculation of saturated hydraulic conductivity of some pedal clay soils using micromorphometric data. *Soil Sci. Soc. Am. J.* **43**: 261–264.

Brewer, R., 1964. *Fabric and Mineral Analysis of Soils.* London: John Wiley & Sons, p. 470.

Brewer, R., 1976. *Fabric and Mineral Analysis of Soils.* Huntington, New York: E. Krieger Publ. Comp., p. 482.

Brewer, R., and Sleeman, J.R., 1988. *Soil Structure and Fabric.* Adelaide: CSIRO, p. 173.

Bullock, P., Fedoroff, N., Jongerius, A., Stoops, G., Tursina, T., and Babel, U., 1985. *Handbook for Soil Thin Section Description.* Wolverhampton, U.K: Waine Research Publications, p. 152.

Callebaut, F., Gabriels, D., and De Boodt, M., eds., 1986. *Assessment of Soil Surface Sealing and Crusting.* Gent (Belgium): Faculty of Agricultural Sciences, State University of Ghent, p. 374.

Chartres, C.J., Ringrose-Voase, A.J., and Raupach, M., 1989. A comparision between acetone and dioxane and explanation of their role in water replacement in undisturbed soil samples. *J. Soil Sci.* **40**: 849–863.

Courty, M.A., Goldberg, P., and Macphail, R., 1989. *Soils and Micromorphology in Archeology.* Cambridge: Cambridge University Press, p. 344.

Coutard, J.P., and Mücher, H.J., 1985. Deformation of laminated silt loam due to repeated freezing and thawing cycles. *Earth Surf. Process. Landforms* **10**: 309–319.

Curmi, P., Soulier, A., and Trolard, F., 1994. Forms of iron oxides in acid hydromorphic soil environments. Morphology and characterization by selective dissolution. In Ringrose-Voase, A.J., and Humphreys, G.S., eds., *Soil Micromorphology: Studies in Management and Genesis.* Amsterdam: Elsevier, pp. 141–148.

Davidson, D.A., Carter, S.P., and Quine, T.A., 1992. An evaluation of micromorphology as an aid to archaeological interpretation. *Geoarchaeology* **7**: 55–65.

Delvigne, J., 1998. *Atlas of Micromorphology of Mineral Alteration and Weathering.* The Canadian Mineralogist, Special Publ. 3. Ottawa, ON: ORSTOM and Mineralogical Assoc. of Canada: p. 494.

Dobrovolski, G.V., ed., 1983. *A methodological Manual of Soil Micromorphology.* Translation 1991, Vol. 3. Gent (Belgium): International Training Centre for Post-Graduate Soil Scientists, Ghent University, p. 63.

Douglas, L.A., and Thompson, M.L., eds., 1985. *Soil Science Society of America Special Publication No 15.* Madison, WI: SSSA, p. 216.

Drees, L.R., and Ransom, M.D., 1994. Light microscopic techniques in quantitative soil mineralogy. In Alonette, J.E., and Zelazny, L.W., eds., *Quantitative Methods in Soil Mineralogy.* Madison, WI: SSSA, pp. 137–176.

Ducloux, J., 1973. Essai de quantification au niveau micromorphologique. Application aux sols d'une toposéquence sur substratum calcaire de la plaine vendéenne. *Sci. du Sol* **2**: 81–90.

Dumanski, I., and St. Arnaud, R.I., 1966. A micropedological study of eluvial horizons. *Can. J. Soil Sci.* **46**: 287–292.

Eswaran, H., 1968. Point-Count analysis as applied to soil micromorphology. *Pedologie*, **18**: 238–252.

Eswaran, H., and Baños, C., 1976. Related distribution patterns in soils and their significance. *Anales de Edafologia y Agrobiologia* **35**: 33–45.

FitzPatrick, E.A., 1984. *Micromorphology of Soils.* London: Chapman & Hall, p. 433.

FitzPatrick, E.A., 1993. *Soil Microscopy and Micromorphology.* Chichester: John Wiley & Sons, p. 304.

Flach, K.W., Cady, J.G., and Nettleton, W.D., 1968. Pedogenic alteration of highly weathered parent materials. *Trans. 9th Int. Congr. Soil Sci.* **4**: 343–351.

Gerasimova, M.I., 1994. Integral micromorphological characteristics of soils. (Micromorphotypes of horizons and morphons). *Eurasian Soil Sci.* **26**: 65–76.

Gerasimova, M.I., 2003. Higher levels of description–approaches to the micromorphological characterisation of Russian soils. *Catena*, **54**: 319–337.

Harris, C., 1985. Geomorphological applications of soil micromorphology with particular reference to periglacial sediments and processes. In Richards, K.S., Arnett, R.R., and Ellis, S., eds., *Geomorphology and Soils.* London: Georges Allen and Unwin, pp. 219–232.

Herrero, J., and Porta, J., 1987. Gypsiferous soils in the North-East of Spain. In Fedoroff, L.M., Bresson, et M.A., Courty eds., Micromorphology des sols – Soil Micromorphology. AFES, Paris, pp. 186–192.

Jongerius, A., Schoonderbeek, D., and Jager, A., 1972. The Application of the Quantimet 720 in Soil Micromorphometry. *The Microscope* **20**: 243–254.

Kubiëna, W.L., 1938. *Micropedology.* Ames, IA: Collegiate Press, p. 242.

Kubiëna, W.L., 1948. *Etwicklungslehre des Bodens.* Wien: Springer Verlag, p. 215.

Kubiëna, W.L., 1956. *The Soils of Europe.* London: Thomas Murby and Co., p. 314.

Kubiëna, W.L., 1967. *Die mikromorphometrische Bodenanalyse.* Stuttgart: Ferdinand Enke Verlag, p. 196.

Kubiëna, W.L., 1970. *Micromorphological Features of Soil Geography.* New Brunswick, NJ: Rutgers University Press, p. 254.

Magaldi, D., and Tallini, M., 2000. A micromorphological index of soil development for Quaternary geology research. *Catena* **41**: 261–276.

van der Meer, J., 1996. Micromorphology. In Menzies, J., ed., *Past Glacial Environments. Sediments, Forms and Techniques,* Vol. 2. Burlington, MA: Butterworth-Heinemann, pp. 335–355.

Mermut, A.R., and Norton, L.D., eds., 1992. Digitization, processing and quantitative interpretation of image, analysis in soil science and related areas. *Geoderma* (Special Issue), **53**: 179–415.

Miedema, R., and Mermut, A.R., 1990. *Soil Micromorphology: An Annotated Bibliography* 1968–1986. Oxon, U.K: CABI, p. 250.

Miedema, R., and Slager, S., 1972. Micromorphological quantification of clay illuviation. *J. Soil Sci.* **23**: 309–314.

Miedema, R., Pape, Th., and Van der Waal, G.J., 1974. A method to impregnate wet soil samples producing high quality thin sections. *Neth. J. Agr. Sci.* **22**: 37–39.

Moran, C.J., 1994. Image processing and soil micromorphology. In Ringrose-Voase, A., and Humphreys, G., eds., *Soil Micromorphology: Studies in Management and Genesis.* Amsterdam: Elsevier, pp. 459–482.

Mücher, H.J., De Ploey, J., and Savat, J., 1981. Response of loess materials to similated translocation by water: micromorphological observations. *Earth Surf. Process. Landforms* **6**: 331–336.

Murphy, C.P., 1986. *Thin Section Preparation of Soils and Sediments.* Berkhamsted, U.K: AB Academic Publishers, p. 149.

Murphy, C.P., and Banfield, C.F., 1978. Pore space variability in a subsurface horizon of two soils. *J. Soil Sci.* **28**: 156–166.

Pape, Th., 1974. The application of circular polarized light in soil micromorphology, *Neth. J. Agric. Sci.* **22**: 31–36.

Parfenova, E.I., and Yarilova, E.A., 1962. *Mineralogical Investigations in Soil Science.* Translation 1965, Jerusalem: IPST, p. 178.

Ross, C.S., 1924. A method of preparing thin sections of friable rock. *Am. J. Sci. Ser.* **5**: 483–485.

Ruark, G.A., Veneman, P.L.M., Mader, D.L., and Waldron, P.F., 1982. Use of circular polarization on soil thin sections to distinguish voids from mineral grains. *Soil Sci. Soc. Am. J.* **46**: 880–882.

Soil Survey Staff. 1975. *Soil Taxonomy. A Basic System of Soil Classification for Making and Interpreting Soil Surveys*. USDA Agric. Handbook No. 436, Washington, DC, p. 754.

Stoops, G., 1978. Some considerations on quantitative soil micromorphology. In Delgado, M., ed., *Micromorphologia de Suelos*. Proc. 5th Int. Working Meeting Soil Micromorphology, Granada 1978, pp. 1367–1384.

Stoops, G., 1994. Soil thin section description: higher levels of classification of microfabrics as a tool for interpretation. In Ringrose-Voase, A., and Humphreys, G., eds., *Soil Micromorphology: Studies in Management and Genesis.* Amsterdam: Elsevier, pp. 317–326.

Stoops, G., 2003. *Guidelines for Analysis and Description of Soil and Regolith Thin Sections.* Madison, WI: SSSA, p. 184.

Stoops, G., and Jongerius, A., 1975. Proposal for a micromorphological classification of soil materials. I. A classification of the related distributions of fine and coarse Particles. *Geoderma* **13**: 189–199.

Tippkötter, R., 1990. Staining of soil microorganisms and related materials with fluochromes. In Douglas, L.A., ed., *Soil Micromorphology: A basic and applied Science.* Amsterdam: Elsevier, pp. 605–611.

Van Vliet-Lanoë, B., 1985. Frost effects in soils. In Boardman, J., ed., *Soils and Quaternary landscape evolution.* Chichester: John Wiley & Sons, pp. 117–158.

Herrero, J., and Porta, J., 1987. Gypsiferous soils in the North-East of Spain. In Fedoroff, N., Bresson, L.M., and Courty, M.A., eds., *Micromorphology des Sols – Soil Micromorphology.* Paris: AFES, pp. 186–192.

Wieder, M., and Yaalon, D.H., 1974. Effect of matrix composition of carbonate nodule crystallisation. *Geoderma* **11**: 95–121.

Wilson, K., Goldstein, A., Falge, E., Aubinet, M., Baldocchi, D., Berbigier, P., Bernhofer, C., Ceulemans R., et al., 2003. Energy balance closure at FLUXNET sites. *Agric. For. Meteor.* **113**: 223–243.

Wyngaard, J.C., Coté, O.R., and Izumi, Y., 1971. Local free convection, similarity, and the budgets of shear stress and heat flux. *J. Atm. Sci.* **28**: 1171–1182.

Cross-references

Cutans
Microhabitats
Microstructure, Engineering Aspects
Soil Engineering

MICRONUTRIENTS

Micronutrients are chemical elements required by plants in relatively small quantities OUP (2000). Table M7 provides context for this definition. The current article is an expanded version of Chesworth (1991), where the original references will be found.

Micronutrients are typically found as constituents of cofactors and coenzymes in living organisms. For the purposes of this article, the micronutrients are taken to be those recognized by the Soil Science Society of America (see Mortvedt et al., 1991): copper, zinc, molybdenum, manganese, cobalt, boron and chlorine (Figure M11). Whitehead (2000) also includes I and Se, which are not considered here.

Basic chemistry

p block elements

Boron

Boron is a group IIIA element, together with Al, Ga, In, and Tl. Atomic size increases in the vertical sequence B to Tl, as with similar groups in the periodic table. Because of the lanthanide contraction, Tl is smaller than would have been predicted. All atoms in group IIIA contain s^2p^1 electrons. Additionally Ga, In and Tl have d electrons, while Tl also has f electrons. Consequently B and Al exhibit simpler chemical behavior than other members of the group.

Boron, in particular, shows little similarity to the others. It is the only element whose outer-shell vacancies outnumber the valence electrons without imparting metallic properties. Yet, it is not a typical nonmetal, since its electrons are not localized in covalent bonds in the elemental state. As a result, B is usually designated a metalloid, a classification borne out by its electronegativity, which, at 2.04, is close to the borderline between metallic and nonmetallic elements. The energy needed to remove its three outer electrons is too high to be compensated by lattice or hydration energies so that B is always covalent in compounds. The quoted ionic radius for B has little meaning, therefore.

The other elements of the group can form trivalent ions, and Tl is also capable of losing the single p electron to form a unipositive ion. The three valence electrons of B can be delocalized between 3 or 4 orbitals to form triangular sp^2 or tetrahedral sp^3 hybrids. These occur as structural units in all the common borate minerals. B is a weak Lewis acid, having the ability to accept an electron pair. The rest of the group is either amphoteric (e.g., Al) or basic (e.g., Tl).

Because the size of atoms or ions in the periodic table increases downwards, and from left to right, atoms or ions that lie diagonally, one beneath the other, tend to be approximately the same size, and to show similar geochemical behavior in instances in which that behavior depends on size. For this reason, the crystal chemistry of borates is generally similar to that of silicates, and B can substitute for Si in silicates and aluminosilicates. It does so especially in sheet silicates. However, because of its ability to assume a three-fold as well as a four-fold coordination, its chemistry is more complex than that of Si.

Chlorine

The halogens, Fl, Cl, Br, I, and At (astatine) are Group VII elements. All have an outer electron configuration of s^2p^5 and so require only one more electron to achieve a stable inert gas configuration. All, therefore, have a high affinity for electrons and all form ions with a single negative charge. The state of condensation increases downwards in the group with F and Cl existing as gases under low temperature, low pressure, conditions, Br as a liquid and I as a solid. All of the foregoing are non-metallic. At is semi-metallic and radioactive, occurring as a daughter product in uranium ores. Its longest lived isotope has a half life of 8.3 hours, so at any one time, the total amount of At in the planet is less than 30 gm. This makes it the rarest of all naturally occurring elements on Earth.

Chlorine gas does not occur in nature; neither do the elemental forms of the other halogens. After F, Ozone and O, Cl has the third highest affinity for electrons in the periodic table. Chloride ion (Cl^-) is the only form in which Cl occurs commonly in nature.

d block elements

Manganese, Fe, Cu, Zn, and Mo all have electronic configurations with d orbitals (Figure M11) and all but Zn are correctly called transition elements. In Zn the d orbitals are completely filled so that it is not technically a transition element, though it is sometimes given that designation. It invariably shows an oxidation state of II in its compounds, whereas the other elements display the multiple oxidation states that are characteristic of elements with incompletely filled d orbitals.

The presence of incompletely filled d orbitals has the further consequence that elements and ions in solids and solutions

Table M7 Terminology relating to nutrient and other elemental abundances. The first five terms reflect biochemical usage; the last three reflect geochemical usage. See Epstein and Bloom (2005); Holland and Turekian (2004)

Nutrient	Required by organisms for their growth and development.
Essential element	Required by organisms to complete their normal life cycles.
Macronutrient	A nutrient found in relatively high concentrations (>500 mg kg^{-1}) in organic tissue: e.g. N, P, K.
Micronutrient	A nutrient found in relatively low concentrations (<100 mg kg^{-1}) in organic tissue. B, Cl, Mn, Fe, Cu, Zn, Mo.
Beneficial element	Elements not known to be essential, but beneficial for plant growth in certain soils and environments: Na, Al, Si, Ni, Co, La, Ce.
Major element	Elements that each constitute more than 1 percent, and together constitute approximately 99 percent, of the mass of the lithosphere: O, Al, Fe, Ca, Mg, Na, K.
Minor element	Elements found in the lithosphere in amounts of 0.01 to 0.99 weight %. e.g. Ti, Mn, P.
Trace element	Elements present in the lithosphere in less than 0.01 weight percentages. Of the micronutrients, all but Fe, and Mn are trace elements in geochemical terms.

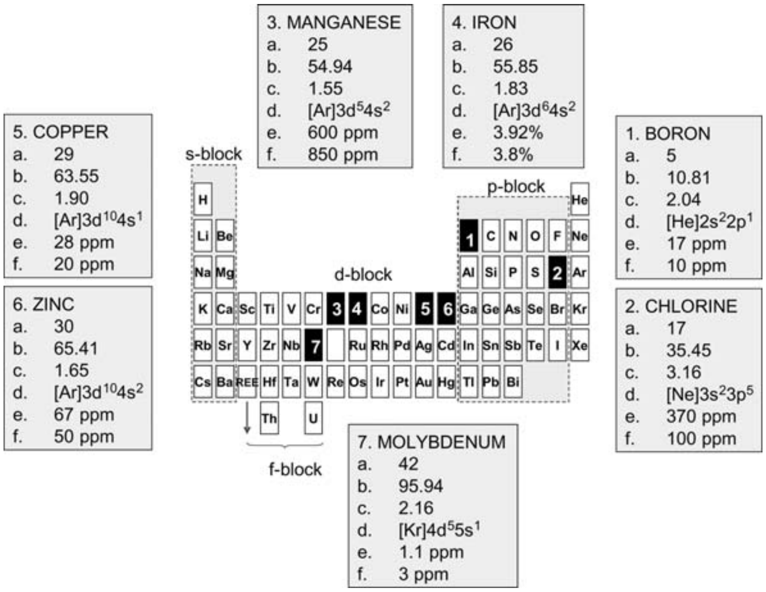


Figure M11 The Periodic Table, highlighting the seven micronutrient elements. *a:* atomic number, *b:* atomic weight, *c:* Pauling electronegativity, *d:* electron configuration, *e:* average abundance in upper continental lithosphere, *f:* estimated average for soils (*Sources:* IUPAC, 2005; Holland and Turekian, 2004; Rössler and Lange, 1972).

of transition elements, may depart notably from the spherical symmetry inherent in the concepts of atomic or ionic radius. Also, the directed nature of d orbitals means that when a transition element is incorporated into a crystal structure or a coordination complex the neighboring atoms or ligands may adjust, so that the geometry of a coordination complex (square planar, tetrahedral, or octahedral configurations are found in nature) becomes distorted. The Jahn-Teller Effect, in which ligands are repelled by d orbitals directed at them, is an example of this. The crystal (or ligand) field exerted by its nearest neighbors on a transition element may also force single d electrons to pair up to occupy the minimum number of d orbitals (low-spin configuration), rather than the maximum number (high spin configuration).

Since transition elements may have several oxidation states, they may also have several ionic radii. Ionic radii will also change with coordination geometry for a given ion, and with the high- and low-spin characteristics of the ion. The tabulation of Shannon (1976) illustrates this fact. The common natural ligands such as O^{2-}, OH^{-}, Cl^{-}, F^{-}, and H_2O, all exert weak fields so that only high-spin complexes involving these species are normally encountered. For this reason, where there was a choice, the ionic radii shown in Figure M11 are for the high-spin case.

First transition series

Manganese, Iron and Copper. The highest valency possible for an element of the first transition series is equal to the sum of all 3d and 4s electrons. This state does not exist for the three elements in nature, though Mn^{VII} is known from the laboratory. The stability of high oxidation states decreases as atomic number increases. As oxidation number increases the oxides of an element become more acidic, while the halides become increasingly covalent and susceptible to hydrolysis. For valence states up to 3, oxy-anions are characterized by octahedral coordination. Tetrahedral coordination is characteristic of higher valence states than this. Complexes in aqueous solution or in crystal structures, with 4, 5, or 6 coordinated cations, are found for oxidation states (II) and (III). Oxidation state (I) is only found in nature for Cu. All three elements form aquo-ions of the type $[M(H_2O)_6]^{2+}$.

Zinc. Zn is grouped with Cd and Hg in Group IIB. All have a $d^{10}s^2$ outer electronic configuration and a common ionic charge of +2, achieved by mobilization of the two s electrons. In addition, Hg also has a +1 ion. Because of the stability of the filled d shell, these elements have few of the characteristics of transition elements. Zinc in particular, shows more affinity to the main group element Mg in its properties, the two being isomorphous in many compounds. Zn is more covalent than Mg (cf. electronegativities: Zn = 1.65, Mg = 1.31). Within the group, Zn and Cd have similarities, while Hg differs markedly from both. In complex formation, the d^{10} configuration imparts no crystal field stabilization so that coordination number is simply a function of size and polarizing power of the cation. For this reason, Zn^{II} forms mainly tetrahedral complexes such as $[Zn(H_2O_4)]^{2+}$.

Second transition series

Molybdenum. First and second row transition elements are similar in general chemistry, though there are significant differences in the stabilities of the various oxidation states. In the second row, lower oxidation states are generally less stable and higher oxidation states are more stable, than the equivalent element in the first series. For example, oxidation state III is relatively unimportant in the chemistry of Mo, though it plays a great role in the chemistry of Cr. The reverse is true for Mo (VI), which is very stable, particularly as MoO_4^{2-}. Unlike the first row ions CrO_4^{2-} and MnO_4^{-} it is not a powerful oxidizer and so has quite a diverse chemistry. Second row elements are followed in the periodic table by the lanthanides, and because of the lanthanide contraction, they are more similar to their related elements in the third row than the first. Mo in particular, is similar in chemistry to W.

Geological provenance

The geological setting is shown in Figure M12. Minerals of the micronutrient elements are listed in Table M8. In the terminology of geology and geochemistry, Fe is a major element (the fourth most abundant in the Earth), Mn is designated a minor element, and B, Cl, Mn, Fe, Cu and Zn are considered to be trace elements.

Boron is not found free in nature. It occurs usually as orthoboric acid in some volcanic spring waters and as borates in the precipitates of natural brines found in some of the saline lakes of arid regions. Ulexite is unusual as a natural fiber optic. Chlorine occurs only in compounds in nature. Its principal minerals are halite, sylvite and carnallite, all to be found in evaporite deposits. Manganese is not found as the free metal in nature, however manganese minerals consisting of oxides, silicates, and carbonates are very common in minor amounts. Most manganese is obtained from ores in Australia, Brazil, Gabon, India, Russia, and South Africa. Manganese nodules on ocean floors contain about 24% manganese. Iron is found free in meteorites (siderites), but does not form as the element under lithospheric conditions. The most common ores are magnetite and hematite. The core of the Earth is considered to be composed largely of iron-nickel alloy. Copper occurs as the native element, as oxides, sulfides, carbonates and a few less common minerals. Major deposits are located in Canada, Chile, Germany, Italy, Peru, USA, Zambia, and Zaire. Zinc is never found as the free metal, but mostly as primary ore minerals such as sphalerite, or secondary alteration products, smithsonite for example. Zinc is widespread around the world. Major deposits occur in North America and Australia. Molybdenum is not found in nature as the free metal. The main ore is molybdenite. It is also recovered as a by-product of copper and tungsten production (Details from Klein and Dutrow, 2008).

Behavior of the micronutrients in the weathering zone

In general, weathering of the primary materials of the lithosphere under humid climates proceeds through three stages of increasing acidification. In the first, incipient stage (in Regosols and Leptosols for example) the micronutrients are locked into the

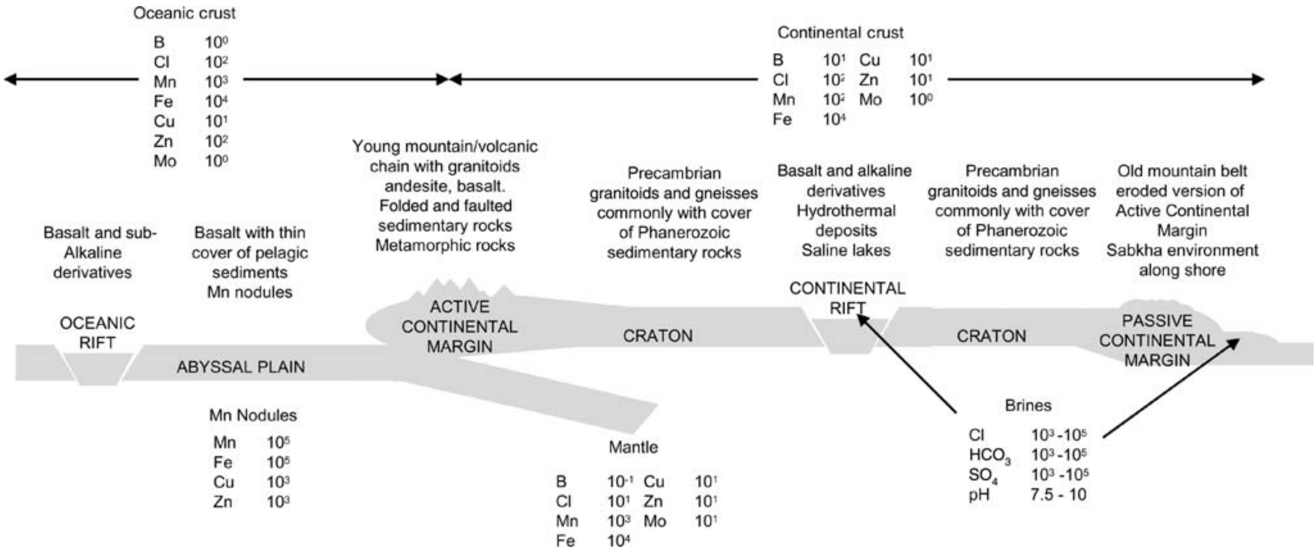


Figure M12 Order of magnitude abundances of the micronutrients in the geological and tectonic environments of the upper 100 km of the Earth. Principal host minerals for the d block nutrients are the ferromagnesian minerals, Fe and Mn oxides and hydroxides and the sulfides pyrite and chalcopyrite. The p block elements are exploited from brines and their related evaporite deposits. Mn nodules are a significant potential source of Mn and other d block elements (*Source:* Holland and Turekian, 2004).

Table M8 Mineralogy of the micronutrients

Material	Formula	%	Occurrence
BORON[a]			
Borax	$Na_2B_4O_7 \cdot 10\ H_2O$	10	Playa lakes are the common evaporite environment for borates.
Tincalconite	$Na_2B_4O_7 \cdot 5\ H_2O$	15	Playa lake deposits. Forms by dehydration of borax. Commercial borax contains both, and is very soluble.
Colemanite	$Ca_2B_6O_{11} \cdot H_2O$	16	Playa lake deposits. Least soluble of common borates. Slow release, useful in coarser soils.
Ulexite	$NaCaB_5O_9 \cdot 8\ H_2O$	13	Playa lake deposits. Used in soil rather than foliar applications by reason of relatively low solubility.
Tourmaline	$NaX_3Al_6(Si_6O_8)(BO_3)_3(OH,F)_4$ where X may be Al, Li and d block elements.	3–4	Accessory mineral in igneous and metamorphic rocks. Detrital mineral in sediments.
CHLORINE[a]			
Halite	$NaCl$	61	Common Na mineral of marine evaporite deposits.
Sylvite	KCl	48	Marine evaporite deposits. Chief source of K, mined as sylvinite, an impure mixture with halite.
Carnallite	$KMgCl_3 \cdot 6\ H_2O$	38	Marine evaporite deposits. Ore of K.
Bischofite	$MgCl_2 \cdot 6\ H_2O$	35	Marine evaporite deposits. Precipitates at late stage.
Manganese[b]			
Rhodochrosite	$MnCO_3$	31	Hydrothermal and alteration product.
Pyrolusite	MnO_2	63	In hydrothermal and detrital deposits.
Psilomelane	$(Ba,H_2O)_2Mn_5O_{10}$	47	Secondary, ill defined alteration product. Wad.
Nodules	Mainly Mn oxides	15–30	Pelagic marine environments and some freshwater lakes. Other d block elements present.
IRON[c]			
Ferromagnesians	Various	5–30	Igneous and metamorphic rocks (olivine, pyroxene, amphibole, mica). Detrital environments (mainly mica). Note that ferromagnesian minerals also accommodate the other micronutrients by isomorphous replacement (B in tetrahedral sites, Cu and Zn mostly in octahedral sites, and Cl for OH in amphiboles and micas).
Magnetite	Fe_3O_4	72	Igneous rocks and skarns.
Hematite	Fe_2O_3	70	Laterites and ferrallitic soils.
Goethite	$FeOOH$	63	Common form in soils.
Pyrite	FeS_2	47	Igneous rocks, hydrothermal veins and highly reduced sedimentary environments.
Chalcopyrite	$CuFeS_2$	30	Igneous rocks and hydrothermal veins.
Siderite	$FeCO_3$	48	Reduced sedimentary environments.
COPPER			
Native Copper	Cu	100	Mostly associated with the reaction of hydrothermal fluids with basaltic rocks. Minor amounts found with other copper minerals in red beds sedimentary environments.
Chalcopyrite	$CuFeS_2$	35	Igneous rocks and hydrothermal veins. The major ore of copper.
Cuprite	Cu_2O	89	Igneous rocks and hydrothermal veins.
Malachite	$Cu_2CO_3(OH)_2$	57	Secondary alteration product of Cu sulfides and oxides. Common in red bed sedimentary copper deposits.
Azurite	$Cu_3(CO_3)_2(OH)_2$	55	Usually accompanies malachite.
ZINC			
Sphalerite	ZnS	67	Hydrothermal veins and limestone-hosted Pb-Zn deposits. About 5% of the metal (octahedral sites) are substituted by Fe. Wurtzite.
Zincite	ZnO	80	Rare, in skarns. Up to 10% Mn substitutes for Zn.
Smithsonite	$ZnCO_3$	52	Alteration product of Zn ore bodies in limestones.
MOLYBDENUM			
Molybdenite	MoS_2	60	In acid igneous rocks. The only important ore.
Molybdite	MoO_3	67	In acid igneous rocks. Rare.
Powellite	$CaMoO_4$	48	In acid igneous rocks. Rare.

[a] Natural brines (for B and Cl) and seawater (Cl) are also exploited.

[b] Mn oxides have a great ability to accept other d block elements in isomorphous replacement for Mn. In soils they adsorb d block cations, as well as the oxyanions of Mo, P, Se, As.

[c] Fe minerals allow for isomorphous replacement of Fe by virtually all the d block elements. The ferromagnesian minerals especially are the major lithospheric depository of the other d block micronutrients. In soils the common iron hydroxide goethite, may accommodate within its structure a similar suite of ions to the Mn oxides.

structures of the minerals of the parent materials. At an intermediate stage of weathering (bisiallitization, as in Luvisols, Phaeozems, Chernozems and Kastanozems) the physical conditions are conducive to the formation of 2 : 1 sheet silicates, such as smectites and vermiculites. These silicates can adsorb nutrients in a form available to plants, and are found in the most fertile soils. An end stage is reached (monosiallitization and allitization as in Ferralsols and Alisols) when advanced weathering and leaching has winnowed the soil down to minerals predominantly made up of the components SiO_2, Al_2O_3, Fe_2O_3 and H_2O. 1 : 1 sheet silicates, oxides, and hydroxides are the main minerals present, and nutrient content is very low. The soil may still support a flourishing vegetation, however. The highly weathered and leached soils of the tropical rain forest, for example, support a flourishing biomass, which contains virtually all the nutrient content of the system, slowly accumulated, and efficiently recycled over millennia.

Two types of environment lead to modification of this simple three-stage progression. Under arid conditions, a trend of alkalinization, rather than acidification, takes place (in Solonchaks and Solonetz for example). Salinization is the common end point. A third trend develops when the soil environment becomes reducing, either by the accumulation of organic matter as in Histosols, or by waterlogging as in Gleysols and Stagnosols.

Acid-base, and redox reactions are the main chemical processes involved in the origin and evolution of soils, so redox-pH diagrams are a useful guide to the behavior of the micronutrients under the three different trends of soil development. Chesworth et al. (2006) provide a theoretical basis for the use of such diagrams in soil science.

Boron

Boron shows two principal patterns of behavior in the weathering regime. The least complicated is its behavior as a residual element. For example, tourmaline from high-temperature rocks is very resistant to chemical breakdown in the weathering zone. As a result, it accumulates in the clastic fraction of soils, sediments and sedimentary rocks.

A second type of behavior is more complex. From primary silicates, in which it occurs as a trace element substituting for Si, it goes into solution, with H_3BO_3 as the dominant species in the zone of soil formation (Figure M13). In this form it is highly mobile and easily leached from the system. Soils therefore tend to have less B than their parent materials. As a nutrient element it is taken up by the soil biomass and may be held temporarily by decayed organic matter, or adsorbed on the fine mineral fraction. A fraction is recycled, but there is an inevitable loss of borate by leaching. Eventually, via ground and river water (0.01 mg kg^{-1}), B is flushed to the sea and accumulates there in solution (4 to 7 mg kg^{-1}). The level in seawater is controlled by adsorption onto clays (especially detrital sericite and illite) and Fe and Al hydroxides. Boron may become incorporated into the clay mineral illite as the ultimate sink. Volcanic emissions are another important source of oceanic B, and for this reason the mean B content of sedimentary rocks (about 100 mg kg^{-1}) is ten times greater than for magmatic rocks. In fact, for illite-rich shales, the enrichment factor is 100. This is probably due to several cycles of weathering, burial, and diagenesis.

Because of the two modes of behavior outlined above, B tends to have a bimodal distribution in soil parent materials of sedimentary origin. The coarse textural fraction will contain any detrital tourmaline, while the fine fraction contains the boron removed from seawater by illite, sericite and Fe hydroxide.

Most of the economic deposits of borate are formed by the evaporation of shallow lakes in the closed basins of arid regions of the Earth. Where late stage hydrothermal processes have been recently active, the B in the lake water may be enriched by hydrothermal fluids as in the southwestern United States.

Figure M13 shows the predominance field of the common dissolved species of B in nature.

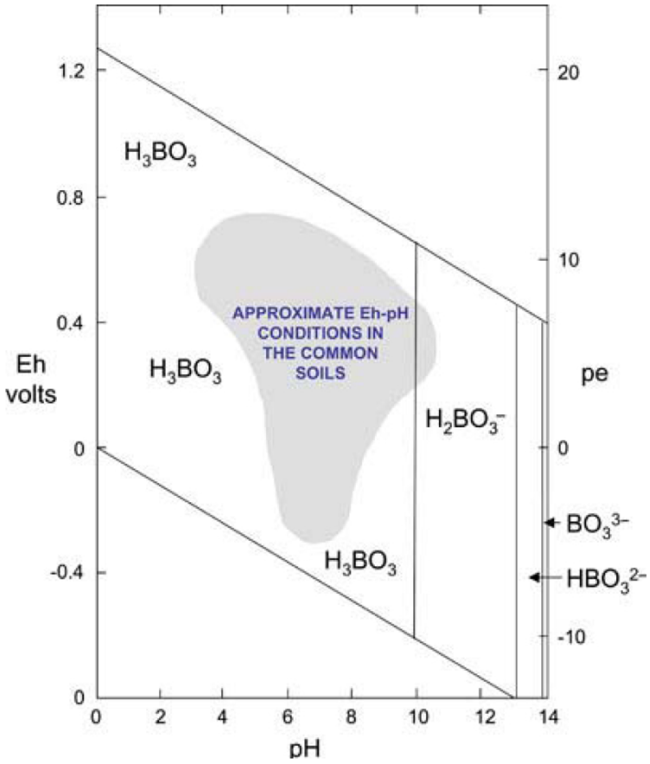


Figure M13 Boron species. The neutral species H_3BO_3 predominates in virtually all soils. Only the soils of environments of extreme alkalinity fall in the predominance field of a charged ion (from Brookins, 1988). All Eh-pH diagrams in this article are constructed for 25 °C and 100 kPa, taken to be representative of Earth-surface conditions. Activity of B is 10^{-5}.

Chlorine

The behavior of Cl in the weathering zone is simple. Cl^- is very mobile in the soil solution and cycles rapidly through the soil provided that atmospheric precipitation is greater than evapotranspiration, and provided that the soils have a pH higher than about 5.5. The ultimate sink for Cl^- in the weathering system is the ocean.

Only in soils with an appreciable number of anion exchange sites (for example Ferralsols and other acid, highly weathered and leached soils with a notable content of kaolinite) is there likely to be any significant (though temporary) immobilization by adsorption of this and other negative ions. With increasing pH available sites disappear and adsorption of Cl^- becomes negligible. In almost all weathering systems Cl^- therefore is highly mobile under sub-humid to humid climates. In arid regions, however, Cl^- may be immobilized in the soil by evaporation, and tends to accumulate in the solum or at the surface, as soluble salts of Na, Ca and Mg.

In spite of the rapid cycling of Cl^- in most soils where precipitation exceeds evapotranspiration, evidence of the effect of deficiencies is rare. Deficiencies have been mainly reported from humid regions in rapidly drained, sandy soils such as Arenosols. The small amounts of Cl^- required for plant nutrition are supplied in most cases from atmospheric precipitations. The provenance is principally oceanic-derived aerosols, with a significant addition from volcanic sources.

Figure M14 shows that Cl^- is the common form of the micronutrient within the complete stability range of water at the surface of the Earth.

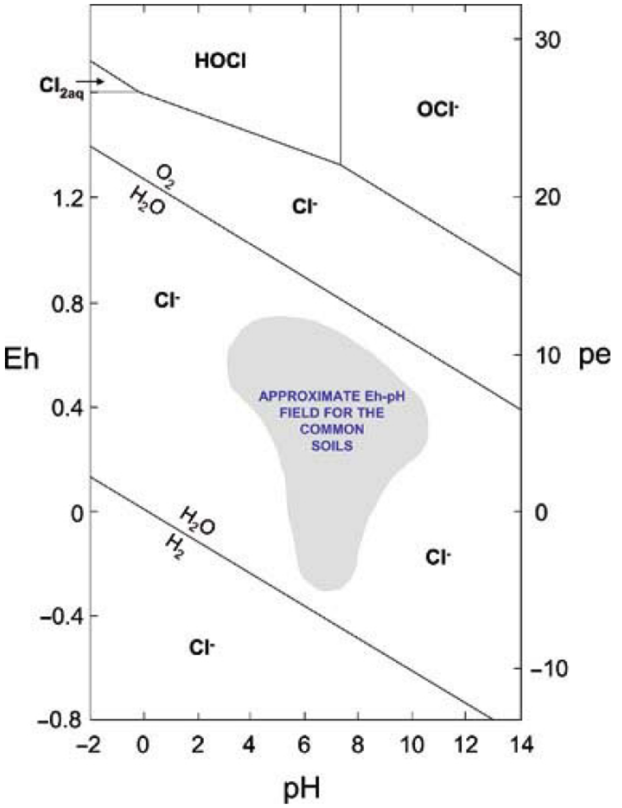


Figure M14 Chlorine species at low temperature and pressure. Chloride ion predominates at the surface of the Earth (after Snoeyink and Jenkins, 1980).

Manganese and iron

By virtue of their proximity as transition elements and the fact that redox plays such a large role in their biogeochemistry, these elements are conveniently discussed together. In general Mn and Fe are sparingly soluble, and therefore relatively immobile, in well aerated soil environments, becoming soluble and mobile under lower redox conditions or at high acidities.

The following factors are important in determining their chemical behavior:

a. The nature of the weathering solid. Taking the primary igneous rocks as the starting point of the weathering process, Fe^{II} is a dominant constituent of the ferromagnesian minerals and metal oxide phases, whereas Mn^{II} is present as a minor or trace element in isomorphous substitution for Fe. The oxide magnetite also contains Fe^{III} and in late stages of magmatic crystallization (in granites and pegmatites for example) Fe^{III} can occur in hematite.
b. Valence of metal in the weathering solid. Leaving aside the exceptions just noted, in primary minerals the lowest valence state (Mn^{2+} and Fe^{2+}) is the most common, on account of the low p_{O_2} of most magmatic and metamorphic formative environments. The Mn^{II} and Fe^{II} compounds are the most soluble at low temperature and pressure.
c. The most active weathering takes place under high p_{O_2} conditions, where oxidization states III and IV (overwhelmingly the commonest form) for Mn and III for Fe predominate. Primary minerals, with the exceptions of the oxide phases mentioned, readily break down.
d. The significant solution field for Fe under conditions of the earth surface is greatest at high acidity (for example in Thionic Fluvisols) and high reduction potential (for example in Gleysols and Histosols). This is also true for Mn, though the predominance field for Mn^{2+} is broader than for Fe^{2+}. There is consequently a significant separation of the two elements during weathering and pedogenesis (Krauskopf and Bird, 1995, p366).
e. The nature of the secondary phase. Under oxidizing and near-neutral conditions, the metals are immobilized principally as hydroxide and oxide phases, as discrete particulate matter or as cutans. The ultimate products of weathering are pyrolusite MnO_2, and goethite FeOOH, though initial metastable precipitates may display various degrees of hydration and crystallinity. The secondary phases, especially those of Fe have an immense role in controlling the level of other metal ions in solution by virtue of the large surface that they make available for adsorption. Under reduced conditions (in Gleysols for example) the metals may be flushed from the soil, though in the presence of the appropriate anion, secondary carbonates or sulfides may form.
f. The behavior of all metals capable of assuming more than one ionic state, is coupled to the chemical behavior of O, S, and C in the weathering zone as a whole, with N having an additional influence in soils.
g. Complex formation. The field of solubility of Mn can be increased by complex formation with both inorganic and organic ligands. Complexation with organic ligands is particularly important in the short-range mobilization of Fe in the formation of Podzols.
h. The geochemistry of both metals at the surface of the Earth is mediated by microbial activity. For example *Gallionella*, *Sphaerotilius*, *Leptothrix* and *Chronothix* are active in the immobilization of Mn, while *Thiobacillus* under oxidizing conditions, and sulfate-reducing bacteria at low redox potentials play significant roles in the geochemistry of Fe (Figure M15).

A notable occurrence of Mn is as nodules rich in Mn hydroxide (and other d-block elements) on the abyssal floor of the ocean. The ultimate source is hydrothermal fluids from oceanic rift systems.

Figures M16 and M17, show the predominance field of the common solid and dissolved species of Mn and Fe respectively, under conditions representative of the surface of the Earth.

Copper

The sulfide chalcopyrite is the commonest Cu mineral, though most of the Cu in the lithosphere is present in ferromagnesian minerals, where it occurs in isomorphous replacement for iron. The ferromagnesian minerals are formed under the relatively high temperatures and pressures and low redox conditions of igneous petrogenesis. They are unstable under the relatively low PT, high redox, water- and CO_2-rich conditions of soil formation, and readily break down to release Cu, among other elements. Within the normal Eh-pH conditions of the soil, Cu mobility is restricted to acid, oxidizing environments. Elsewhere, mobility is restricted by the precipitation of carbonates, such as malachite, by $Cu(OH)_2$, and by CuS. An important sink for Cu in soil is the clay fraction: Cu^{2+} is adsorbed preferentially on fine-grained Mn hydroxy, rather than Fe hydroxy or

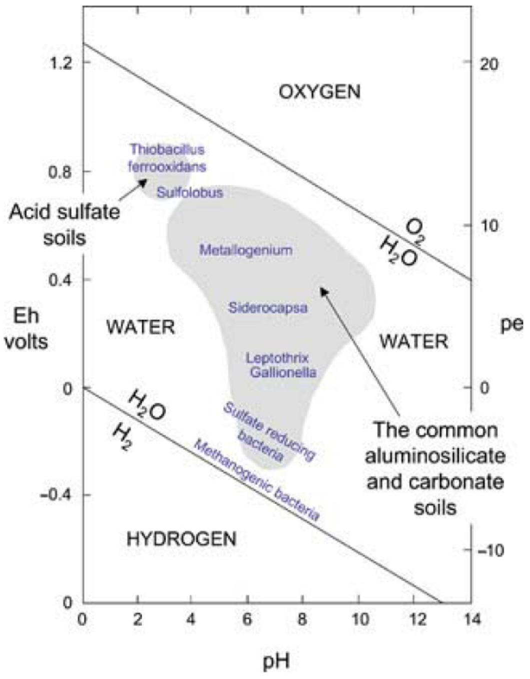


Figure M15 Bacteria responsible for mobilization and immobilization of Fe and Mn in soils and other weathered products, in relation to the Eh-pH ranges of mineral soils (adapted from Trudinger and Swaine, 1979).

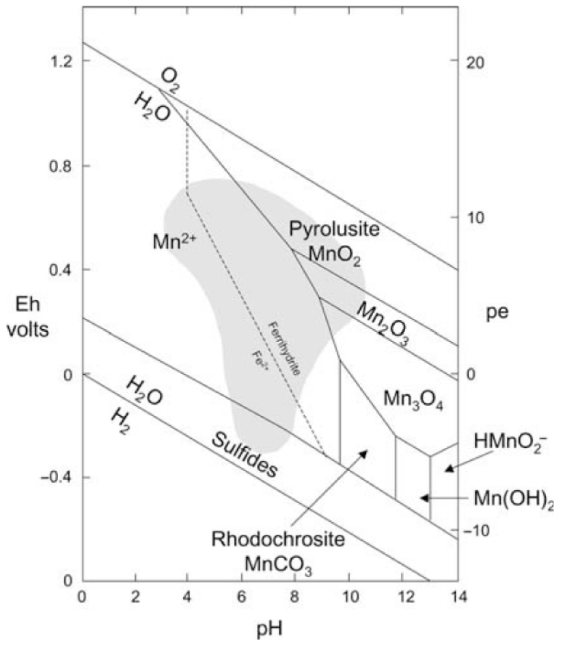


Figure M16 Mn species under Earth surface conditions (adapted from Hem, 1972). The potential mobility of Mn as the dipositive ion is considerably reduced by the presence of Fe hydroxides represented in the diagram by ferrihydrite, which adsorbs and co-precipitates with Mn. Activity of Mn 10^{-5}. Lower pH limit of predominance field of Fe plotted for an activity of Fe of 10^{-5}. Activity of CO_2 is $10^{-3.5}$. Sulfur activity is unspecified in order to show the approximate maximum extent of the predominance field of sulfide minerals.

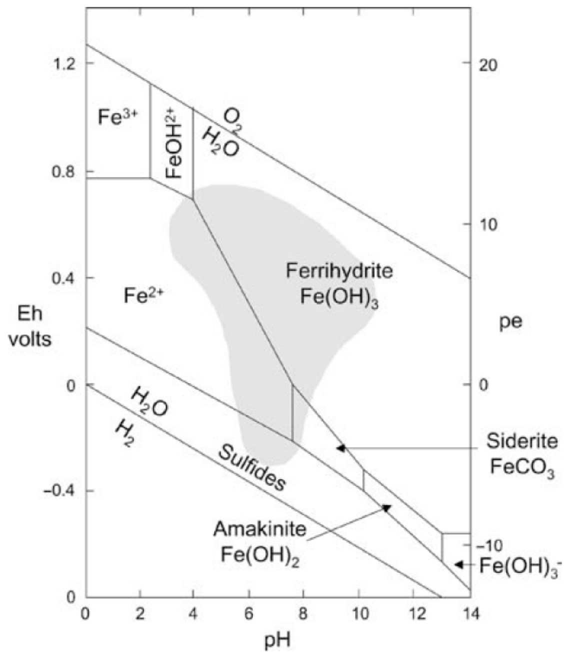


Figure M17 Iron species under Earth surface conditions. Modified from Jenne (1968) and Hem (1972). Activity of Fe is 10^{-5}. Activity of CO_2 is $10^{-3.5}$. S activity is assumed to be negligible except for the sulfide field, which is shown at its approximate maximum extent.

aluminosilicate phases. The result is that Cu is relatively immobile in the weathering zone. Complexation, particularly with Cl (in the connate waters of marine sediments, or conceivably in sabhka and similar type pedological environments) and with organic ligands in common pedological environments, may increase the mobility of Cu in favored circumstances.

In spite of the zone of alteration in sulfide deposits being ideal for Cu mobilization (i.e., acid and oxidizing), Cu shows a low mobility in gossans. It precipitates as secondary hydroxy carbonates (usually as malachite rather than azurite), and is adsorbed onto the plentiful Fe hydroxides, which accompany this kind of weathering. It has also been suggested that malachite is the solution-limiting phase for Cu in the sea.

Figure M18 shows the predominance field of the common solid and dissolved species of Cu in nature.

Zinc

The primary source of Zn is the sulfide, sphalerite (ZnS), though most Zn in the lithosphere is present as an isomorphous replacement of Fe in the ferromagnesian minerals. Sphalerite may accumulate in the detrital fraction, but normally Zn^{II} will be released into the environment when the ferromagnesians (or sphalerite break down). Since Zn has only one valence state, its solution chemistry is simple compared to the other d-block elements. Whether or not there is significant leaching of Zn in a weathering material depends mainly on pH. The more basic conditions lead to the immobilization of Zn as carbonate or hydroxy solids. Under low redox conditions and in the presence of HS^-, ZnS may precipitate, or Zn may become incorporated into other sulfides, most notably pyrite.

Although the Eh-pH diagram shows a large predominance field for Zn^{2+} in solution, in soil the ion tends to become

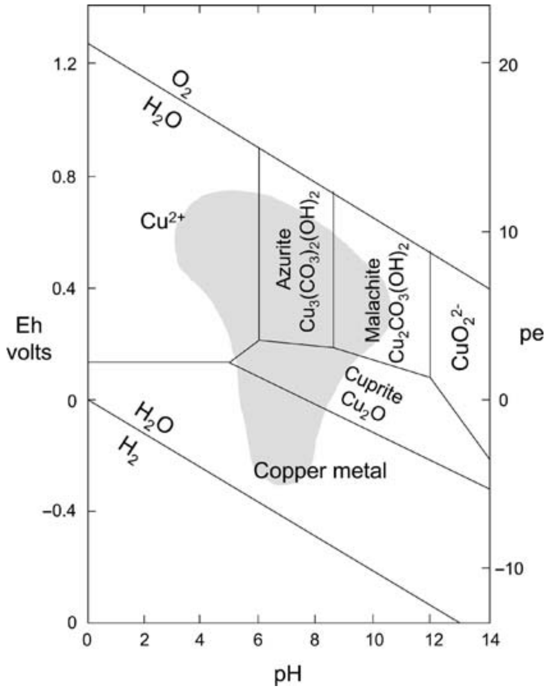


Figure M18 Copper species under Earth surface conditions. Activity of CO_2 is $10^{-3.5}$. Activity of Cu is 10^{-5} (after Vink, 1986). In the presence of S species at low Eh, a predominance field for Cu sulfides, similar in maximum extent to the equivalent fields in Figures M16, M17, M19 and M20, occupies the lower part of the field of Cu metal.

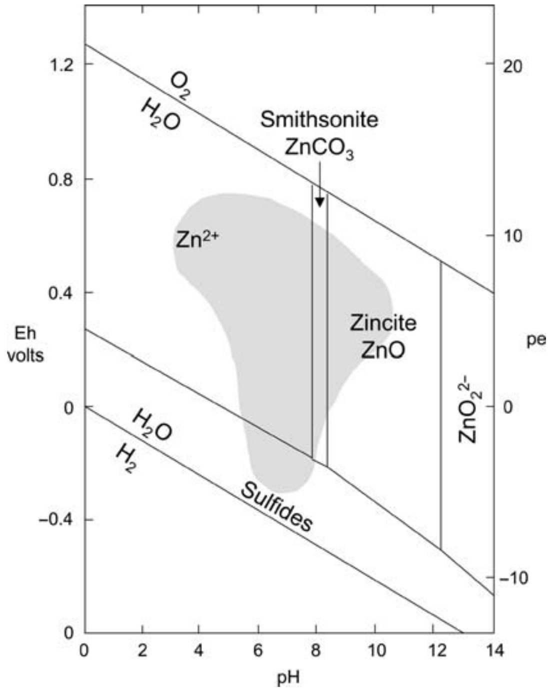


Figure M19 Zinc species under Earth surface conditions. Activity of zinc is 10^{-5}, $P_{CO_2} = 10^{-1}$ kPa. Sulfur activity is unspecified in order to show the approximate maximum extent of the predominance field of sulfide minerals (after Brookins, 1988). In the aqueous environment of soil the predominance field of the hydroxide $Zn(OH)_2$ covers the fields of Smithsonite and Zincite between pH 8–12 (Wu and Hsu, 1986).

immobilized in soil, on the cation exchange sites of organic matter and the high surface area solids of the clay fraction (Mn hydroxides are preferred). Immobilization by this mechanism is common among the d-block elements.

Plants accumulate Zn by a factor of about 10. Coupled with the generally low mobility of Zn during weathering, this commonly leads to soils having a slightly higher Zn content than their parent material. The same point is generally true for other d-bloc elements.

Cadmium has similar crystallochemical properties to Zn and tends to be present in high concentrations in ZnS. Potentially; this could cause toxicity problems in the vicinity of weathering Zn deposits (Martinez et al., 2002).

Figure M19 shows the predominance field of the common solid and dissolved species of Zn in nature.

Molybdenum

The sulfide molybdenite is the commonest primary molybdenum mineral (particularly in granitoid rocks). The usual source of Mo in the weathering zone, however, is the ferromagnesian minerals. When released into the Earth-surface environment, there is a slow oxidation to Mo^{VI} and it enters solution as one of a number of (usually oxy-) anions. Figure M20 shows some of the possibilities, although higher molybdates and thiomolybdates (which may form in waters of neutral or basic pH) were ignored in constructing the diagram.

Because of the wide range of conditions under which Mo is soluble, it is potentially very mobile (probably the most mobile of all metallic elements next to the alkalies, alkaline earths and possibly Re. As with other examples discussed, Mo precipitation and adsorption will tend to reduce expected mobility, with the behavior of Fe and Mn exerting the dominant control. Virtually all the Mo in the lithosphere is associated with Fe and Mn (the preferred adsorbing substrate) hydroxides and Fe sulfide.

Molybdenum (together with other d-block elements, including the micronutrients Mn, Fe, Cu and Zn) is enriched in pelagic, highly reducing, organic-rich sedimentary environments. The main source is hydrothermal additions from vents at mid-oceanic ridges. Pelagic materials are found on land only in such relatively rare occurrences as ophiolite complexes (fragments of oceanic lithosphere thrust into mountain belts during plate collisions). They are therefore hardly ever found as the parent materials for soils.

Figure M20 shows the predominance field of the common solid and dissolved species of Mo in nature.

Micronutrients in agriculture

Boron is required by green algae and higher plants. It is probably not required in the diet of humans but it might be a necessary “ultratrace” element. Its function is not clear. Chlorine as chloride is the most recently designated micronutrient (Mortveldt et al., 1999). Cl^- is a nutritional element in small grains, corn and sorghum. Again, its function is not clear. It is essential for mammals; digestive juices for example, contain hydrochloric acid. It also decreases the incidence of fungus infections in small grains. Manganese is an essential component of about

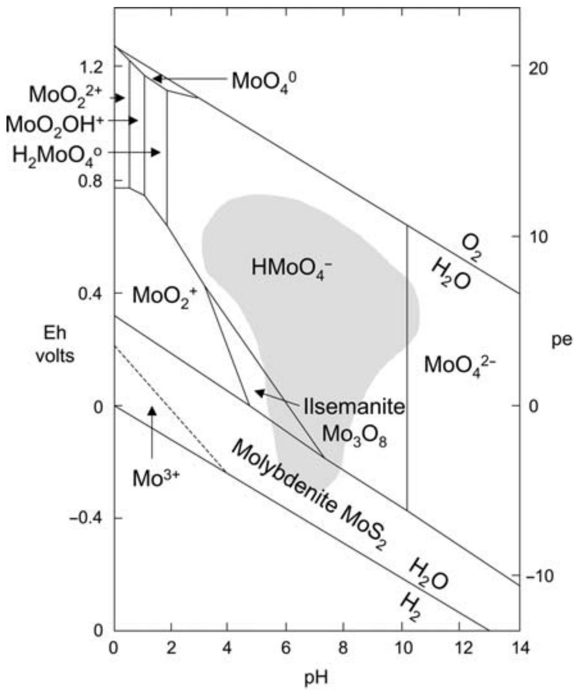


Figure M20 Mo species under Earth surface conditions. Mo activity is 10^{-5}. Sulfur activity is unspecified in order to show the approximate maximum extent of the predominance field of sulfide minerals (adapted from Brookins, 1988).

20 enzymes and proteins for the action of some enzymes. Soil deficiencies lead to infertility in mammals and to bone malformation in growing chicks. Iron compounds are essential to all life. For example, the iron atom in hemoglobin is responsible for carrying oxygen around the blood stream. Copper is also essential for all life. It is the key component of redox enzymes and of hemocyanin. Zinc is essential in the diets of plants and animals. It is the key component of many enzymes and of the protein-hormone insulin. Zinc deficiency results in stunted growth and in male sexual immaturity. Molybdenum appears to be a necessary element for all species. It plays a role in nitrogen fixation enzymes, and nitrate reduction enzymes. Details of the occurrence and functions of the micronutrients in living organisms can be found in Fraústo da Silva and Williams (2001).

Although the micronutrients are necessary for plant growth and development, high concentrations lead to toxicities. Under acid conditions Mn, Cu and Zn are readily mobilized and may reach toxic levels, whereas the easily leached boron is more likely to build up to toxic levels in the soils of drier climates.

Before micronutrients were recognized as such, they were added to agricultural soils incidently, in manures and composts or as impurities in fertilizers. The environment of formation of sedimentary phosphates for example, is conducive to the precipitation of d block elements (and Zn appears to be a particularly significant minor element in these deposits). As a result, phosphate fertilizers may contain enough of the d block micronutrients to satisfy the needs of a crop.

In less industrialized agricultural systems it is still true that micronutrients are added to soil serendipidously. In the agriculture of the developed world however, supplementary materials are added during fertilizer application, where soil tests reveal micronutrient deficiencies. Mortvedt et al. (1999) have produced a useful handbook on the supplements and technologies available.

Ward Chesworth

Bibliography

Brookins, D.G., 1988. *Eh-pH diagrams for geochemistry.* Berlin, New York: Springer, 176 pp.

Chesworth, W., 1991. In Mortvedt et al., eds., *Geochemistry of Micronutrients,* Chapter 1, pp. 1–30.

Chesworth, W., Martinez Cortizas, A., and Garcia-Rodeja, E., 2006. The redox-pH approach to the geochemistry of the Earth's land surface, with application to peatlands. Chapter 8 in Martini, I.P., Martinez Cortizas, A., and Chesworth, W., eds., *Peatlands: Evolution and Records of Environmental and Climate Changes.* New York: Amsterdam, Elsevier. pp. 175–195.

Epstein, E., and Bloom, A.J., 2005. *Mineral Nutrition of Plants: Principles and Perspectives*. New York: Wiley & Sons, 400 pp.

Fraústo da Silva, J.J.R., and Williams, R.J.P., 2001. *The Biological Chemistry of the Elements: the inorganic chemistry of life.* 2nd ed. Oxford; New York: Oxford University Press. 575 pp.

Hem, J.D., 1972. Chemical factors that influence the availability of iron and manganese in aqueous systems. *Geol. Soc. Am. Bull.* **83**: 443–450.

Holland, H.D., and Turekian, K.K., 2004. Treatise on Geochemistry, Vol. 3. *The Crust* (Rudnick, R.L., vol. ed.); Vol. 5. *Surface and Ground water, Weathering, and Soils* (Drever, J.I., vol. ed.); Vol. 8. *Biogeochemistry* (Schlesinger, W.H., vol. ed.). Amsterdam; Boston: Elsevier/Pergamon.

IUPAC, 2005. International Union of Pure and Applied Sciences website at http://www.iupac.org/reports/periodic_table/index.html.

Jenne, E.A., 1968. Controls of Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. In *Trace Inorganics in Water.* Adv. in Chem. Ser. 73. Washington, DC: Am. Chem. Soc., pp. 337–387.

Klein, Cornelis, and Dutrow, Barbara. 2008. *Manual of Mineral Science*: (23rd edition after James D. Dana). Hoboken, N.J.: Wiley. 675 pp.

Krauskopf, Konrad B., and Bird, Dennis K. 1995. *Introduction to geochemistry.* 3rd ed. New York: McGraw-Hill. 647 pp.

Martinez, Carmen E., Mcbride, M.B., Kandianis. Michael T., Duxbury, John M., Yoong, Soh-Joung, and Bleam, William F., 2002. Zinc-Sulfur and Cadmium-Sulfur association in metalliferous peats: evidence from spectroscopy, distribution coefficients, and phytoavailability. *Environmental Science and Technology* **36**: 3683–3689.

Mortvedt, J.J., Cox, F.R., Shuman, L.M., and Welch, R.M., 1991. *Micronutrients in Agriculture*, 2nd edn., Madison, WI: Soil Science Society of America, 760 pp.

Mortvedt, J.J., Murphy, L.S., and Follett, R.H., 1999. *Fertilizer Technology and Application*. Willoughby, OH: Meister Publishing Co., 199 pp.

OUP, 2000. *A Dictionary of Biology*, 4th edn. Oxford: Oxford University Press, 641 pp.

Rössler, H.J., and Langer, H., 1972. *Geochemical Tables*. Amsterdam: Elsevier, 468 pp.

Shannon, R.D., 1976. Revised effective ionic radii in oxides and fluorides. *Acta Crystallogr.***25**925–946.

Snoeyink. V.L., and Jenkins, D., 1980. *Water Chemistry.* New York: Wiley, 463 pp.

Trudinger, P.A., and Swaine, D.J., 1979. *Biogeochemical Cycling of Mineral-forming Elements.* Amsterdam: Elsevier, 612 pp.

Vink, B.W., 1986. Stability relations of malachite and azurite. *Min. Mag.* **50**: 41–47.

Whitehead, D.C., 2000. *Nutrient Elements in Grassland: Soil–Plant–Animal Relationships.* Wallingford, Oxford: CABI Pub., 369 pp.

Wu, J.K., and Hsu, Y.S., 1986. Electrochemical corrosion of zinc in sodium chlorite. *Journal of Materials Science.* **21**: 3475–3478.

Cross-references

Geochemistry in Soil Science
Macronutrients
Periodic Table in Soil Science
Plant Nutrients
Trace Elements

MICROSTRUCTURE, ENGINEERING ASPECTS

The structure of fine soils is mainly studied using the techniques of electron and optical microscopy; engineers, geologists and pedologists have all contributed. Various methods were reviewed by Smart and Tovey (1982) and Bisdom et al. (1988). Leng et al. (1993) summarized methods of analyzing electron micrographs. Optical micrographs are often reduced to black-and-white before analysis. Polarizing microphotometry is used to measure anisotropy; the values quoted here are for anisotropy index, A:

$$A = \frac{\mathrm{MAX} - \mathrm{MIN}}{\mathrm{MAX} + \mathrm{MIN}} \qquad (1)$$

where MAX and MIN are the maximum and minimum intensities of light transmitted by a thin section, which is rotated between crossed polarizers. (Jarrett, 1972, found that photometric analyses gave measurements which depended upon the impregnant used in preparing samples.) Smart et al. (1992) combine image analysis with polarizing microscopy. Computerized tomography is also a useful interpretive tool.

Computer simulations of the internal mechanics of large groups of particles are also made (e.g., Cundall and Strack, 1979). Before discussing the effect of various modes of deformation on soil structure, the nature of soil particles and the characteristics of pores will be considered.

Particles

Beutelspacher and van der Marel (1968) and Gard (1971) reviewed the electron microscopy of clay particles. Even though some minerals have characteristic shapes, there is no one-to-one relationship between morphology and mineralogy. Table M9 gives the most important of the engineers' concepts.

Because particles are often "dispersed" and "cleaned" for microscopy, there are doubts concerning their true size and shape. For example, Weir (1960) demonstrated the breakdown of smectite particles in water, and Tovey and Wong (1973) the breakdown of kaolinite particles during oven drying. Crystal structure may be studied by electron diffraction (Gard, 1971), with which Mering et al. (in Gard, 1971) compared Camp-Berteaux and Wyoming bentonites; in water, one forms particles 100 Å in diameter, the other thin extensive flakes. These findings suggest that reclamation, drainage, wetting cycles, and freezing may induce physical changes in some clay particles.

Pictures of dispersed and cleaned particles and early hypothetical sketches of soil structure inferred that clay particles behaved like slippery rigid pennies (the phrase is due to A. W. Bishop). While there is some support for this view for dispersed kaolin (and illite perhaps), it is not general, as evidenced by Weir's (1960) pictures of folded smectite plates. Further, the springiness of large mica plates has long been recognized.

Table M9 Simplified classification of small soil particles

Concept	Example
All diameters approximately equal	Fine quartz
Rigid platy particles with small colloidal effect	Kaolinite
Rigid platy particles with large colloidal effect	Illite
Flexible platy particles with large colloidal effect	Montmorillonite
Laths	Attapulgite
Tubes	Halloysite
Minute particles	Ferrihydrite

Contrast effects, e.g., Moire fringes, may indicate crystal defects, etc. (Gard, 1971). High-voltage electron microscopes are useful for studying these effects. Wet or vacuum decoration may locate electrostatic charges within crystals. Care is needed because (1) microtomy or rough treatment may cause artifacts, (2) the electron beam may break particles down causing artifacts, (3) regular features may be growth steps, and (4) irregular decoration features occur if the decorating material condenses at positions which have no particular significance. These methods have shown that under suitable circumstances, clay plates have positive edges, the faces generally being negative. The methods may also show the extent of local concentrations of negative charges; but such concentrations may be insignificant in chemical and mechanical phenomena, because they seem to be small and free to move within the crystal.

Another problem in determining the true nature of clay particles is that of differentiating them from stacks, packets, and quasi-crystals. Stacks are groups of plates cemented together tightly, often by a true mineral-to-mineral bond (Figure M21a). They are found as growth features in kaolin. Packets are small groups of plates arranged face-to-face with water between them (Figure M21c). In micrographs, packets are indistinguishable from stacks except that the arrangement is irregular in packets. Quasicrystals are expanded smectite particles; the individual layers of smectite 10 or 20 or 30 Å thick are separable by water layers. It is debatable whether a quasicrystal is a particle or whether each of the thin smectite layers should itself be treated as a particle. The identification is complicated when the amount of water available for expansion is limited so that only part of the quasicrystal is expanded. It thus seems preferable to avoid a rigid definition of "a particle" but to allow it to include aggregates and crumbs. Although a stack is clearly a particle, severe mechanical disturbances can reduce it to its component plates, in which case one particle is turned into several.

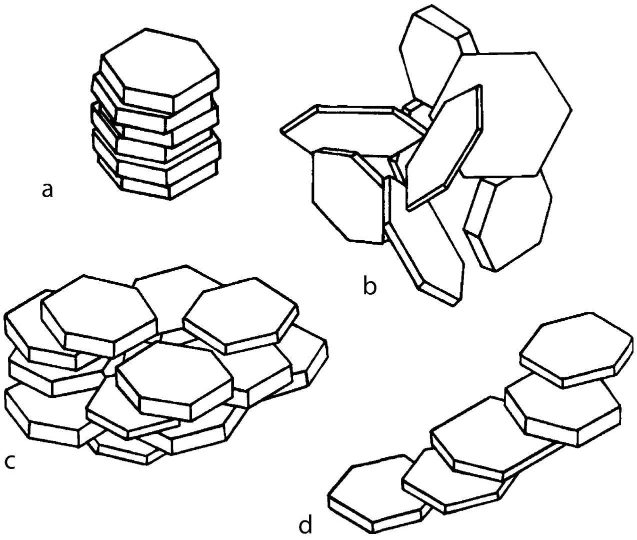


Figure M21 (**a**) Stack; (**b**) single-plate card-house; (**c**) packet, a small domain; (**d**) stepped cluster, tile-like.

Pores

Pores are important elements of structure; they weaken soil, store water, and form the transport pathways through the soil. Pores are usually classified by type following either Brewer (1964) or Bullock et al. (1985). The least unsatisfactory classification by size is probably that of Bullock et al. (1985), which uses the 1–2–5-system (see *Soil pores*); but engineers may prefer to keep to the 2–6-system which they use for particles (Smart, 1975). It seems to be generally agreed that the sizes of pores should be measured at their minimum diameters. A practical expedient is to use moisture desorption to calculate the equivalent cylindrical diameter, d (cm), from:

$$hd = 0.3 \tag{2}$$

where h (cm) is the moisture tension. This corresponds to a surface tension of 73.5 dyne cm^{-1} at 15 °C and is accurate within ±3% for ±15 °C. Gas permeability is often used instead of pore size distribution to monitor changes during cultivation and compaction.

Pore characteristics may be studied experimentally by image analysis. Usually a view of a planar surface is reduced to black-and-white solid-and-pore. Some problems can be solved by using only horizontal sections; others require only a few vertical sections. Ringrose-Voase (1990) gives a good introduction to the stereological approach to a three-dimensional analysis; Glasbey et al. (1991) demonstrate the alternative approach of modeling. Bartoli et al. (1991) and Young and Crawford (1991) give intelligible and useful accounts of fractals. Bhatia and Soliman (in Bennett et al., 1991) use Oda's method to analyze local void ratios. A corollary to Nyquist's Theorem is that pores less than 2 pixels wide cannot be found reliably. Leng et al. (1993) evade this by estimating the porosity of individual pixels in gray back-scattered scanning electron micrographs.

Table M10 gives a preliminary interpretation of pore size data.

Concepts of clay microstructure

The terminology used here follows Smart and Tovey (1981), but see also Collins and McGown (1974) and Grabowska-Olszewska et al. (1984). It is convenient to start by defining single-grain structure as a structure formed by clean silt or sand particles. This leads to Collins' subdivision:

- granular arrangement: relatively large occurrence of single-grain structure;
- clay arrangement: relatively large occurrence entirely of clay;
- clay-granular arrangement: relatively large occurrence of clay mixed with silt or sand particles.

Table M10 Notable pore sizes, approximate

Width	Accessible to	Visible by	Drainage	pF
60 mm	Moles			
2 mm	Worms			
200 μm	Silt	Eye		
60 μm			Free draining	1.7
30 μm			Field capacity	2.0
6 μm	Root hairs	Macrophotograph		
200 nm		Microscope		
190 nm			Wilting point	4.2
200 pm	Water			

It would be convenient to distinguish between:

- cement: material, which bonds particles together;
- mortar: material, which fills voids without bonding to the particles.

In practice, it is often only possible to distinguish:

- bridge: long thin connection of cement, mortar, or clay between (large) particles;
- buttress: a similar short stout connection;
- cutan: coating around or beside another feature;
- plasma: space-filling material.

However, diagnosis may be aided by Kubiena's subdivision:

- porphyropectic structure: larger particles show clean faces in fracture surfaces, presumably uncemented;
- porphyropeptic structure: larger particles show unclean faces in fracture surfaces, presumably cemented.

Clay particles tend to form groups as follows:

- domain: group of plates parallel to a surface, which may be curved Figures M21c and M22, subdivided into:
  - overlap domain: the plates are separate particles;
  - intergrown domain: the crystal lattices are continuous from plate to plate, perhaps imperfectly;
- bundle: group of fibers, rods or tubes; subdivided principally into parallel, sub-parallel, and radiating bundles; radiating bundles are subdivided as sparsely filled, close packed (i.e., more densely filled), or spherulite;
- spherulite: completely filled radiating bundle;
- globular cluster: roughly spherical cluster of particles; subdivided principally into types with radial or circumferential plates;
- stepped cluster: a sheet of plates with face-to-face contacts with a relatively small overlap between adjacent plates; subdivided according as successive plates are joined randomly to either face of the last plate or to the same face like the tiles on a roof (Figure M21d);
- random cluster: group of particles, which has a random or almost random internal structure, and possibly an anisotropic external shape; subdivided principally into loose and dense types;
- loose floc: the term appears to mean a loose random cluster formed in suspension by flocculation and partly bounded by large voids.

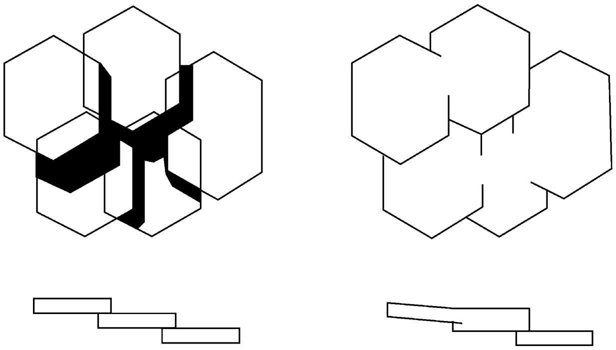


Figure M22 Details of domains. *Left:* overlap domain; shadows would be seen in replicas. *Right:* intergrown domain; the plates seem to merge together.

The three types of clusters are quite different, the concepts having arisen historically.

The groups of clay particles then tend to form structures as follows. These terms have also arisen historically, and there is some overlap between some of the concepts.

- random structure: particles and voids arranged randomly; often close packed, a reasonable proportion of face-to-face plates being permitted within this class;
- single-plate card-house structure: plates arranged singly with angular or perpendicular edge-to-face contacts presumably governed by some definite phenomena (Figure M21b); subdivided principally into flocculated, cemented, and authigenic versions;
- bookhouse structure: small packets arranged with angular or perpendicular edge-to-face contacts;
- lamellar structure: apparently a synonym for bookhouse structure;
- salt-flocculated structure: strictly bookhouse structure, which has been formed by salt-flocculation; often applied somewhat thoughtlessly without evidence;
- Brownian structure: relatively large plates lying horizontally in a matrix of smaller particles, which themselves form any relatively unoriented and relatively open type of structure;
- honeycomb structure: particles grouped in sheets or chains, which are themselves grouped into a loose inter-connecting framework with relatively large voids between the sheets;
- flocculent structure: particles grouped in loose flocs, which are themselves grouped loosely, i.e., there are small intra-floc voids and larger inter-floc voids;
- Pusch's structure: clusters and loose flocs all grouped loosely with relatively large voids between these units;
- cluster structure: clusters, often with definite inter-cluster voids; subdivided according as anisotropy, etc., is evident;
- turbostratic structure: large domains, sometimes curved, inter-domain boundaries may be diffuse, few or no large voids;
- discrete domain structure: small domains, sometimes too small to be curved, well-defined domain boundaries, definite inter-domain voids;
- cpo-structure or structure with complete preferred orientation: plates, fibers, etc., all parallel to a single direction; subdivided according as discrete domains or larger voids or neither are present;
- tactoid structure: the original idea was of a very large quasi-crystal with most of the flakes say 1 nm apart and with a few isolated swollen voids within it;
- dispersed structure: strictly any structure in which mutual repulsions between the particles control the structure; often applied somewhat thoughtlessly to turbostratic or cpo-structures, either of which could be intergrown or cemented;
- herring-bone structure: plates, etc., oriented to give a zigzag pattern.

Figure M23 illustrates several of these structures as they might occur in a two dimensional view.

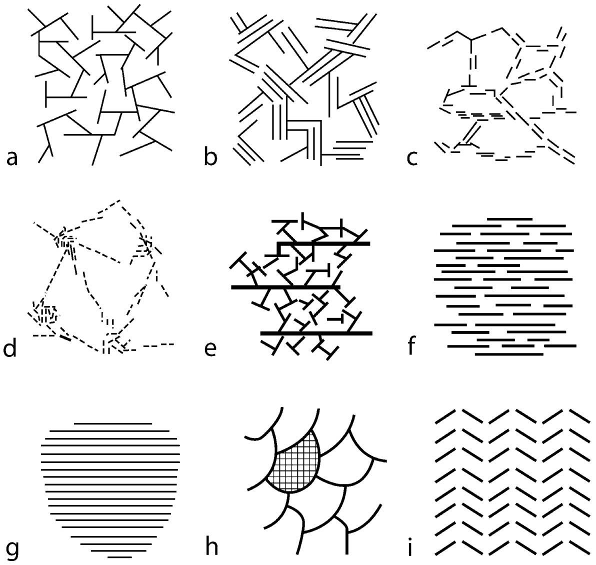


Figure M23 Types of structures as seen in two dimensions; (**a**) card-house structure, two-dimensional analog, each stroke represents a platy particle; (**b**) book-house structure, analog; (**c**) flocculent structure, cross-section; (**d**) Pusch's structure, cross-section; (**e**) Brownian structure, analog; (**f**) domain, cross-section; (**f**) packet, cross-section; (**h**) kidney structure, sketch; (**i**) Herringbone structure, cross-section.

Natural clay microstructure

At one time, hypotheses involving single-plate card-house structure were common; but this type of structure appears to be rare, and some of the observations are of material formed in situ, whereas the hypotheses concerned sediments or suspensions. Smart (1975) shows an example of single-plate card-house structure that was tentatively attributed to microbiological activity. This suggests that in cultivated soils with high bulk densities, crumbs are formed as follows: (1) relatively large pores are first formed by cultivation, etc.; (2) bacteria then rearrange the particles near the surfaces of these pores one by one to form open structures stabilized by soft organic matter; and (3) this organic matter condenses, drawing the particles together and forming stronger bonds.

Book-house structure has been frequently observed. Flocculent structures made of long loose flocs or stepped clusters are also fairly common; sometimes random clusters have been mixed among the flocs, forming Pusch's structure, or the clusters have occurred alone, cluster structure. Brownian structure, which is fairly rare, would result if larger particles were sedimented quickly with horizontal attitude while smaller particles sank slowly with random orientation, in which case the larger particles may collect flocs of smaller particles before reaching the bottom.

Generally, these open structures occur either (1) in an uncemented form as unconsolidated muds which would change on reclamation, (2) as small occurrences within clay-granular arrangements, or (3) as cemented sediments, in which case one obtains a quick clay (see *Volume on Sediments and Sedimentary Rocks*).

Domains occur under natural conditions and in laboratory studies. Overlap domains tend to occur (1) by weathering of a layered parent material, (2) by slips under a one-dimensional compressive stress, (3) by re-orientation by movement within failure zones, or (4) as cutans by precipitation or deposition from flowing water within pores. Dispersing conditions favor overlap domains. Intergrown domains may occur in other cutans or inside peds. The concept of an intergrown domain was suggested by electron micrographs of shales; and presumably more severe conditions are required for their formation than for overlap domains. Perhaps the best method of diagnosis today would be to examine ion-beam thinned ultra-thin sections in a transmission electron microscope.

Close packed random structures have also been observed. These are denser than card- and bookhouse structures. If card-house structures resulted from stable edge-to-face contacts, then the angles of contact would be distributed about a certain value, and the structure would be systematic not random. Close-packed random structures, card-house structures, and probably book-house structures are expected to extinguish between crossed polarizers.

Consolidation

Consolidation, in the engineering sense, follows from a decrease in volume of saturated clay as water is expelled by pressure. In laboratories, the sample is often confined laterally, and the pressure doubled daily. There are three models:

1. Mechanical: the particles slip, bend, or break (very thin layers of adsorbed water may separate the particles).
2. Physicochemical: double-layer effects dominate.
3. Mineralogical: strain is accommodated by migratory recrystallization.

The mineralogical model perhaps requires a ‘geological’ setting. Agreement between some observations and Gouy-Chapman theory support the physicochemical model (Warkentin et al., 1957); but this is not general. Olson and Mesri (1970) suggested the following discriminatory tests:

1. If the pore fluid is water, changes in either the type or concentration of electrolyte will affect physicochemical but not mechanical properties.
2. Replacement of the pore water by a fluid in which double layers cannot develop would result in substantial reductions in void ratio if physicochemical effects govern, whereas such a substitution will usually increase surface friction and reduce compressibility if mechanical effects control.

They concluded that mechanical effects dominate in sand, muscovite, and kaolinite, and at high pressures in illite, whereas physicochemical effects dominate in smectite and at low pressures and during rebound in illite.

Slipping under pressure leads to anisotropic structures, and these in turn lead to anisotropic properties. For example, permeability may vary with orientation, since the morphology of interdomain voids in the vertical section may differ from their morphology in a horizontal section.

Reorientation of clay plates has been measured using optical microphotometry, X-ray texture diffraction, and electron microscopy. For example, McConnachie (1974) found that in flocculated kaolin at high water contents, considerable reorientation occurred below 15 kPa (0.15 kg cm^{-2}) approximately. Thereafter, there was less, if any, reorientation up to 105 kPa (1 000 kg cm^{-2}), at which pressure the preferred orientation was still imperfect. The observations did not continue that far, but there was a suggestion that the curves would converge on $A = 0$ and void ratio $= 0.1$ at pressure $= 6 \times 106$ Pa (60 000 kg cm^{-2}). At low pressures, any natural bonding prevents both reorientation and consolidation (Jarrett, 1972). On the other hand, Brindley (1953) was unable to find preferred orientation in compressed halloysite.

Figure M24 gives an impression of the size of domains in a consolidated kaolin. There was triple anisotropy: domain lengths are larger than breadths; horizontal domains are larger than vertical; and there was also an overall preferred horizontal orientation of the particles. The domains were irregular in shape and there were no interdomain voids. In another kaolin, McConnachie (1974) found that domain size decreased little with pressure. At 400 kPa, his domains were approximately 1 μm × 0.4 μm on average. McConnachie’s domains were discrete, smaller, and tighter than in the first kaolin, and there were interdomain voids between them. These differences were probably due to physicochemical factors. In contrast to this work on kaolin, Blackmore and Miller (1961), in a study of calcium montmorillonite, using X-ray analysis, inferred from line broadening that the number of single clay sheets per tactoid (quasicrystal, domain) increased linearly with log pressure. It is not clear whether sheets were added one by one or whether quasicrystals coalesced.

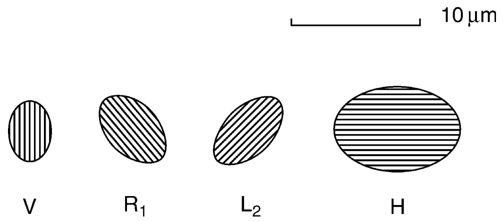


Figure M24 Average domains. Kaolin, consolidated to 400 kPa (4 kg cm^{-2}). Major and minor diameters of these ellipses equal the average lengths and breadths of nearly vertical, inclined, and horizontal domains, *V*, *R* and *L*, and *H*, respectively (based on Smart, 1966b, Figure 3).

McConnachie (1974) also mapped the inter-domain voids at higher pressures. These were irregular in outline, anisotropic in shape, anisiotropic in orientation, and decreased in size with pressure. The geometric mean breadth, as seen in two dimensions in ultrathin sections, fell to 0.2 μm at 2 000 kPa (300 lb in^{-2}). These observations suggest that micropores accessible to bacteria may survive the stresses of cultivation but that these might be anaerobic for much of the time. Figure M25 shows the intradomain void ratio. It suggests that at high pressures the domains are themselves compressed.

Secondary consolidation

During consolidation, the expulsion of water is usually accompanied by an increase of pore water pressure. However, in some soils, the volume continues to decrease after the excess pore water pressure has disappeared. This continued consolidation is called secondary consolidation; it may progress at a diminishing, steady, or increasing rate, and it is similar to or identical with creep or viscous flow. Three explanations have been offered:

1. When the particles slip into fresh positions, they are at first help apart by their adsorbed water layers, which are slowly squeezed out.
2. Secondary consolidation is caused by recrystallization of the particles themselves.
3. The initial structure consists of groups of particles with large voids between. During primary consolidation, the groups slip, setting up pore water pressures throughout all the voids; but, during secondary consolidation, there is yielding only within the groups, any intragroup pore water pressure increase being inaccessible to measuring instruments.

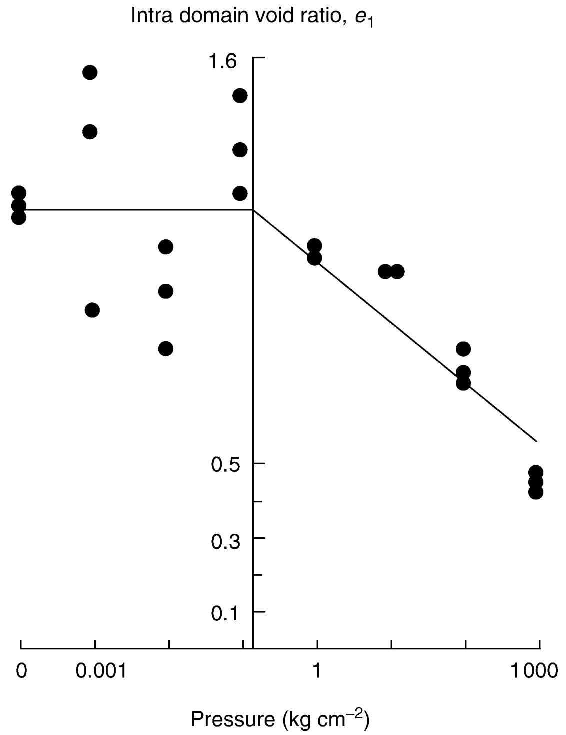


Figure M25 Intradomain void ratio during consolidation of kaolin. The term e_1 is the intradomain void ratio, i.e., the volume of voids within domains divided by the volume of solids, calculated from total void ratio and domain packing density (data of McConnachie, 1974).

Creep, whether involving change of size or shape or both, may lead to a deterioration of structure in wet, heavy subsoils. Natural structures are unlikely to be affected unless the conditions under which they were formed are altered; but mole drains and the structures formed by subsoilers would be liable to this form of deterioration.

Reclamation

Reclamation may be thought of as the opposite of consolidation. For example, Magaldi (1985) showed that subsoils became more isotropic as they aged: A fell from 0.2 for soils reclaimed this century to 0.07 for those reclaimed three centuries ago. There is also a seasonal variation of structure (e.g., Mackie-Dawson, 1989).

Failure

Complete preferred orientation of clay particles occurs within slickensided failure zones. Depending on the stress and strain conditions, these occur singly, singly with complementary zones at approximately 45° + $\phi/2$, in oblique sets at this same orientation, or possibly as omnisepic fabric (ϕ = angle of internal friction). There may be water migration either into or out of the failure zone. Within failure zones, the particles seem to have been separated from each other and to be moving singly, i.e., there has been mechanical dispersion. Comminution of the particles has been postulated, but it is difficult to demonstrate in soils. Recrystallization has been observed in wear surfaces of alumina, snow-rolls have been found under avalanches, and a curved drag zone is often seen alongside the main failure zone in rocks; but observations of similar features in soils are almost non-existent. In dense sands, the failure zones are dilatent; and loose sands tend to collapse. Mixed soils combine these effects. Vermeer (1990) has shown theoretically that the orientation of shear zones in sand is not unique but unstable within a range which is typically from 45° + $\phi/2$ to about 3° lower. This could conceivably be the case in clay too.

Shear failures are damaging to the structure of the soil; so implements should be designed and used to produce tensile failures either directly or induced by dilation, or to minimize shear strains. For example, digger ploughs probably induce tensile failures in dry soils; but, when very wet soil must be ploughed, there is no hope of inducing tensile failure. Helical moldboards were used to invert the furrow slice without inducing shear strain except near the share. Similarly, although Suffolk coulters and triple-disk coulters work well for seed drills under suitable conditions, single disk coulters and arrow coulters could be used under wetter conditions with less risk of smearing the bottom of the seed furrow.

Deformation

Here, deformation means a change of shape less drastic than failure. During deformation, dense sands tend to dilate, and loose sands to contract; clays also dilate or contract according to circumstances. The void ratio separating these two states is known as the critical void ratio. Various apparatus and procedures are used for shear testing. Almost all apply one stress to deform the soil while using other stresses to confine it. When the confining stress is itself too low to break the initial structure of the soil, saturated clays dilate when deformed under drained conditions, whereas they contract under much higher confining stresses. In unsaturated soils, the moisture tension will tend to act as a confining stress, and water scarcity may result in the adsorbed layers becoming more ordered and thus increase the rigidity and tendency to dilate; but shrinkage cracks would weaken the soil. Presumably, dispersing conditions, whether due to changes in pH or ionic composition or to dispersing agents, will tend to permit clay particles to slip individually, thereby facilitating contraction; whereas flocculating conditions and cementation would tend to cause the particles to move in groups and cause dilation. There may also be an intermediate state in which the groups retain their identity but fail to bond to each other, so that the soil behaves as if dispersed.

In a brief study of a dispersed kaolin, domains increased in size during shearing (cf. Smart, 1966b). In a flocculated kaolin, both the length and breadth of domains increased by 50% during pre-peak deformation and decreased with further shear, suggesting perhaps that some of the domains had been pressed together under stress (Smart and Dickson, 1979). The hypothesis that particles would gradually turn into the direction of the failure plane was eliminated in this study: the direction of preferred orientation remained constant throughout; and the failure plane, when it did occur, cut straight through the preferred orientation. This and other studies led to the hypothesis that deformation increases the anisotropy of isotropic clays and decreases that of strongly anisotropic clays; the critical anisotropy index would presumably vary from clay to clay.

Figure M23i illustrates a herringbone structure or kinking which may occur under some conditions.

Kirby (1991) used measurements of air permeability to extend the critical state theory to soils with large pores.

Compaction

This section discusses compaction of unsaturated soils by various combinations of compressive and shearing stresses applied for brief periods, e.g., by wheels or in laboratory tests, and resulting in increased dry density, and usually increased strength and decreased permeability to water, air, and root penetration.

The response of a soil to compaction depends on both the method of compaction and the moisture content. All other things being equal, the amount of compaction is greatest at an "optimum moisture content"; the terminology comes from engineers. In general, soils compacted "wet-of-optimum" are more liable to either swell or to collapse when wetted, having higher permeability, a lower air entry value, greater ultimate strength at the molding moisture content, and greater rigidity both at the molding moisture content and when swollen. Molding moisture content, however, seems to have little effect on strength when swollen; judging from tests on foundry sands, dry strength increases with the molding moisture content. There are reports of failure by piping erosion of earth dams that had been compacted dry-of-optimum.

With wet-of-optimum compaction, there is generally an increase in local preferred orientation of clay plates, sometimes an increase in overall preferred orientation, sometimes the formation of short failure planes, and generally a uniform large-scale structure. With dry-of-optimum compaction, crumbs tend to persist, and relatively large intercrumb pores are formed. Because there are no large intercrumb pores wet-of-optimum, it follows that the intracrumb pores formed by compaction dry-of-optimum are smaller than the pores in a similar sample compacted wet-of-optimum to the same bulk density. Some moderations to these generalizations are to be expected, for example, in strongly flocculated soils or highly plastic soils that resist compaction. Table M11 classifies soil on the basis of their behavior during compaction.

In general, it seems that the effect of the method of compaction increases in the following order: static, vibratory, impact, kneading compaction, the differences being more pronounced wet-of-optimum. Thus, dynamic and shearing effects are generally more severe; but machines traveling faster usually produce less compaction, presumably because the stresses, which they produce, act for shorter times.

Several phenomena may be involved in resisting compaction. It seems that wet-of-optimum, the compacting stresses are applied for too brief a time to expel appreciable quantities of water, so that the volume may be reduced only to the sum of the volumes of the solids and the water, a little air being trapped as isolated bubbles. Dry-of-optimum, a high pore water tension will tend to strengthen the crumbs. Further, the small amount of water will have a higher electrolyte concentration, assuming that the total quantity of electrolyte present depends only on the amount of solids present, so that the double layers will contract and may become ordered, and tendencies to flocculate will increase. Further, interparticle contacts may also form and strengthen the crumbs. During compaction wet-of-optimum, the crumbs are squeezed together like plasticine; whereas dry-of-optimum, the crumbs probably break and slip to fill the largest voids, but relatively large voids remain between the pieces thus explaining the good aeration and permeability and permitting root penetration. These voids also explain the piping failure of dams; with the velocity of water flow through a large void high, the probability of eroding particles from the side of the void will also be high.

Similar internal erosion may also occur in cultivated soils and in backfills over underdrains. Further, when crumbs are formed by fracturing, either by compaction dry-of-optimum or by cultivation, many could be left partly fractured, so that particles are more likely to be eroded from them, or the crumbs are more likely to collapse entirely when wetted. During compaction wet-of-optimum, soils tend to become mechanically dispersed; the clay particles become separated from each other and slip into domains or shear zones. This partly-sheared structure explains the small rigidity when saturated. When dried, the particles would move closer together face-to-face, and a dense rigid state would result.

Tensile failure

Tensile failure is used by: microscopists preparing fracture surfaces for SEM; pedologists inspecting fields; and farmers cultivating. Surprisingly little attention has been paid to it, but see Grant et al. (1990). Surface roughness is usually measured from a moving average position which depends on the length of the window in which it is defined; Leng et al. (1993) relate this to the range of the semi-variogram. Cultivation and weather must be considered together: for example, C. M. Darlow (pers. comm., 1985) reported that a heavy clay, which dried immediately after cultivation, crumbled down nicely; whereas, soil which was immediately wetted by rain ran together into a gluey mess. This might be explained by cracking followed by shrinkage or wetting up respectively.

Table M11 Soil classification for compaction (modified and adapted from Seed and Chan, 1959)

	Cause		Static		Kneading	
	Dry-of-optimum	Wet-of-optimum	Wet	Dry	Wet	Dry
4	Strong tendency to disperse		D[1]	D	D	D
1	Naturally flocculates	Naturally disperses	F[2]	D	F	D
2	Strong tendency to flocculate		F	F	F	D
3	Very strong tendency to flocculate		F	F	F	F
5	Colloidal actions overborne by other effects					
6	Highly plastic soils which resist compaction and shrink and swell					
7	Thoroughly unsuitable soils					

[1] $D =$ dispersed structure.
[2] $F =$ flocculated structure.

Further topics

This brief review omits reference to early electron microscopy of inorganic clay-chemical interactions, work on organic clay-chemical interactions, natural inorganic dispersants (Søderblom, 1966), soil formation and bacteria, and gassy sediments. Bennett et al. (1991) and the Proceedings of the International Working-Meetings on Soil Micromorphology provide a comprehensive introduction that is still useful.

Peter Smart

Bibliography

Andrawes, K.X., Krishnamurthy, D.N., and Barden, L., 1975. Fabric changes during deformation of oriented clays, *Proc. 1 Baltic Conf. Soil Mech. Found Eng.,* 15–23.

Bartoli, F., Philippy, R., Doirisse, M., Niquet, S., and Dubuit, M., 1991. Structure and self-similarity in silty and sandy soils: the fractal approach. *J. Soil Sci.* **42**: 167–185.

Bennett, R.H., Bryant, W.R., and Hulbert, M.H., eds., 1991. *Microstructure of Fine-Grained Sediments, from Mud to Shale.* New York: Springer, 582 pp.

Beutelspacher, H., and van der Marel, H.W., 1968. *Atlas of Electron Microscopy of Clay Minerals and Their Admixtures – A Picture Atlas.* Amsterdam: Elsevier, 333 pp.

Bisdom, E.B.A., Tessier, D., and Schoute, J.F.T., 1988. Micromorphological techniques in research and teaching (submicroscopy). In Douglas, L.A., ed., *Soil Micromorphology: A Basic and Applied Science.* Amsterdam: Elsevier, pp. 581–603.

Blackmore, A.V., and Miller, R.D., 1961. Tactoid size and osmotic swelling in calcium montmorillonite. *Soil Sci. Soc. Am. Proc.* **25**: 169–173.

Bondarik, G.K., Berexinka, G.M., Tsareve, A.M., and Ierusalimskaya, E.N., 1970. Deformation and texture of water-saturated clay soils. *Proc. 1 Internat. Cong. Eng. Geol.* **1**: 165–179.

Brewer, R., 1964. *Fabric and Mineral Analysis of Soils.* New York: Wiley, 470 pp.

Brindley, G.W., 1953. An X-ray method for studying orientation of micaceous minerals in shales, clays and similar materials. *Min. Mag.* **30**: 71–78.

Bullock, P., Fedoroff, N., Jongerius, A., Stoops, G., and Tursina, T., 1985. *Handbook of Soil Thin Section Description.* Albrighton: Waine Research Publishing.

Collins, K., and McGown, A., 1974. The form and function of microfabric features in a variety of natural soils. *Geotechnique* **24**: 223–254.

Cundall, P.A., and Strack, O.D.L., 1979. A discrete numerical model for granular assemblies. *Geotechnique* **29**: 47–65.

Gard, J.A., ed., 1971. *The Electron-Optical Investigation of Clays.* London: Mineralogical Society, 383 pp.

Glasbey, C.A., Horgan, G.W., and Darbyshire, J.F., 1991. Image analysis and three-dimensional modelling of pores in soil aggregates. *J. Soil Sci.* **42**: 479–486.

Grabowska-Olszewska, B., Osipov, V., and Sokolov, V., 1984. *Atlas of the Microstructure of Clay Soils.* Warsaw: Panstwowe Wydawnictwo Naukowe.

Grant, C.D., Dexter, A.R., and Huang, C., 1990. Roughness of soil fracture surfaces as a measure of soil microstructure. *J. Soil Sci.* **41**: 95–110.

Jarrett, P.M., 1972. The effects of soil structure on the engineering behaviour of a sensitive clay. *Q. J. Eng. Geol.* **5**: 103–110.

Kirby, J.M., 1991. The influence of soil deformation on the permeability to air. *J. Soil Sci.* **42**: 227–235.

Leng, X., Hounslow, M.W., Bai, X., Luo, D., Costa, L.da F., Xue, X., Tovey, N.K., and Smart, P., 1993. Image analysis of clay microstructure. In Frost, J.D., and Wright, J.R., *Digital image processing: techniques and applications in civil engineering.* Proceedings of Engineering Foundation Conference, Hawaii, 1993. New York: American Society of Civil Engineers, pp. 77–86.

Mackie-Dawson, L.A., et al., 1989. Seasonal changes in the structure of clay soils in relation to soil management and crop type. Parts I and II. *J. Soil Sci.* **40**: 269–292.

Magaldi, D., 1985. Degree of soil plasma orientation in relation to age in some hydromorphic soils of Tuscany, Italy. *Proc. 7 Int. Working-Meeting Soil Micromorphology, Paris*. Plaisir: Association Française pour l'Etude du Sol, pp. 605–609.

McConnachie, I., 1974. Fabric changes in consolidated kaolin. *Geotechnique* **24**: 207–222.

McKyes, E., and Yong, R.N., 1971. Three techniques for fabric viewing as applied to shear distortion of a clay. *Clays Clay Min.* **19**: 289–293.

Olson, R.E., and Mesri, G., 1970. Mechanisms controlling compressibility of clays. *Am. Soc. Civil Eng. Proc.* **96SM6**: 1863–1878.

Omer, B.M.A., 1978. A study of a layered clay from Grangemouth. Glasgow Ph.D. Thesis.

Ringrose-Voase, R.J., 1990. One-dimensional image analysis of soil structure. I. Principles. *J. Soil Sci.* **41**: 499–512.

Seed, H.B., and Chan, C.K., 1959. Structure and strength characteristics of compacted clays. *Trans. Am. Soc. Civil Eng.* **126**: 1343–1407.

Shibakova, V.S., 1970. Effect of clay texture upon its shearing strength. *Proc. 1 Int. Cong. Eng. Geol.* **1**: 419–435.

Smart, P., 1966a. Optical microscopy and soil structure. *Nature* **210**: 1400.

Smart, P., 1966b. Particle arrangements in kaolin. *Proc. 15th Natl Conf. Clays Clay Miner.*, 241–254.

Smart, P., 1975. Soil microstructure. *Soil Sci.* **119**: 385–393.

Smart, P., and Dickson, J.W., 1979. Deformation and shear of normally consolidated flocculated kaolin. *Mechanisms of Deformation and Fracture – Proc. Interdisciplinary Conf.* Lule, Oxford: Pergammon, pp. 129–136.

Smart, P., and Tovey, N.K., 1981. *Electron Microscopy of Soils and Sediments: Examples.* Oxford: Oxford University Press.

Smart, P., and Tovey, N.K., 1982. *Electron Microscopy of Soils and Sediments: Techniques.* Oxford: Oxford University Press.

Smart, P., Leng, X., and Bai, X., 1992. Image analysis of soil microstructure, pp. 905–912. In *Géotechnique et Informaqtique - Colloque International, Paris.* Paris: Presses de l'Ecole National des Ponts et Chaussées.

Søderblom, R., 1966. Chemical aspects of quick clay formation. *Eng. Geol.* **1**: 415–431.

Tovey, N.K., and Wong, K.Y., 1973. The preparation of soils and other geological materials for the S.E.M.. *Proc. Int. Symp. Soil Structure, Gothenburg*. Stockholm: Swedish Geotechnical Institute, pp. 59–67.

Vermeer, P.A., 1990. The orientation of shear bands in triaxial tests. *Geotechnique* **40**: 223–236.

Warkentin, B.P., Bolt, G.H., and Miller, R.D., 1957. Swelling pressure of montmorillonite. *Soil Sci. Soc. Am. Proc.* **21**: 495–497.

Weir, A.H., 1960. A study in the relationships between certain physical properties and structure and composition of montmorillonitic group minerals. Ph.D. thesis, Rothamsted, London, 226 pp.

Young, I.M., and Crawford, J.W., 1991. The fractal structure of soil aggregates: its measurement and interpretation. *J. Soil Sci.* **42**: 187–192.

Cross-reference

Soil Engineering
Soil Pores

MIDDEN

A heap of organic debris made up of kitchen waste, food remains, excreta or the like, associated with human habitation. Prehistoric middens may be loosely cemented with calcite and minor amounts of calcium oxalate. Evidence of the use of midden materials to fertilize soil, and of the direct ploughing and planting of middens is found from the Neolithic on (Guttman, 2005).

Bibliography

Guttman, E. B. A. 2005. Midden cultivation in prehistoric Britain: arable crops in gardens. World Archaeology. 37, 224–239.

Cross-reference

Anthrosols

MINERAL ANALYSIS

See the articles *Analytical Geochemistry* and *Analytical Techniques in the Geochemistry* volume of the *Encyclopedia of Earth Sciences Series*.

Cross-references

Chemical Analyses
Micromorphology
Soil Chemistry
Soil Mineralogy

MINERAL SOIL

A soil composed primarily of mineral material, with usually no more than about 20 percent organic matter below the A horizon. This does not preclude an organic rich A, which may be up to 30 cm thick.

MINERALIZATION

In soil science the conversion by microbial action of organic matter into simple inorganic compounds, as part of a nutrient cycle e.g., the conversion of nitrogen-bearing materials into ammonia.

Cross-references

Carbon Sequestration in Soil
Nitrogen Cycle
Phosphorus Cycle
Sulfur Transformations and Fluxes

MINESOIL

An artificial land cover derived from the solid wastes of mining processes, with or without the admixture of natural soil. Now included in the WRB designation Technosols. Many minesoils contain sulfides (especially pyrite), which on oxidation become a source of acid leachates (acid mine drainage, AMD).

Cross-references

Redox-pH Reactions and Diagrams in Soil
Technosols

MIRE

As active peat-forming wetland ecosystems, mires are peatlands, but not all peatlands are mires. Some peat deposits (buried peat layers, perturbed peatlands) currently lack the ability to form peat. The formation and accumulation of the peat (see *Peat*) occurs because plant biomass production exceeds decomposition, on account of the strong limiting conditions for the activity of microorganisms. These include permanent (or quasi-permanent) water-logged conditions with low oxygen availability, low temperatures, high rainfall and a number of physico-chemical properties such as low nutrient content or low pH. The living vegetation of mires is typically composed of mosses, sedges and herbs – plants of relatively slow growth, highly efficient in nutrient uptake from dilute solutions and usually having mechanisms for the preservation of the nutrients. Some investigations suggest that this active nutrient depletion from the waters helps to create a highly acid environment, which prevents colonization by more exigent plant species. Although mire vegetation is certainly specialized to this harsh environment, it is not restricted to it. The typical plants can be found in other environments, but mires are the only ones where the vegetation lives over an exclusively organic substratum.

Thus mires develop where all or a set of the mentioned limiting conditions are met, but hydrology is probably the fundamental factor in the evolution of these wetlands. Depending on the main source for the water mires are classified into ombrotrophic and minerotrophic. The former, also called bogs (Figure M26), receive the water exclusively from precipitation, while the later, called fens (Figure M27) are also fed by run-off and subsuperficial waters. This key difference strongly affects the geochemistry of the waters and the composition of the vegetation. Fens are usually less oligotrophic than bogs and richer in plant diversity.

When a mire begins to form as an ombrotrophic wetland (the process is called paludification) for example as a hilltop bog, it is said to be ombrogenic. If run-off and subsuperficial waters are involved in its hydrology from the very beginning of its formation (in basins or valleys for example) it is said to be minerogenic and the process is called terrestrization. In some cases mires that started as minerogenic systems develop a domed ombrotrophic superficial layer of varying thickness (up to a few meters) due to intense peat accretion, and thus will contain both ombrotrophic and minerotrophic layers. Despite their minerogenic origin they are considered to be bogs – raised bogs, specifically (Figure M28).

Regarding the internal hydrology, there is another fundamental difference between fens and bogs, since the later have a watertable mimicing the shape of the surface of the bog

Figure M26 Bog.

Figure M27 Fen with Histosols.

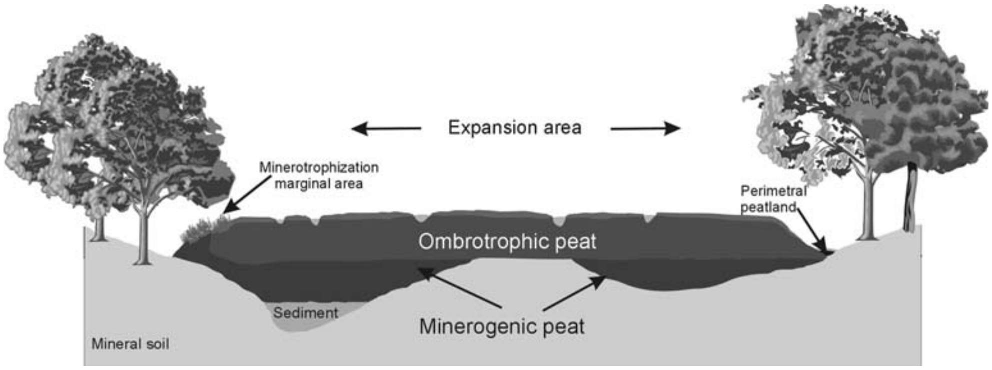


Figure M28 Raised bog.

and thus usually domed. This implies that water will not flow into the bog from the surroundings but will tend to slowly flow outwards.

The water table in fens is usually flat and, since they occupy depressions in the landscape, waters flow into the mire. The water table is also responsible for the presence of two distinct layers in the peat soil. Above the water table and therefore unsaturated for at least some period of the year, is the acrotelm. The acrotelm is an oxic, highly acidic superficial layer of peat, a few tens of centimeters in thickness. Below the water table (and the acrotelm) is the permanently saturated and more extensive part of the peat soil called the catotelm. Hydraulic conductivity is higher in the acrotelm than in the catotelm and most of the mass and volume transformations (decomposition, structural collapse and compaction) take place there. By contrast the accretion of peat and the increase in thickness occurs in the catotelm by the upward movement of the water table. In other words, the hydrology of the mire is crucial in understanding the coupling between the structural evolution and the internal geochemical conditions of this landscape component.

In certain sectors mires expand over vast areas forming a continuum in the landscape. These are blanket mires and represent the highest level in the hierarchy of the mire (Lindsay, 1995), the macrotope, in which the hydrology of each morphological unit is connected to that of neighboring formations. Each identifiable morphological unit (spur, saddle, valleyside or watershed bog) of a macrotope and the individual units (usually the fens) represent the second level: the mesotope. The lowest level is the microtope, the superficial pattern of specialized features that depend on the hydrology and the plant communities of the carpet of living vegetation. Among the later several features have been described, such as low and high ridges, hummocks, haggs, mounds, hollows, permanent pools or erosion gullies.

Mires have a worldwide distribution covering about 3% of the continental land (some 4×10^6 km^2), from arctic to tropical regions, though they are more intensely expressed in oceanic and low temperature areas of the Northern Hemisphere. They also occur in a variety of topographical locations, from mountain summits to slopes and basins. While fens and raised bogs are present in continental and oceanic areas, blanket bogs seem to be restricted to the mountains of Atlantic Europe, from Norway to northwestern Spain, where a high rainfall prevails.

The characteristic soils of mires are Histosols (see *Histosols*), soils having organic material, which in this case refers to the active, superficial layer of the mire. Other soil types associated with the dominant Histosols are Podzols, Umbrisols, Gleysols, Regosols and Leptosols.

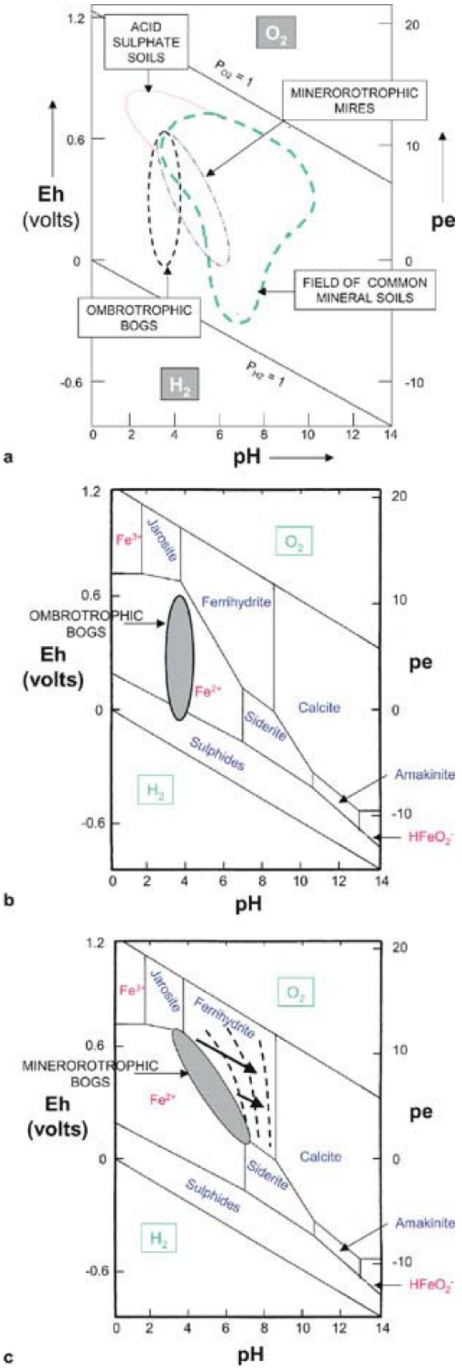


Figure M29 Three Redox-pH diagrams from Chesworth et al. (2006). (**a**) Redox and pH conditions of bogs and fens in comparison to mineral soils. (**b**) fens in the framework of the system Fe–Ca–K–S–CO_2–H_2O. Ombrotrophic bogs are essentially uninfluenced by the geology, geochemistry and groundwater of the surrounding environment. (**c**) Minerotrophic mires showing the influence of local conditions. Ferrous-ferric reactions account for the slope of the main area. The two parallel dark arrows (essentially following Nernst Equation slopes) and the dashed lines indicate the expansion of the minerotrophic field in response to additions of more alkaline waters. In practical terms this evolution to higher pH terminates at the predominance field of calcite (calcite acting as buffer).

Mires play important roles in the environment. One of the aspects that have received considerable attention is their role on the hydrology of catchments. Because the peat deposit stores water, mires were thought to be significant water reservoirs able to diminish run-off during rainfall events and decrease the probability of floods. Recent work suggests that storage is unlikely to contribute to attenuation of winter floods because the whole mire is already saturated with water. However they may delay storm run-off following long dry periods (Bragg, 2002). Nevertheless peat deposits work as effective covers protecting soils and sediments from erosion. On the other hand the high affinity of the organic matter of the peat for cations, means that mires act as environmental filters for many toxic elements and compounds, thereby improving the water quality.

It has been estimated that mires contain 300–500 Pg of carbon, which perhaps represents half of the atmospheric carbon pool (Gorham, 1991; Immirzi et al., 1992). The carbon accumulates at about 0.1 Pg per year, actively sequestering atmospheric CO_2. On the other hand, mires also emit CH_4 to the atmosphere as a result of the slow decomposition of organic matter under the anoxic conditions of the catotelm. Thus mires are both sinks and sources of atmospheric greenhouse gases (CO_2 and CH_4), with the net budget depending on the stage of formation of the mire. This ranges from a negative greenhouse effect in early stages to slightly greenhouse-positive condition for well-developed peat deposits (that is, those having a thick catotelm). If drained, the decomposition of the peat may accelerate, in which case a greater, positive greenhouse effect can be expected.

Mires are important ecosystems in terms of biodiversity. Although not particularly rich in number of species, they are important to natural diversity in terms of the composition of vegetation-communities, the presence of some plant and animal species restricted to the mire-ecosystem, and their role as wetlands for migratory birds.

However, present biodiversity is only a snapshot of the evolution of a dynamic, historical system and mires also contain a detailed record of changes in biodiversity through millennia. The record concerns not only the vegetation and fauna of the mire but also of the surrounding areas, and is revealed through the analysis of pollen and spores. Mires are also archives of other environmental and cultural changes that permit the reconstruction of (for example) climate change, volcanism, soil erosion, and metal pollution of the atmosphere by human activities. This requires the analysis of both biotic (pollen, spores, diatoms, plant and animal remains) and abiotic (major, minor and trace elements, isotopes) signals.

A. Martínez Cortizas, X. Pontevedra Pombal,
and J. C. Nóvoa Muñoz

Bibliography

Bragg, O.M., 2002. Hydrology of peat-forming wetlands in Scotland. *Sci. Total Environ.* **294**: 111–129.

Chesworth, W., Martinez Cortizas, A., and Garcia-Rodeja, E., 2006. The redox-pH approach to the geochemistry of the Earth's land surface, with application to peatlands. Chapter 8 in Martini, I.P., Martinez Cortizas, A., and Chesworth, W., eds., Peatlands: Evolution and Records of Environmental and Climate Changes. New York: Amsterdam, Elsevier. pp. 175–195.

Gorham, E., 1991. Northerns peatlands: role in the carbon cycle and probable responses to climatic warming. *Ecol. Appl.* **2**: 82–195.

Immirzi, C.P., Maltby, E., and Clymo, R.S., 1992. *The Global Status of Peatlands and Their Role in Carbon Cycling. A Report to Friends of* *the Earth.* London: Wetland Ecosystems Research Group, Dept. Geography, Univ. Exeter. Friends of the Earth.

Lindsay, R.A., 1995. *Bogs: The Ecology, Classification and Conservation of Ombrotrophic Mires.* Perth, Sctoland: UK.Scottish Natural Heritage.

Cross-references

Histosols
Peat

MOISTURE REGIMES

The following terms are used in Soil Taxonomy to indicate the degree to which water is naturally available in the soil depth of maximum root proliferation.

- *aquic:* A mostly reducing soil moisture regime nearly free of dissolved oxygen due to saturation by groundwater or its capillary fringe and occurring at periods when the soil temperature at 50 cm below the surface is >5 °C.
- *aridic:* A soil moisture regime that has no water available for plants for more than half the cumulative time that the soil temperature at 50 cm below the surface is >5 °C, and has no period as long as 90 consecutive days when there is water for plants while the soil temperature at 50 cm is continuously >8 °C.
- *perudic:* An udic soil moisture regime in which water moves through the soil in all months when it is not frozen.
- *torric:* A soil moisture regime defined like aridic moisture regime but used in a different category of the U.S. soil taxonomy.
- *udic:* A soil moisture regime that is neither dry for as long as 90 cumulative days nor for as long as 60 consecutive days in the 90 days following the summer solstice at periods when the soil temperature at 50 cm below the surface is above >5 °C.
- *ustic:* A soil moisture regime that is intermediate between the aridic and udic regimes and common in temperate subhumid or semiarid regions, or in tropical and subtropical regions with a monsoon climate. A limited amount of water is available for plants but occurs at times when the soil temperature is optimum for plant growth.
- *xeric:* A soil moisture regime common to Mediterranean climates that have moist cool winters and warm dry summers. A limited amount of water is present but does not occur at optimum periods for plant growth. Irrigation or summerfallow is commonly necessary for crop production.

MONADNOCK

A hill, mountain, or ridge rising above a peneplain, commonly of a more erosion-resistant rock than the material surrounding it. An erosional remnant.

MOR

A generally acid forest humus forming a discrete layer, separate and distinct from the A horizon, and containing little or no mineral matter. By contrast mull grades into the mineral soil via an organic A horizon. Moder is intermediate in characteristics between mor and mull.

MORAINE

Earth-materials transported by ice and left covering a landscape as a mound, ridge, or other feature, when the ice melts. Terminal or end moraines are deposited at the end of a glacier, lateral moraines at its sides. A more regional deposit in the form of an undulating land surface, laid down by a large ice sheet is called a ground moraine.

Cross-reference

Ice Erosion

MORPHOLOGY

The macroscopic form or shape of an object, for example a landform. In soil science, the overall form of a soil resulting from the ensemble of macroscopic elements such as horizonation, texture, structure and so on.

Bibliography

Fanning, Delvin S., and Fanning, Mary Christine. 1989. *Soil: morphology, genesis, and classification.* New York: Wiley. 395 pp.

MOTTLE

A circumscribed patch or blotch within a soil body, differing in color from the soil around it. Commonly caused by local variations in drainage conditions and the redox state of iron in inorganic mineral phases.

Cross-references

Gleysol
Micromorphology
Planosol
Redoximorphic Features
Saprolite, Regolith and Soil
Stagnosol

MUCK

Soil material consisting of highly decayed plant remains, suitable for use as manure, similar to peat but more decayed and with a higher mineral content. A muck soil is one with a predominance of muck horizons over mineral horizons. Loose synonym of Histosols.

Cross-reference

Histosols

MULCH

Loose material used as a top dressing on soil in order to provide insolation, conserve soil moisture or to deter weeds and pests. Organic materials, dead leaves, bark, wood chippings and similar materials are commonly used for the purpose. Less common is the use of volcanic ash, scoria, coarse sand and gravel as mulch in dry-lands agriculture. Figure M30 shows the use of rock mulch (basaltic scoria) in the Canary Islands to conserve soil-moisture for the benefit of a variety of horticultural and vegetable crops (Tejedor et al., 2003a and 2003b). Similar rock mulches are a feature of indigenous agriculture in the southwestern USA (for example, amongst the Anasazi and latterly the Hopi).

Bibliography

Lightfoot, Dale. 1993. The cultural ecology of Puebloan pebble-mulch gardens. *Human Ecology.* **21**: 115–143.

Tejedor, M., Jiménez, C., and Díaz, F., 2003a. Volcanic materials as mulches for water conservation. *Geoderma* **117**: 283–295.

Tejedor, M., Jiménez, C., and Díaz, F., 2003b. Use of volcanic mulch to rehabilitate saline–sodic soils. *Soil Science Society of America Journal* **67**: 1856–1861.

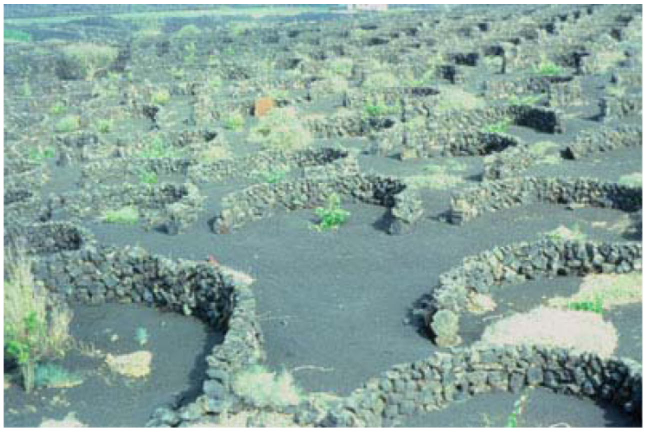


Figure M30 Use of rock mulch to conserve soil-moisture (Canary Islands). Credit: Credit: J. M. Hernández Moreno.

MULL

Humus on the surface of a forest soil mixed with the underlying mineral soil, and gradually transitional into the A horizon. Generally weakly acid to weakly alkaline in reaction.

MUNSELL CHART

A color classification based for any particular color, on three quantifiable characteristics: hue, value (lightness or brightness), and chroma, each of which can be assigned a numerical value on prescribed scales.

Cross-reference

Soil Color

MUSKEG

North American term (Algonquin in origin) for sphagnum peatland. Sphagnum peatland develops in bogs, fens and swamps, and is especially characteristic of wetlands in the Taiga and Tundra.

Cross-references

Biomes and their Soils
Peat
Wetland

N

NEAR-NEUTRAL SOILS

The field of soils with a near neutral reaction is shown in Figure N1. Krumbein and Garrels (1956), in their original development of the idea of the geochemical fence, erected a fence at pH 7. It was not given a mineralogical justification, its significance arising solely from the fact that it divided the redox-pH field at low temperature into acid and alkali divisions. This alone would not tend to buffer a soil at a pH close to neutrality.

In fact, the buffering of soil pH at values close to seven appears to be brought about by two mineralogical features. The first relates to calcite dissolution. Where calcite is present in a weathering system, the pH could rise to as high as 8 or slightly more if the equilibrium between the mineral and water saturated with atmospheric CO_2 were achieved. Soil conditions would then lie along the calcite fence of Figure N2. Although a pH this high may be established in the semi-arid conditions under which calcite precipitates (in Calcisols for example), under humid conditions there is a constant supply of H^+ from atmospheric precipitations, and a steady removal of reaction products, so that a near neutral pH (around 7.5 in many Luvisols for example) is not uncommon.

The second mineralogical feature that may justify a geochemical fence at about pH 7 relates to the smectites. Using an average montmorillonite (Weaver and Pollard, 1973) in which the Cation Exchange Capacity is satisfied by so-called basic cations (mainly Ca and Mg), a fence has been constructed (Chesworth, 1992) on the basis of the reaction:

$$\begin{aligned}&\overset{\text{smectite}}{Si_{3.81}Al_{1.71}Fe_{0.22}Mg_{0.49}O_{10}(OH)_2} + 0.98H^+ + 0.22e^-\\&\quad + 0.33H_2O\\&\rightleftharpoons \overset{\text{kaolinite}}{0.86Al_2Si_2O_5(OH)_4} + \overset{\text{goethite}}{0.22FeOOH} + \overset{\text{quartz}}{2.1SiO_2}\\&\quad + 0.49Mg^{2+}\end{aligned}$$

The fence has a negative slope in Eh-pH space, by virtue of the presence of iron in the system, which therefore brings ferrous/ferric equilibria into play. It is shown in Figure N2 as the smectite fence. It does not mark the absolute appearance or disappearance of smectite in soils, since the total range of conditions under which smectites form is from between about 3.5–4 in Podzols (where beidellite may occur) to 9 of more in alkali soils. In general, conditions on the acid side of the fence result in the exchange positions becoming more H^+ and Al^{3+} saturated, while conditions on the alkali side of the fence result in an increasing dominance of Na^+ on the exchange complex (Figure N3).

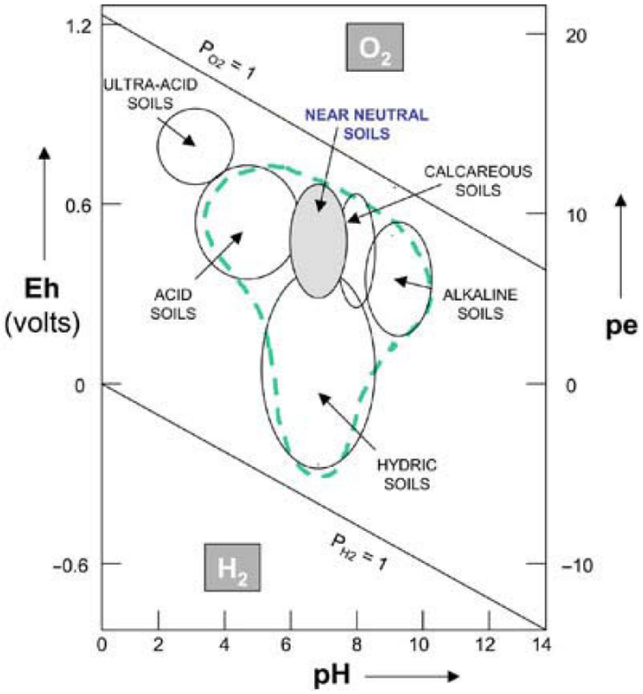


Figure N1 Near neutral soils (*gray shaded area*) defined in terms of the Eh-pH diagram.

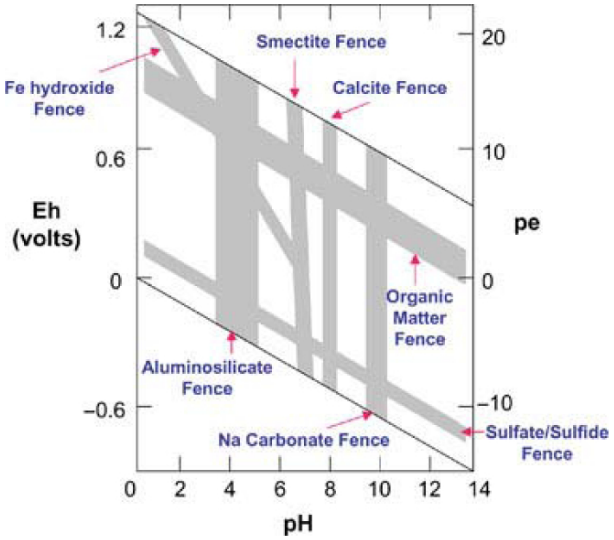


Figure N2 Geochemical fences of significance to the soil-forming environment.

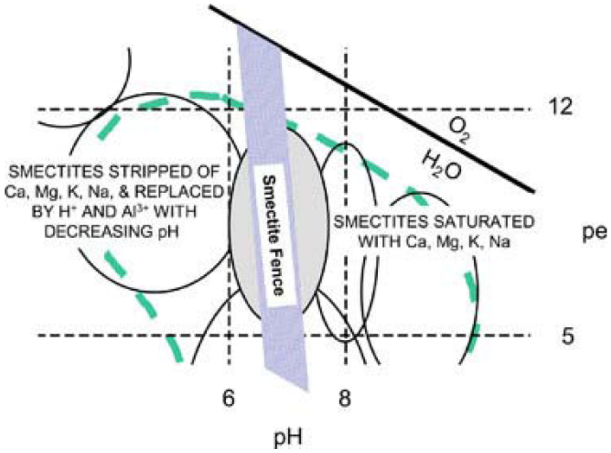


Figure N3 Detail of the near neutral field of Figure N1, in the vicinity of the Smectite Fence of Figure N2. Emphasis is on variations in composition of the exchange complex.

Luvisolic soils may be the largest group to fall in the near neutral category, but any soil with calcite and/or Ca-saturated smectite dominating the clay fraction, occurring in regions with a humid climate where precipitation exceeds evapotranspiration for all or most of the year, can be expected to qualify for inclusion.

A final, non-mineralogical feature may also give rise to pH values close to 7, and that is water saturation. Under waterlogged conditions, where the water is not carrying a high concentration of dissolved materials (organic matter, anions, bicarbonate and carbonate in particular, as well as metallic and other ions) the pH will naturally fall close to 7. Consequently, gleysolic soils will tend to neutrality, unless they are subject to wetting and drying cycles, in which case ferrolysis may lead to the generation of acid conditions.

M. Camps Arbestain, F. Macías, and W. Chesworth

Bibliography

Chesworth, W., 1992. Weathering in soils, Chapter 2. In Martini, and Chesworth, eds., *Weathering, Soils and Paleosols*, New York: Elsevier, pp. 19–40.

Krumbein, W.C., and Garrels, R.M., 1952. Origin and classification of chemical elements in terms of pH and oxidation–reduction potentials. *J. Geol.*, **60**: 1–33.

Martini, I.P., and Chesworth, W., 1992. *Weathering, Soils and paleosols*. New York: Elsevier, 618 pp.

Weaver, C.E., and Pollard, L.D., 1973. *The Chemistry of Clay Minerals*. New York: Elsevier, 213 pp.

NEOFORMATION

As a noun, neoformation means a mineral or inorganic phase, newly formed in a soil during the process of pedogenesis. Includes clay minerals, hydroxides, carbonates and amorphous phases. Also used to mean the process by which new phases are formed. The implication of the term is that the new phases are formed *ab initio* i.e., a new phase does not inherit any part of its structure from a pre-existing mineral.

Bibliography

Erhart, H., 1971. *Itinéraires géochimiques et cycle géologique du silicium: katamorphisme des silicates primaires, genèse et évolution de la silice de néoformation.* Paris: Doin, 217 pp.

Cross-references

Clay Mineral Alteration in Soils
Clay Mineral Formation

NEOLITHIC REVOLUTION

The Neolithic Revolution brought about the greatest material transformation in human history, being directly responsible for the transition of humanity to a civilized form of existence. The label is something of a misnomer as Harris (1971, p. 174) points out: "*Although Neolithic literally means 'new stone age', it is not stone working methods but rather the technology of food production that distinguishes this period from previous phases of human history*".

Specifically, the Neolithic transformation marks a change from a predominantly hunting and gathering style of survival to one based on agriculture. Some object to the word revolution in this context, since the transformation took a few thousand years to complete, but the fact that agriculture makes possible a settled, sedentary society, leading to the invention of "*metallurgy, writing, the city and the state*" (Hobsbaum, 1962), and "*changed Homo sapiens from a rare to an abundant species*" (Harris, 1971), effectively justifies the term. Agriculture opened "*a radically new phase of human history*" and was "*perhaps the most basic of all human revolutions*" (McNeill, 1991).

Soil and the climatic parameters temperature and precipitation, are normally considered to be the primary arbiters of food production. Little can be done about climate, at least on a large scale, so that soil, "*common brown earth, is the limiting factor which shall determine not only the number of people the world* *can contain but also the comfort and therefore the final trend of their civilization*" (East, 1924). Manipulation ("husbandry") of the soil, on an increasingly large scale, begins with the Neolithic Revolution. It was not the first technology available to humans for modifying the planetary surface. That was fire, first controlled by *Homo erectus* (Stearns, 2001), possibly as early as 1.8 million years ago, though evidence for this (from Kenya) is controversial. Australia for example, appears to have been transformed by burning soon after *Homo sapiens* arrived there some 40 000 years ago, and long before agriculture was invented (Head, 2000).

On the scale of the landscape, weathering and the erosional cycle are the natural maintenance systems of soil fertility that the early farmers depended upon. The highland arc that stretches from southern Turkey to the Zagros Mountains of Iran provides some of the earliest archeological sites for agriculture, for example at Çatal Hüyük (Hodder, 2004). Not only does the soil tend to be young (since mountain slopes are prone to erosion) and fertile (because of the exposure of fresh parent material), but also orographically controlled rainfall is generally adequate to sustain a crop. After considerable trial and error, farming was introduced into the valleys of the Tigris and Euphrates, where extensive areas of soil with a high inherent fertility (river alluvium derived from the erosional material washed down from the mountains) occur. The rivers themselves delivered water more reliably than the serendipity of rainfall could, and the resulting surplus of food became large enough to sustain a non-farming population and thus to allow the invention of those cultures that we call civilized. Agriculture is the prerequisite of civilization. Civilization cannot arise "*on the go*" (Bronowski, 1974), nomadic societies are too busy "*carrying around their spears and their babies*" (Diamond, 1997).

The earliest civilizations in the old world, in the valleys of the Tigris and Euphrates, the Nile, Indus and Huang Ho, are all based on large river systems, draining an area where freshly exposed and lightly weathered geological materials provide nutrient-rich sediment for distribution lower down the valley, where they weather predominantly to fertile Fluvisols. Because of this association with rivers, they are often referred to as "hydraulic civilizations". The earliest was in Sumer or Sumeria, at the head of the Persian Gulf in what is now Iraq. Sumeria is considered to be the site of the fabled Garden of Eden. Eden is believed to be cognate with the Sumerian word Edin that referred to the wild uncultivated grassland of southern Mesopotamia. In other words the first civilization on Earth took over a grassland habitat, a pattern that continued throughout human history so that the loessial soils of the major grassland regions such as the prairies of North America and the steppe of Eurasia, are now largely taken over for agricultural purposes. The agricultural surplus in Sumer, allowed the support of full time specialists, specialization led to a stratification of society, the rise of urban and administrative centers, as well as trade with neighboring peoples for raw materials that Sumer lacked (Crawford, 2004, p. 14).

The darker consequences of the Neolithic Revolution must also be acknowledged. Societies based on farming "*tend to breathe out nastier germs, to own better weapons and armor, to own more powerful technology in general, and to live under centralized governments with literate elites better able to wage wars of conquest*" (Diamond, 1997). In addition, it must be recognized that agriculture as practiced from the start, has never been sustainable. It has always resulted in a drawdown of the natural capital of the Earth (Jackson, 2004) to the degree that human beings have become a dominating geological force on the planetary surface, and the long-term persistence of human civilization has become problematical. In the words of Angus Martin (1975): "*How many millennia of deforestation, dust storms and soil erosion has it taken for us to realize that our agricultural methodology has had serious flaws in it from the start.*"

Ward Chesworth

Bibliography

Bronowski, J., 1974. *The Ascent of Man.* Boston: Little, Brown, 448 pp.

Crawford, H.E.W., 2004. *Sumer and the Sumerians.* Cambridge, UK: Cambridge University Press, 252 pp.

Diamond, J., 1997. *Guns, Germs, and Steel: The Fates of Human Societies.* New York: W.W. Norton & Co., 480 pp.

East, W.G., 1924. *The Geography behind History.* London: Nelson, 203 pp.

Harris, M., 1971. *Culture, Man, and Nature; An Introduction to General Anthropology.* New York: Crowell, 660 pp.

Head, L., 2000. *Second Nature. The History and Implications of Australia as Aboriginal Landscape.* New York: Syracuse University Press, 272 pp.

Hobsbawm, E.J., 1996. *The Age of Revolution 1789–1848.* New York: Vintage Books, 356 pp.

Hodder, I., 2004. Women and men at Çatalhöyük. *Sci. Am.*, **290**: 77–83.

Jackson, W., 2004. Agriculture, the primary environmental challenge of the 21st century. In Chesworth, W., Moss, M., and Thomas, V., eds., *The Human Ecological Footprint.* Guelph, ON: University of Guelph, pp. 85–99.

Martin, A., 1975. *The Last Generation: The End of Survival?* Glasgow: Fontana, 188 pp.

McNeill, W.H., 1991. *The Rise of the West: A History of the Human Community: With a Retrospective Essay.* Chicago: University of Chicago Press, 828 pp.

Stearns, P.N., 2001. *The Encyclopedia of World History: Ancient, Medieval, and Modern,* 6th edn., Boston: Houghton Mifflin Company, 1243 pp.

NET PRIMARY PRODUCTIVITY

NPP: the net flux of carbon into green plants from atmospheric CO_2 per unit time. It is the amount of vegetable matter produced per day, week, or year. It may also be expressed as the equivalent amount of energy per unit time. The range (from about 9,000 to less than 200 kcal/m^2/year) is highest in the tropical rainforest biome, and lowest in the desert and tundra biomes (Aber and Melillo, 2001). The main determining physical factors are temperature and water availability. Soil texture has a notable influence on these, with sandy and gravelly soils tending to be excessively well drained in many cases (leading to drought) and clay-rich soils tending to be poorly drained (leading to waterlogging and gleying) and also slow to heat up at the beginning of a growing season. Chemically, the inherent fertility of the soil is an important factor, though paradoxically the tropical rainforest, where some of the least fertile (ferralitic) soils are to be found, has the highest NPP. High temperatures, a year round growing season, and reliable rainfall, account for much of this, but an additional important factor is geological/pedological. Weathering in the soil provides only a meager supply of nutrients, but most regions of extensive tropical rainforest are to be found on stable landscapes without major geological upheavals for millions of years (Amazon and Congo regions for example). Consequently, by efficiently recycling the nutritional content of dead vegetation (soil organic matter), the standing biomass has slowly accumulated a sufficiency of nutrient elements, generation by generation.

Bibliography

Aber, J.D., and Melillo, J.M., 2001. *Terrestrial Ecosystems*. 2nd edn., San Diego: Harcourt Academic Press, 556 pp.

Cross-reference

Biomes and their Soils

NITISOLS

Nitisols are deep, strongly weathered, well-drained tropical soils with a clayey subsurface horizon made up of angular, blocky structural elements that easily crumble into polyhedric ('nutty') peds with shiny faces. The soils have a high cation exchange capacity compared to associated Ferralsols. This article is based on the descriptions in FAO (2001).

Connotation. From the Latin *nitidus* meaning shiny.

Synonyms. 'Terra roxa estruturada' (Brazil), kandic groups of alfisols and ultisols (Soil Taxonomy), 'sols fersialitiques' or 'ferrisols' (France); cinnamonic soils (Russia). A common term is 'red earths'.

Definition. Nitisols are defined by FAO (2001) as soils having

1. a nitic horizon starting within 100 cm from the soil surface, and
2. gradual to diffuse horizon boundaries, and
3. no ferric, plinthic or vertic horizon within 100 cm from the soil surface.

Parent material. Intermediate to basic parent rock, possibly rejuvenated by recent admixtures of volcanic ash.

Environment. Nitisols are predominantly found in level to hilly land under tropical rain forest or savannah vegetation.

Distribution. More than half of the approximately 200 million ha of Nitisols that occur on the Earth's land surface are found in tropical Africa. The Ethiopian volcanic plateau, and volcanic highlands in East and Central Africa, and in Cameroon have Nitisols above 1 000 m. In tropical Asia, South and Central America, Australia and in other places, Nitisols are found at lower elevations. Figure N4 shows the global extent of this reference group.

Characteristics. The clay assemblage of Nitisols or their finely textured weathering products are dominated by kaolinite/(meta) halloysite. Nitisols are rich in iron and have little water-dispersible ('natural') clay. The AB(t)C-profiles are usually deeper than 150 cm. They are red or reddish brown clayey soils with a '*nitic*' subsurface horizon of high aggregate stability. Black, reticulate segregation of Mn hydroxides occur on ped surfaces in the lower part of the nitic horizon. The soils range from hard when dry, through friable to firm when moist, to sticky and plastic when wet. Gravelly or stony Nitisols are uncommon, but may contain fine iron-manganese concretions known as shot. Horizon boundaries are normally gradual, and in addition gradual transitions into other horizons take place (cambic, for example) laterally. Also the nitic horizon may wedge out laterally, or dip below a ferralic or argic horizon.

The clay fraction is dominated by kaolinite and (meta)halloysite, with minor amounts of illite, chloritized vermiculite and randomly interstratified clay minerals. Oxide-hydroxide phases are represented by hematite, goethite and gibbsite. The mineralogical composition of the sand fraction depends strongly on the nature of the parent material. Weatherable primary minerals persist, their nature depending on the parent material.

The soil fauna (termites in particular) is very active which probably accounts for the gradual nature of boundary-transitions. Faunal activity is accountable for the typical gradual horizon boundaries of Nitisols.

Origin. The formation of Nitisols involves three processes. (*a*) '*Ferralitization*'; intense hydrolysis and leaching to leave residua rich in minerals such as goethite, gibbsite, (meta)halloysite, and kaolinite. The process is an early stage of the one that produces Ferralsols. (*b*) '*Nitidization*'; formation of angular, shiny peds in the nitic horizon. Probably caused by swelling and shrinking on a micro-scale. (*c*) '*Homogenization*' by termites, ants, worms and other soil fauna (sometimes referred to as '*biological pedoturbation*'). Particularly affects the top 100 cm of soil where it produces a crumb and/or subangular blocky soil structure, and results in gradual or diffuse boundaries between horizons.

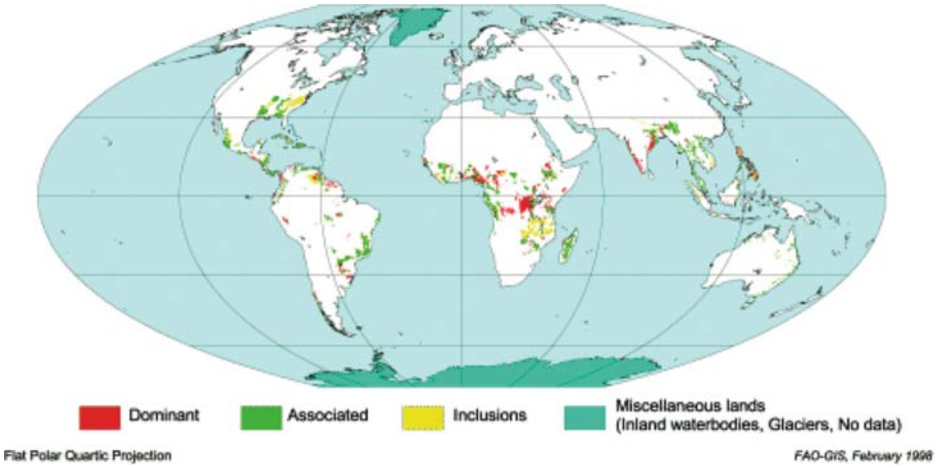


Figure N4 Global distribution of Nitisols.

Use. Nitisols are planted to farm and plantation crops. They are generally considered to be 'fertile' soils in spite of their low level of 'available' phosphorus and their normally low base status. Nitisols are deep, stable soils with favorable physical properties for agriculture. From the standpoint of their deep and porous solum, stable soil structure, good workability, good internal drainage, fair water holding capacity and relative good fertility, they are among the best of the tropical soils.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science,* 2nd ed. Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W. and Hintermaier-Erhard, G. 2007. Soils of the world. Heiderberg, Berlin: Springer-Verlag. 130 pp.

Cross-references

Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils

NITRIFICATION

The oxidation of ammonia to nitrite then nitrate mediated by bacteria. An energy producing activity for the bacteria. See *Nitrogen Cycle*.

NITROGEN CYCLE

As a constituent of cell proteins nitrogen is an indispensable nutrient for all living organisms, and although approximately three quarters of the atmosphere (about 386×10^{13} t) is made up of dinitrogen gas (N_2) the element is always a limiting factor in the growth of plants and animals since it cannot be assimilated by most organisms in elemental form. Animals derive their nitrogen from plant sources, and plants manufacture their protein mostly from soil nitrogen. The latter is present in complex organic combinations, which, like nitrogen gas, cannot be used directly by plants. Only one to two percent of the total nitrogen in the soil is present in inorganic forms (mostly as ammonium or nitrate, occasionally as nitrite) and it is this that can be assimilated by plants. Nitrite, which at high levels is toxic to plants, has only a transitory existence in aerated soils, being readily oxidized to nitrate.

The path of nitrogen in the biosphere can be viewed as a cycle of reactions through which elemental nitrogen enters into the soil from the atmosphere, undergoes a series of transformations due to organic activities, and eventually goes out of the soil back into the atmosphere. The complete process is collectively known as the nitrogen cycle (Figure N5). The important steps in the nitrogen cycle are nitrogen fixation, mineralization, immobilization and volatilization each of which is mediated by different microorganisms (Figure N6). Wolstenholme (2004) provides an excellent review in the practical context of the avocado industry.

The ultimate source of soil nitrogen is atmospheric nitrogen. Generally between 1 and 10 kg ha^{-1} is transformed to ammonium and nitrate forms by electrical discharges during thunderstorms and washed into the soil through precipitation. However the bulk of N_2 incorporated directly into soil is converted into organic nitrogenous compounds by certain microorganisms, with or without the association of a host. This is known as biological nitrogen fixation, and the fixed nitrogen reaches the soil upon the death of the organisms affecting the original nitrogen fixation from the atmosphere. In the soil, the conversion of organic into inorganic forms, again mediated microbiologically, is known as mineralization. The mineralized nitrogen may be used up by microorganisms or by plants, where it is converted

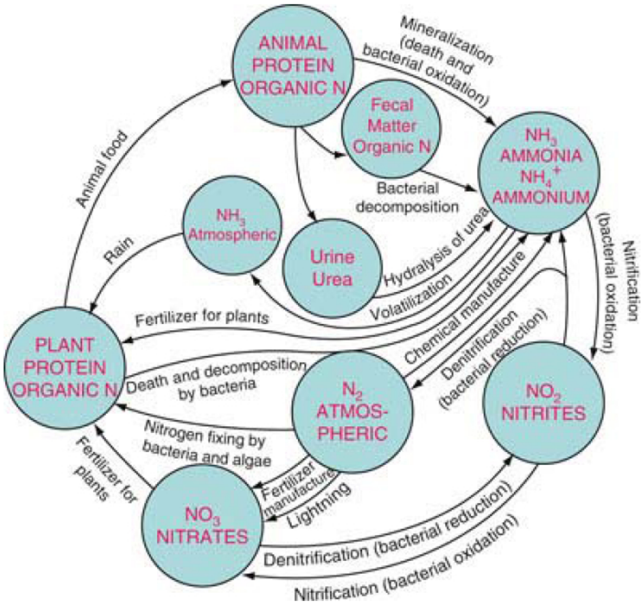


Figure N5 The nitrogen cycle (adapted from Baskin, 2002).

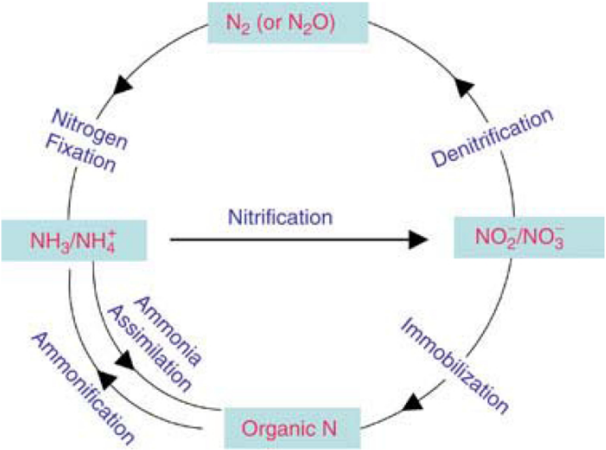


Figure N6 Biogeochemical transformations in the nitrogen cycle in soils (adapted from Jaffe, 1992).

into organic nitrogen in the cells. This process of converting of inorganic (or mineral) nitrogen to organic forms is called immobilization.

All of the foregoing occurs under well-aerated conditions. Where the oxygen supply is depleted or anaerobic conditions prevail a different microbiological process operates whereby elemental nitrogen is formed from nitrates and nitrites. This results in the loss of nitrogen from the soil by volatilization, and the process is called denitrification.

Nitrogen fixation

Nitrogen fixation is the term used to describe the conversion of gaseous N_2 into any chemically bound form including fixation by lightening strikes or by industrial techniques. Biological nitrogen fixation is the enzyme-catalyzed reduction of N_2 to ammonia, ammonium ion or to any organic compound. In soils, biofixation is the commonest natural process. This is accomplished (1) by *Rhizobium* bacteria symbiotic with legumes and living in nodules on the plant roots, (2) by such free living bacteria as *Azotobacter* (mainly in neutral to alkaline soils) and *Beijerinckia* (in tropical acid soils) (Table N1), and (3) by cyanobacteria. In agricultural soils the plant available nitrogen is augmented by the use of fertilizers, manures and crop residues.

The amount of nitrogen fixed asymbiotically is not definitely known, but is relatively small, perhaps 7 to 10 kg N ha^{-1} yr^{-1}. Cyanobacteria can fix a considerable amount of nitrogen in flooded rice fields, between 15 to 50 kg N ha^{-1} annually. By contrast the symbiotic bacteria in the root nodules of legumes is considerable (Table N2).

Table N1 Distribution of *Azotobacter* and *Beijerinckia* in some soils of Tanzania (from Urio et al., 1979)

Location	Soil	Number/g in soil	
	pH	*Azotobacter*	*Beijerinckia*
Inyala, Mbeya	6.4	549	9 524
Mwakaleli, Mbeya	5.9	1 402	48 042
Nsiansia Masoko, Mbeya	6.0	4 813	5 552
Kiyungu, Tanga	6.8	14 694	297
Livestock Breeding Station, Tanga	7.1	1 503	1 337
Kange Farm, Tanga	4.7	187	1 850
Lyamungu, Moshi	6.7	7 566	685
Mlama Coffee Estate, Moshi	5.8	1 265	792
Kindi Coffee Estate, Kibosho, Moshi	6.1	506	2 579
Marangu Teachers College, Moshi	5.9	178	4 034
Olomotonyi Forest, Arusha	6.1	774	2 346
University Farm, Morogoro	5.7	2 500	15 783

Table N2 Nitrogen fixation by different legumes (from Urio et al., 1979)

Crop	Nitrogen fixed (kg ha^{-1})
Cowpea	73–80
Soybean	up to 206
Greengram	61
Groundnut	72–240
Pigeonpea	96–280
Chickpea	103
Centrosema	128–395
Desmodium	up to 400

Mineralization

The main sources of soil nitrogen are the proteins (in particular) as well as purines and pyrimidines, in crop residues, farm manures, green manures and composts. Mineralization is brought about by two distinct microbiological processes. The first, ammonification breaks down organic N compounds to NH_3 or NH_4^+ with the enzymatic breakdown to amines (called proteolysis or aminization) as an initial step. The second, nitrification is the oxidation of NH_3 or NH_4^+ to NO_2^- or NO_3^- (the latter being the predominant available form of nitrogen in well-aerated, cultivated soils).

Nitrification is used by several organisms as an energy source (Delwiche, 1981), the energy yielding steps being

$$NH_4^+ + 1.5O_2 \rightleftharpoons NO_2^- + H_2O + 2H^+$$
$$\Delta G^0 = -290\,\mathrm{KJ\,mol^{-1}}$$

principally mediated by *Nitrosomonas*, and

$$NO_2^- + 0.5O_2 \rightleftharpoons NO_3^- \quad \Delta G^0 = -82\,\mathrm{KJ\,mol^{-1}}$$

principally mediated by *Nitrobacter.*

Immobilization

The incorporation of inorganic nitrogen into an organism is called immobilization. In algae, fungi and the higher plants, the principal pathway is by assimilatory nitrate reduction. Assimilatory pathways are methods for taking a nutrient in the soil, moving it into the cell and using it for biosynthesis of macromolecules. Following transportation across the cell membrane and into the cell, nitrate is reduced enzymatically, to provide nitrogen for incorporation into amino acids. These then become the building blocks of proteins.

The C/N ratio is an approximate indicator of the extent to which nitrogen contained in organic residues in soil, may become reincorporated (i.e., immobilized) in growing organisms. Residues with C/N ratios above about 30, (nitrogen contents of about 1.5% or less) cause a net immobilization of nitrogen, thereby lowering the reserve of plant available N. By contrast, if the C/N ratio is less than about 20 (nitrogen contents above about 2.5%) mineralization occurs, which increases the reserve.

Losses of soil nitrogen

Biological volatilization. Nitrate is the most oxidized form of nitrogen, and can act as an oxidant or electron acceptor. In environments where oxygen supply is limited, as under waterlogged conditions, certain microorganisms can use nitrate in the place of oxygen for their respiration. In such respiration, nitrate is reduced to gaseous species, which will tend to escape to the atmosphere, usually as N_2 but also to N_2O. The process is called denitrification (or nitrate respiration). The following diagram shows possible pathways (Stevenson, 1986).

Non-biological volatilization. (*i*) Volatilization of ammonia is another potential source of nitrogen loss from soil. The amount lost increases with pH, becoming significant in calcareous soils. Appreciable losses of N as ammonia can also occur when manures decompose on the soil surface, even on acid soils, since ammonia formation in the rotting manure locally raises pH. (*ii*) In acid soils (pH 5.5 or less) nitrates may decompose to oxide gases of nitrogen. Nitrous acid may also react non-enzymatically with amines, amino acids or ammonia, to produce nitrogen gas.

Leaching. Nitrogen in the soil solution as nitrate ions is readily lost from the soil by leaching. In sandy soils, ammonium losses may be significant. The extent of nitrate leaching is determined by several factors including (*i*) quantity of nitrate, (*ii*) amount and time of rainfall, (*iii*) infiltration and percolation rates, (*iv*) evapotranspiration, (*v*) water-holding capacity of the soil, and (*vi*) presence of growing plants.

Erosion. Since soil nitrogen is intimately associated with soil organic matter, and since the latter is concentrated in the A horizon, sheet erosion, which strips off the surface layers of the soil, will tend to deplete this and other plant nutrients.

Fertilizer nitrogen

The yield of intensive agriculture is virtually always limited by the availability of the nitrogen needed to produce the proteins in living cells (Leigh, 2004). Natural sources provide only about half the global N requirement in agriculture, and we are completely reliant on inorganic nitrogen fertilizers for the rest. Smil (1999) points out that of all the technological inventions of the 20th century, the Haber-Bosch process has made the most difference to the survival of humanity. This is the industrial technique that is used to synthesize nitrogen fertilizer using the atmosphere as nitrogen source. Smil (2001) claims that approximately 40% of the world's dietary protein supply in the mid-1990s originated from fertilizer produced in this way. The Haber-Bosch technique, though improved and more energy efficient nowadays, is still recognizably the process that first went into commercial production to convert atmospheric nitrogen into ammonia, just before the First World War began.

Currently, global output of ammonia is now about 130 million t yr^{-1}. Eighty percent is used in fertilizers, with urea the most important. Without the Haber-Bosch synthesis of ammonia, almost two-fifths of the world's population would not be here – and our dependence will only increase as the global count moves from six to nine or ten billion people (Leigh, 2004).

Environmental consequences

Nosengo (2003) points out that over the last century, the impact of human activity on the nitrogen cycle has become global. At the beginning of the twentieth century most reactive nitrogen in soil was produced bacterially amounting to about 100 million t yr^{-1}. Now, anthropogenic production accounts for some 160 million t yr^{-1} (Galloway et al., 2003), mostly as fertilizer (more than 100 million t), with much of the rest being added to the biosphere inadvertently as a by-product of the burning of fossil fuels for transport, industrial and domestic purposes. At current rates of increase, Nosengo (2003) reports that global production of reactive nitrogen could reach between 250 million and 900 million t yr^{-1} by 2100.

A major problem arises from the fact that the efficiency with which organisms pick up nitrogen in the soil is low (generally in the range 25 to 50%), with the excess leached and washed from the soil predominantly as nitrate (Smil, 2001, chapter 9). The resulting massive introduction of nitrogen into the natural system creates problems in a wide variety of terrestrial and marine ecosystems (Vitousek et al., 1997; Mosier et al., 2004). Eutrophication, recognized as an endemic problem in the surface waters of agricultural areas of the developed world in the 1960s and 1970s, has now extended to the marine environment, causing hypoxia (so called "dead zones") in near shore waters. The most notorious extends for about 500 kilometers along the shore of the Gulf of Mexico, where the Mississippi brings nitrates and phosphates from the agricultural hinterland to fertilize algal growth (Figure N7). Decomposition of the algae deoxygenates the water and leads to the death of aquatic species (CENR, 2003).

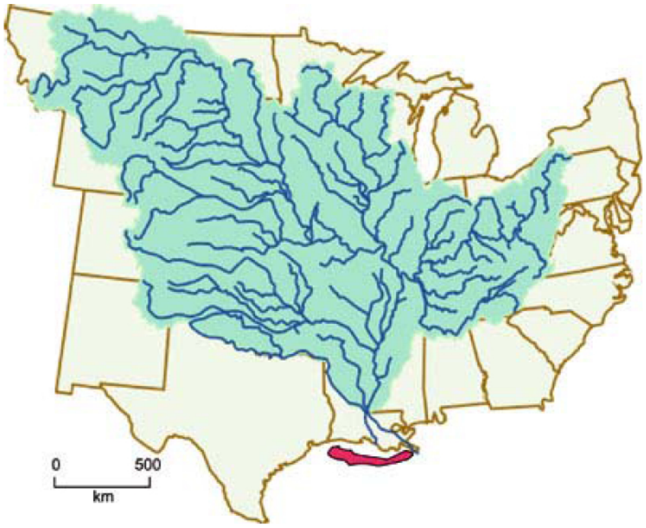


Figure N7 Hypoxia in the Gulf of Mexico. The Mississippi watershed is the proximate source of nutrients for the hypoxic zone. It is now largely transformed for human use: 58% cropland, 21% grazing, and 0.6% urban After Goolsby (2000).

Excess nitrate may also contaminate groundwater. In southern Ontario, Canada, for example a third of the rural drinking water resource is contaminated in this way (Goss et al., 1998), and potentially threatens the occurrence of methaemoglobinaemia or blue baby syndrome. This is a rare condition that prevents red blood corpuscles from transporting in an affected child.

Finally, nitrogen in oxidized form may remain in the atmosphere to cause smog, or, by dissolving in atmospheric precipitation, to produce acid rain.

Johnson Semoka

Bibliography

Baskin, V.N., 2002. *Modern Biogeochemistry.* London: Kluwer, 561 pp.

CENR, 2003. *An Assessment of Coastal Hypoxia and Eutrophication in U.S. Waters.* Washington, DC: National Science and Technology Council Committee on Environmental and Natural Resources, 82 pp.

Delwiche, C.C., 1981. The nitrogen cycle and nitrous oxide. In Delwiche, C.C., ed., *Denitrification, Nitrification and Atmospheric Nitrous Oxide.* New York: Wiley, pp. 1–15.

Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., and Cosby, B.J., 2003. The nitrogen cascade. *BioScience*, **53**: 341–356.

Goolsby, D.A., 2000. Mississippi basin nitrogen flux believed to cause Gulf hypoxia. *Trans. Am. Geophys. Union*, **81**: 325–327.

Goss, M.J., Barry, D.A.J., and Rudolph, D.L., 1998. Contamination in Ontario farmstead domestic wells and its association with agriculture: 1. Results from drinking water wells. *J. Contam. Hydrol.*, **32**: 267–293.

Jaffe, D.A., 1992. The nitrogen cycle. In Butcher, S.S., Charlson, R.J., Orians, G.H., and Wolfe, G.V., eds., *Global Biogeochemical Cycles.* New York: Academic Press, pp. 263–284.

Leigh, G.J., 2004. *The World's Greatest Fix: A History of Nitrogen in Agriculture.* Oxford: Oxford University Press, 254 pp.

Mosier, A., Syers, J.K., and Freney, J.R., 2004. *Agriculture and the Nitrogen Cycle: Assessing the Impacts of Fertilizer Use on Food Production* *and the Environment.* International Council for Science. Scientific Committee on Problems of the Environment; Washington, DC: Island Press, 296 pp.

Nosengo, N., 2003. Fertilized to death. *Nature*, **425**: 894–895.

Smil, V., 1999. Detonator of the population explosion. *Nature*, **400**: 415.

Smil, V., 2001. *Enriching the Earth.* Cambridge, MA: MIT Press, 338 pp.

Stevenson, F.J., 1986. *Cycles of soil: Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients.* New York: Wiley, 380 pp.

Urio, A.P., Mongi, H.O., Chowdhury, M.S., Singh, B.R., and Semoka, J.M.R., 1979. *Introductory Soil Science.* Dar es Salaam: Tanzania Publishing House, 232 pp.

Vitousek, P.M., Aber, J., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., and Tilman, G.D., 1997. Human alteration of the global nitrogen cycle: causes and consequences. *Issues Ecol.*, **1**: 1–17.

Wolstenholme, B.N., 2004. Nitrogen – The Manipulator Element: Managing Inputs and Outputs in Different Environments. *South African Avocado Growers Association Yearbook*, **27**: 45–61.

NITROGEN FIXATION

The conversion of atmospheric nitrogen into oxidized forms available to plants. Some genera of bacteria important in soils (eg, Rhizobium sp.; Azotobacter sp.) and cyanobacteria, are capable of biochemically fixing nitrogen. The process is catalyzed by the enzyme nitrogenase. Such bacteria are important symbionts for peas, beans, vetches and other legumes. See *Nitrogen Cycle*.

NODULE

A small rounded lump of material distinct from the soil matrix, formed in situ by the deposition of such minerals as calcite and silica (in Calcisols and Durisols respectively, for example), pyrolusite and/or goethite (in gleyic varieties of many soil groups). Presence of Mn/Fe nodules in soil is a redoximorphic feature. Alternations of oxidation and reduction (as would accompany fluctuations in a water table for example) cause solution of Mn or Fe during reduction cycles and precipitation (as hydroxides) during oxidation cycles. Presence of a nucleating agent (a pre-existing mineral for example) begins the process of nodular growth (Taylor et al., 1983, p. 322). Refer to diagram under *Ortstein*. See also *Concretion*.

Bibliography

Taylor, R.M., McKenzie, R.M., Fordham, A.W., and Gillman, G.P., 1983. Oxide minerals (Chap. 23). In *Soils: An Australian Viewpoint.* Australia. Commonwealth Scientific and Industrial Research Organization, Division of Soils, pp. 309–334.

NUTRIENT

Any substance that is used by an organism to provide nourishment, and to build and repair tissues.

Cross-references

Macronutrients
Micronutrients
Nutrient Potentials
Plant Nutrient

NUTRIENT CYCLING

See *Biogeochemical Cycles*; *Plant Nutrients*.

NUTRIENT POTENTIALS

The term nutrient potential means the amount of plant nutrients in the rooting depth of soils being directly or indirectly accessible to plant roots. The total amount of a plant nutrient in the rooting depth can be higher by some orders of magnitude than the amount required by plants during a growth period. Potassium in mineral soils for example may amount to 3×10^6 kg K ha^{-1} at a rooting depth of 1 m while a heavy potassium feeder, such as sugar beet requires about 3×10^2 kg K per growth period. According to this assessment the total amount of K should be sufficient for about 10^4 years. This simple calculation, however, is not correct because most of the K in soils present in the interlayers and interstices of various minerals is so strongly bound that it cannot be exploited by plants or is released at low rates due to weathering processes and attack by plant roots, rates that are insuffcient for normal growth. This situation applies also to plant nutrients mainly released by physicochemical processes such as Mg^{2+}, Ca^{2+}, heavy metals and phosphate. Release of nutrient ions from minerals may be associated with a degradation of soil minerals. This is particularly true if the release extends over a long period. Otherwise the structure of minerals is not profoundly changed and the sites from which the ions were released may be refilled with the nutrient ion in question. Nutrient amounts, which can be adsorbed at these sites, indicate roughly the nutrient potential of this particular nutrient in a given soil. In Figure N8 the relationship between the exhaustion of the nutrient potential and the strength of nutrient binding by soils is shown. This relationship, which is particularly true for soil water, shows that the strength of binding is the stronger the more the pool of nutrients is exhausted, and that release rates decrease with the exhaustion of the pool.

Plant nutrient dynamics in soils are controlled by physicochemical and biological processes the latter comprising root growth, excretion of organic and inorganic solutes as well as nutrient uptake by roots and microbial enzyme activity. This is particularly true for potassium, ammonium, sulfur, phosphorus, and some heavy metals. Nutrient potentials and their relevant dynamics are discussed for the most important nutrients, below.

Nitrogen

Nitrogen in the rooting depth of arable soils amounts to about 10^3 to 10^4 kg N ha^{-1} and is mainly present in organic form. The most important inorganic forms are nitrate and ammonium. Plant roots can directly absorb them when both are present in the soil solution. Nitrate, which is not adsorbed to soil particles,

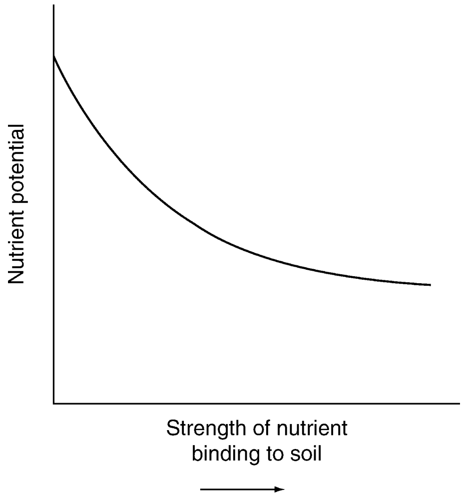


Figure N8 General relationship between the nutrient potential and the strength of nutrient binding to the soil matrix.

so that all the amount present in the rooting zone is available. Ammonium dissolved in the soil solution and adsorbed nonspecifically to soil colloids is also easily accessible to plant roots and hence an important component of the nitrogen potential. This is especially true for flooded soils in which nitrification is hampered because of a lack of oxygen (Savant and De Datta, 1982; Schön et al., 1985). Some soils abundant in 2:1 clay minerals may adsorb NH_4^+ specifically in their interlayers (Scherer, 1993). This “fixed” NH_4^+ is protected against nitrification and therefore indirectly against leaching and denitrification. A significant proportion of the interlayer NH_4^+ is available to plant roots and represents an important amount of the soil nitrogen potential (Scherer, 1993). In arable soils only about 2% of the total organic soil N is available to crops during a season. These are low molecular amino compounds such as amino sugars and oligopeptides (Mengel et al. 1999, Mulvaney and Khan 2001).

The estimation of the soil organic nitrogen contributing to the nitrogen potential meets with difficulties because only the mineralizable nitrogen is potentially available to plants which are no clear-cut fraction and various chemical groups of organic soil nitrogen are prone to mineralization. Nitrogen mineralisation is high in fallow soils while immobilization of inorganic N (assimilation by soil bacteria) in soils is high if a crop is grown on the soil as was recently shown by Maci et al. (2007). Incubation experiments were used to assess the mineralization potential of organic soil N by Stanford and Smith (1972), who established the following equation for N mineralization potential of soils.

$$\log(N_0 - N_t) = \log N_0 - kt$$

where N_0, is the N mineralization potential at the beginning of mineralization, N_t the cumulative N mineralized at time t, and k the mineralization rate constant. According to this equation, nitrogen mineralization related to time is a non-linear process, which is in contrast to the results of Tabatabai and Al-Khafaji (1980) and Appel and Xu (1995) who found a linear relationship for the cumulative N quantities mineralized vs. the time of mineralization.

Mineralization of organic soil N depends on soil moisture, soil temperature, C/N ratio of the organic matter, soil pH, and particularly on soil texture. Peptides, proteins and also enzymes involved in the mineralization may be adsorbed to clay minerals and therefore less prone to mineralization (Loll and Bollag, 1983). For this the reason N mineralization in sandy soils proceeds more rapidly than in loamy and clay soils (Mengel, 1996). For the assessment of the soil nitrogen potential net mineralization is of utmost importance, and is expressed as N mineralization minus N immobilization. The latter is mainly due to the incorporation of inorganic N into the microbial biomass. Nitrogen immobilization rates are high for N-poor organic matter such as cereal straw (Gok and Ottow, 1988), and high for young N-rich organic matter (Appel et al., 1995; Mengel, 1996). Net mineralization rates and hence also the soil nitrogen potential declines the longer soils are undersupplied with nitrogen. This means that the quantity of nitrogen removed from the soil is higher than the quantity of nitrogen added to it, so that the pool of mineralizable soil nitrogen is gradually exhausted.

The potential of nitrogen net mineralization is very important for adjusting nitrogen fertilizer rates to the crop demand. In recent years models for net mineralization for soil nitrogen were elaborated (Otter-Nacke and Kuhlmann, 1991) and efforts were made to quantify the mineralizable nitrogen by means of the electro-ultrafiltration method (EUF) and by extracting the soil with a $CaCl_2$-solution (Appel and Mengel, 1992; Groot and Houba, 1995).

Sulfur

For S, as for N, the organic form is dominant. Only soils of arid areas commonly contain larger amounts of inorganic than organic S (Wainwright, 1984). Organic sulfur occurs as reduced S in which the S is bound to a C atom (C–S), and in sulfate esters. According to Nguyen and Goh (1992) C-bound S is less prone to mineralization than the sulfate esters and therefore the latter contribute more to the sulfur potentials of soils than the C bound sulfur. The potential of S mineralization can be estimated by the following equation (Pirela and Tabatabai, 1988):

$$S_m = S_0[1 - \exp(-kt)]$$

where S_m is the mineralized S at the time t, S_0 the potentially mineralizable S, t the time of mineralization and k a coefficient. The sulfur potential of soils in tropics and subtropics is frequently poor due to the low organic matter of these soils (Pasricha and Fox, 1993).

The total amount of S in temperate climate, arable soils is in the range of 1 000 to 4 000 kg S ha^{-1} and is much higher than the S requirement of crops with a high S demand such as rape which takes up about 15 to 30 kg S ha^{-1} (Schnug, 1991). For this reason moderate mineralization rates of organic S may suffice to meet the demand of many crop species.

Unlike nitrate, sulfate can be adsorbed to soil colloids in substantial amounts and therefore adsorbed sulfate may contribute to the S potential of soils. Sulfate adsorption occurs on surfaces of Al/Fe oxides/hydroxides and clay minerals and generally increases with soil clay concentrations (Martini and Mutters, 1984; Pasricha and Fox, 1993). Sulfate adsorption is strong at low soil pH and decreases as pH increases (Nodvin et al., 1986). For this reason liming may increase the potential of plant available sulfate. According to investigations of Turner and Kramer (1991) carried out with hematite and goethite, sulfate adsorption is a ligand exchange for OH^- and mono- and binuclear sulfate complexes can be formed. In pervious soils sulfate can be easily leached out of the rooting depth and highly weathered soils low in organic S, have a poor sulfate potential (Pasricha and Fox, 1993).

Phosphorus

The phosphate concentration in the soil solution is very low and therefore the phosphate potential depends greatly on the soil phosphate fractions, which provide phosphate to the soil solution. There are three main fractions directly related to soil solution phosphate: the Ca phosphates (Mengel, 1994), the adsorbed phosphates (Parfitt, 1978) together with the occluded phosphate, and the organic phosphates (Dalai, 1977). The main forms of the Ca phosphates are Ca monohydrogen phosphate, octo-Ca-phosphate, and apatites. The latter are unstable in acid soils.

The dissolution of the Ca phosphates is mainly controlled by the pH and the Ca^{2+} concentration in the soil solution; the low pH favoring dissolution, high Ca^{2+}, precipitation. The solubility products of Ca monohydrogen phosphate and even of octo-Ca-phosphate are high enough to give sufficient phosphate rates to plant roots even under alkaline soil conditions. Hence these phosphates contribute 100% to the phosphate potential. This is not true for apatites under near neutral to alkaline conditions.

Phosphate can be adsorbed to surfaces of soil particles such as Al/Fe oxides/hydroxides, clay minerals, and carbonates. The adsorption is a ligand exchange reaction for OH^- and therefore it is pH dependent. The lower the pH the stronger the adsorption. Low soil pH also favors binuclear relative to mononuclear adsorption, the latter being much weaker than the former. Strong phosphate adsorption (a severe problem in oxisols – van Wambeke, 1991) contributes only the relatively minor amount of desorbable P to the phosphate potential, only that part which is desorbable. Increasing the soil pH (by liming for example) increases the availability of the adsorbed phosphate and hence has a beneficial impact on the phosphate potential (Sturm and Isermann, 1978). Phosphate adsorption follows approximately a Langmuir Equation (Nair, 1996). Phosphate adsorption dominates in mineral soils with a low pH. With an increase in pH the Ca phosphates increase in their importance. Occluded phosphate is adsorbed to a Fe^{3+} oxide/hydroxide layer forming a mantle around the phosphatic core which is not available to plant roots. Under anaerobic conditions, however, the Fe^{3+} may be reduced by microbes with release of phosphate, thereby making it plant-available (Sah and Mikkelsen, 1982).

The percentage of total phosphate, which is organic, is between 20 to 80%. Virtually all organic phosphates are present as *ortho*-phosphate esters, with the inositol esters dominant. Phosphate can be split off from the esters by the attack of phosphatases originating from plants and/or microbes. Particularly in the rhizosphere the activity of phosphatases is high (Tarafdar and Jungk, 1987) and hence this biological factor may contribute much to the soil phosphate potential (Tarafdar and Claassen, 1988; Helal and Dressler, 1989). Phosphate released from the organic phosphate pool by phosphatases may be directly absorbed by plant roots, otherwise it is exposed to the characteristic phosphate dynamics of the soil in question, which mainly means precipitation or adsorption. Both forms of phosphate are in an equilibrium relationship with the dissolved inorganic phosphate in the soil solution. When plant roots feed from this soluble phosphate pool phosphate will be replenished by the adsorbed phosphate fraction and/or by the precipitated phosphate fraction, which mainly consists of Ca phosphates. This relationship is shown in Figure N9. Steiffens (1994) found that regardless of the type of phosphate fertilizer applied, phosphate availability was well reflected by phosphate extraction with the electro-ultrafiltration (EUF) technique. Cumulative phosphate uptake of various crops tested in pot experiments followed the algorithm

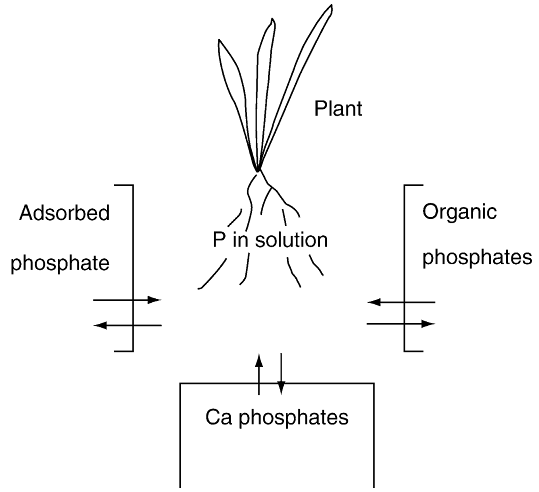


Figure N9 Soil solution phosphate related to the three main phosphate pools: adsorbed phosphate, Ca phosphates and organic phosphates.

$$Y = 27.8 + 0.4\text{CAL-P} \qquad r^2 = -0.97$$

where Y = P uptake, CAL-P = extractable phosphate by calcium ammonium lactate (a quantity term) and b is the constant of the Elovich Equation and indicates the phosphate release rate (an intensity term) which was obtained by EUF (Elovich Equation).

The actual accessibility of phosphate to plant roots depends on a number of factors as described by a model of Silberbush and Barber (1983). The most important are physico-chemical (such as the phosphate concentration in the soil solution and the phosphate buffer power of the soil), and biological (such as root growth and metabolic activity of roots). Poor soil structure may impede root growth and thus affect the accessibility to soil phosphates (Keita and Steffens, 1989). Biological parameters include the mycorrhization of plant roots (Barea and Azcon-Aguilar, 1983) thereby enlarging the soil volume, which can be exploited, by roots for phosphate. Some plant species may respond to an insufficient supply of phosphate (phosphate stress) by the excretion of organic molecules. Grinstedt et al. (1982) reported that rape undersupplied with phosphate increased the supply by excreting higher amounts of protons into the rhizosphere. Proton excretion by roots induced by an insufficient plant phosphate status favors the dissolution of phosphate but may hinder the desorption of phosphate adsorbed to Fe/Al oxides/hydroxides in the rhizosphere. A prominent example of phosphate acquisition is by the excretion of citrate by the proteoid roots of *Lupinus albus*. This induces an exchange of phosphate for citrate (Gardner et al., 1983) and is particularly efficient at mobilizing phosphates adsorbed to Al/Fe oxides/hydroxides.

Gerke et al. (1995) reported that also *Trifolium pratense* excretes citrate into the rhizosphere when grown under insufficient phosphate supply and in a similar way to proteoid roots red clover exploits less soluble soil phosphate by citrate/phosphate exchange. In an analogous way organic anions produced by the decomposition of farmyard manure may mobilize adsorbed phosphate and thus enlarge the phosphate potential of soils (Werner and Scherer, 1995).

Potassium

Potassium ion concentration in the bulk soil solution of arable soils ranges between 0.1 and 2.0 mM and is generally higher in sandy than in loamy or clay soils. Potassium in soil solution is directly available to plant roots and hence contributes almost 100% to the nutritive potential of soil K^+. There are three main sources by which soil solution K^+ is replenished: K^+ from unspecific sites of soil colloids, K^+ from specific sites of clay minerals, and K^+ from K-bearing minerals. The former two fractions are in an equilibrium relationship with K^+ in soil solution. Potassium electrostatically adsorbed to unspecific sites, such as sites of kaolinites, organic matter, planar sites of clay minerals, and inner sites of expanded clay minerals can be easily exchanged by other cation species, especially by Ca^{2+} and is therefore readily available to roots and therefore an important component of the K^+ potential (Mengel, 1985).

Specific K adsorption sites are present in 2:1 phyllosilicate minerals (mainly illite and micas) with K^+ as an integral ion in their crystalline structure. Potassium ions released from interlayer sites give rise to free K^+ specific binding site. Release of interlayer K^+ occurs if the soil solution is low in K^+ concentration (Martin and Sparks, 1983) because of K^+ leaching into deeper soil layers or because of K^+ uptake by crops which are removed from the field. The K^+ potential of this interlayer K^+ fraction can be high and depends mainly on the concentration of non expanded 2:1 K^+ bearing minerals, especially micas (Fanning et al., 1989). The strength of interlayer K^+ binding differs for the various minerals and increases with the following sequence: biotite > muscovite > orthoclase > microcline (Sparks, 1987). Interlayer K^+ contributes only partially to the K^+ potential of soils because K^+ release rates from this pool decrease with its depletion. The cumulative amount of interlayer K^+ released at time t is well reflected by the Elolovich Equation (Martin and Sparks, 1983; Mengel and Uhlenbecker, 1993):

$$K_t = a + b \text{ Int}$$

where K_t is the cumulative K^+ released at time t and a and b are constants, and b is indicative of the rate of K^+ release and therefore has a direct impact on the K^+ supply of plants.

Potassium released from interlayers may simply result in an expansion of the mineral and thus increase the number of specific binding sites. K^+ release, however, may also be associated with destruction of the mineral particularly under acid soil conditions (Feigenbaum et al., 1981). This observation is in line with results of Tributh et al. (1987) who found that cropping a soil for an extended period without fertilizing with K^+ leads to an alteration of illites. At neutral pH illites were altered to smectites, at slightly acidic pH they were degraded to transitional minerals. Both degradation and alteration must be considered as a loss in K^+ potential. A major loss of interlayer K^+ without a degradation of the mineral may give rise to K^+ fixation meaning that K^+ added to such soils is adsorbed by K^+ specific binding sites, replacing other bound cationic species. The process is associated with a shrinkage of the mineral. The K^+ fixed in this way is not easily available to plant roots (Burkart and Amberger, 1978). Besides micaceous K-bearing minerals, feldspars may also contain K^+ in substantial quantities. It is not yet clear whether the release rates from such minerals are high enough to contribute substantially to crop supply.

In soils with virtually no interlayer K^+ the K^+ potential equals approximately the amount of exchangeable K^+ (exchangeable by NH_4^+). Such soils are sandy soils, organic soils, and highly weathered soils with mainly kaolinitic clay minerals (oxisols) having a poor K^+ potential. In soils with a higher concentration of micas, especially biotite, high K^+ potentials may prevail even if the concentration in exchangeable K^+ is low: for example, young less-weathered soils (entisols) may release interlayer K^+ in remarkable quantities from the mica-silt fraction (Mengel and Rahmatullah, 1994).

The K^+ buffer power of soils is represented by the plot quantity of K^+, which can be fed into the soil solution (exchangeable K^+ + available non-exchangeable K^+) versus the K^+ concentration of the soil solution (x-axis). Such curves are known as quantity/intensity curves (Q/I curves). The steeper the slope the higher is the K^+ buffering power (Nair, 1996). This is not identical to the K^+ potential since a high buffering power may be associated with a low amount of exchangeable K^+ and vice versa. The buffering power gives a reliable indication of the amount of available K^+ a soil can store. This depends mainly on the clay concentration of soils and the type of clay minerals (Sharpley, 1990).

Magnesium

The nutrient potential of Mg^{2+} depends almost exclusively on the concentrations of clay and Mg^{2+} bearing minerals present in the silt fractions of soils. The most important Mg^{2+} bearing minerals are olivine, serpentine, biotite, pyroxene, amphibole, and dolomite. Mg^{2+} release from mica is particularly high in acid soils (Feigenbaum et al., 1981). Released Mg^{2+} may be quickly adsorbed to soil colloids and this fraction represents the exchangeable Mg^{2+}. It is frequently used as an indicator for available soil Mg^{2+}. Exchangeable Mg^{2+} together with the Mg^{2+} bearing minerals are the most important components of the Mg^{2+} potential in soils. Since the Mg^{2+} demand of crops is low in comparison with the demand for K^+, Mg^{2+} weathering rates frequently are sufficient for an optimum Mg^{2+} supply of crops (Christenson and Doll, 1973). In pervious, light-textured soils the released Mg^{2+} can be easily leached out of the rooting zone. Highly weathered soils under the humid conditions of the tropics and the temperate zone are those with a low Mg^{2+} potential and on these soils crops may suffer from Mg^{2+} deficiency. Young soils (entisols) are generally rich in Mg^{2+} bearing minerals and have therefore a high Mg^{2+} potential. The same is true for soils derived from dolomitic limestone, for river alluvial soils of which the parent material comes from dolomite areas and for young sea-marsh soils. In serpentinized soils the Mg^{2+} potential can be extremely high while the available Ca^{2+} is comparatively low. In such cases the extreme low Ca/Mg ratio may be harmful to plants (Rodenkirchen and Roberts, 1993).

Calcium

The Ca^{2+} potential of soils mainly depends on the content of Ca^{2+} bearing amorphous and crystalline material. The principal source is Ca-carbonate, and, in some soils, gypsum. Soils containing these minerals are characterized by a high degree of

Ca^{2+} saturation on exchange sites. The fraction of exchangeable Ca^{2+} is in an equilibrium relationship with the Ca^{2+} concentration of the soil solution and hence soils with a high Ca^{2+} potential are characterized by high Ca^{2+} soil solution concentrations. Acidic organic soils (histosols) and highly weathered soils of the humid climate (oxisols) commonly have a low Ca^{2+} potential (van Wambeke, 1991).

The Ca^{2+} potential of soils can be considered either from the standpoint of the Ca^{2+} demand of plants or from that of the Ca^{2+} demand of soils. Soil structure, particularly of silty to clay soils with 2:1 clay minerals predominating, depends largely on the degree of Ca^{2+} saturation. About 70 to 80% of the cation exchange capacity (CEC) should be occupied by Ca^{2+} in order to maintain a satisfactory soil structure. Insufficient Ca^{2+} saturation may not only occur in acidic soils but also in saline soils. In the acid case liming is recommended, in the saline case, the addition of gypsum (Shainberg et al., 1989). In routine analysis, the Ca^{2+} requirement of soils is not assessed directly but by measuring soil pH from which parameter the liming requirement is derived. There may be cases, however, in which the pH is not growth limiting but the concentration of exchangeable Ca^{2+} is. Leguminous species are particularly sensitive to low soil pH (Mahler and McDole, 1987) and low available Ca^{2+} (Schubert et al., 1990).

The Ca^{2+} demand of crops differs much among plant species, generally dicots having a higher Ca^{2+} demand than monocots (Loneragan and Snowball, 1969) because the latter bind comparatively low amounts of Ca^{2+} in the cell wall. Species developed on low-Ca^{2+} soils generally do not need much Ca^{2+} and are known as calcifuge species in contrast to the calcicole species, which are typical representatives of calcareous soils. Calcium deficiency, such as bitter pit in the fruit of apples or tomato end-rot may occur even where the Ca^{2+} potential of soils is high. Such deficiencies result from physiological disorders.

Micronutrients

For plant micronutrients the term potential is rarely used because the physiological demand of plants for micronutrients is low.

Iron. Iron is present in soils in huge quantities but its solubility is very low (Lindsay, 1991) and plants would suffer from Fe deficiency, if other factors did not come into play. These are the production of numerous siderophores by microbes (Crowley et al., 1991) and higher plants. Siderophores are organic compounds which dissolve Fe^{3+} from soil minerals and which form Fe^{3+} complexes soluble over a broad pH range. According to Romheld and Marschner (1986) monocot roots excrete highly selective siderophores (phytosiderophores) into the soil and make iron thus available to plants by attacking ferric minerals. The process is particularly intense in the case of an insufficient Fe status of plants. Iron deficiencies in crops occur almost exclusively on calcareous soils (Loeppert and Hallmark, 1985). Interestingly enough the deficient plants often contain high concentrations of Fe in roots and leaves. This however, is physiologically inefficient and presumably bound in the apoplast of leaf and root cells (Mengel, 1994). Obviously it is not so much the poor physico-chemical solubility of Fe^{3+} in calcareous soils responsible for Fe chlorosis since sufficient Fe is transported to the roots. There is evidence that in such cases Fe^{3+} reduction by the plasma membrane Fe^{3+} reductase is hampered because of too high a pH. This is particularly true for calcareous soils where the soil solution has a high pH much buffered by the elevated concentrations of dissolved HCO_3^- characteristic of calcareous soils (Mengel, 1994). The potential of available Fe therefore is not so much a question of total Fe concentrations in soils being high in mineral soils and low in organic soils (histosols), but a question of microbial activity in soils as was recently shown by Ammari and Mengel (2006). Organic soils are generally low in Fe-bearing minerals and here an absolute Fe deficiency in crops may occur, but this is uncommon. The potential of available Fe may be very high under anaerobic conditions (flooded rice soils) because of the reduction of mineral Fe^{3+} associated with a dissolution of Fe^{2+} which may even induce Fe toxicity in rice plants (Savant and De Datta, 1982).

Manganese. Manganese in soils is mainly present in Mn oxides and in Mn-bearing minerals. Its availability to plants depends much on soil pH, soil redox potential and microbiological activities in soils. A decrease of the redox potential as occurs after flooding soils results in an immense increase in soluble Mn, almost exclusively in the form of Mn^{2+}, produced by microbial reduction according to the following equation (Schwertmann et al., 1987):

$$Mn^{IV}O_2 + 2e^- + 4H^+ \rightleftharpoons Mn^{2+} + 2H_2O$$

The resulting Mn^{2+} is readily available to plants in solution. Under aerobic conditions Mn solubility decreases with an increase in soil pH by a factor of 10 for each pH unit (Lindsay, 1972). Thus insufficient Mn supply to crops is likely to occur on alkaline soils. The pH effect is enforced by microbial activity since at neutral to alkaline soil pH, Mn oxidizing microbes dominate relative to Mn reducing microbes. This is particularly true for soils high in organic matter and if such soils also have a high pH, crops may suffer from Mn deficiency. Excretion of chelating organic anions and of protons by roots renders insoluble Mn forms soluble and makes the Mn available to plants (Uren and Reisenauer, 1988).

Zinc. Zinc in soils is mainly incorporated as structural cations in phyllosilicate minerals, oxides and carbonates, and also sequestered in organic complexes. Its concentration may be very low in highly weathered aid soils, but frequently Zn deficiency occurs on calcareous soils where it is adsorbed to $CaCO_3$. Its solubility decreases with an increase in soil pH. A substantial amount of Zn is complexed by organic molecules and hence soluble in the soil solution. According to Zhang et al. (1989) phytosiderophores excreted by roots attack insoluble Zn compounds and make the Zn available to roots. Insufficient Zn supply to crops, particularly cereals, is mainly observed in arid areas on calcareous soils rich in clay (Cakmak, 1996).

Copper. Copper in soils is almost exclusively present in bivalent form in Cu salts. In soil minerals it may substitute Mg^{2+} or Fe^{2+}. A substantial proportion of Cu in soils is present in organic complexes. Copper can also be chelated by phytosiderophores, a process presumably of importance for improving its availability to plants (Romheld, 1991). Copper deficiency in crops frequently occurs on humic podzolic soils (Henkens, 1965).

Molybdenum. Molybdenum in soils is mainly present as Mo^{IV} in oxyanionic form. The soluble molybdate ions, HMO_4^- and MO_4^{2-}, can be strongly adsorbed to Fe/Al oxides/hydroxides (Kingston et al., 1972). The process is a ligand exchange analogous to that of phosphate. The adsorption is the stronger the lower the soil pH (Barrow, 1970) and it is for this reason that Mo deficiency mainly occurs on acid soils and often can be simply cured by liming.

Boron. Boron is present in various minerals where it may substitute for Si. Also boric acid may form esters with soil organic matter. Young soils and marine sediments are generally rich in B. Boron may also accumulate in alkaline soils even to levels which are toxic to plants. Highly weathered soils in humid areas are often absolutely low in B and crops on these soils may suffer from B deficiency. On such sites boron can be easily leached out of the root-zone. The soluble B in soils is mainly present in the form of boric acid $B(OH)_3$ or as $B(OH)_4^-$ The latter anion is formed under alkaline pH conditions. Since boric acid is a Lewis acid, the anion is formed according to the following reaction:

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \quad pK = 9.0$$

The anion is adsorbed by Al/Fe oxides and clay minerals and the adsorption is the stronger the higher the soil pH (Goldberg and Forster, 1991). It is for this reason that B deficiency in crops frequently occurs on clay soils high in pH. On sandy soils a substantial portion of B is bound as ester to soil organic matter (Goldberg and Glaubig, 1986).

Konrad Mengel

Bibliography

Ammari, T., and Mengal, K., 2006. Total soluble Fe in soil solutions of chemically different soils. *Geoderma*, **136**: 876–885.

Appel, T., and Mengel, K., 1992. Nitrogen uptake of cereals on sandy soils as related to nitrogen fertilizer application and soil nitrogen fractions obtained by electro-ultrafiltration (EUF) and CaCU extraction. *Eur. J. Agron.*, **1**: 1–9.

Appel, T., and Xu, F., 1995. Extractability of ^{15}N labelled plant residues in soil by electroultrafiltration. *Soil Biol. Biochem.*, **27**: 1393–1399.

Appel, T., Sisak, I., and Hermanns-Sellen, M., 1995. $CaCl_2$ extractable N fractions and K_2SO_4 extractable N released on fumigation as affected by green manure mineralization and soil texture. *Plant Soil*, **176**: 197–203.

Barea, J.M., and Azcon-Aguilar, C., 1983. Mycorrhizas and their significance in nodulating nitrogen-fixing plants. *Adv. Agron.*, **36**: 1–54.

Barrow, N.J., 1970. Comparison of the adsorption of molybdate, sulfate and phosphate by soils. *Soil Sci.*, **109**: 282–288.

Burkhart, N., and Amberger, A., 1978. Einfluss der Kaliumdimgung auf die Verfugbarkeit des Kaliums in K-fixierenden Boden im Verlaufe der Vegetationszeit. *Z. Pflanzenernahr. Bodenk.*, **141**: 167–179.

Cakmak, I., Yilmaz, A., Torun, M., Kalayci, B., Erenoglu, B., and Braun, H.J., 1996. Zinc deficiency as a critical problem in wheat production in Central Anatolia. *Plant Soil*, **180**: 165–172.

Catroux, G., and Schnitzer, M., 1987. Chemical, spectroscopic, and biological characteristics of the organic matter in particle size fractions separated from an Aquoll. *Soil Sci. Soc. Am. J.*, **51**: 1200–1207.

Christenson, D.R., and Doll, E.C., 1973. Release of magnesium from soil clay and silt fractions during cropping. *Soil Sci.*, **116**: 59–63.

Crowley, D.E., Wang, Y.C., Reid, C.P.P., and Szaniszlo, P.J., 1991. Mechanisms of iron acquisition from siderophores by microorganisms and plants. In Chen, Y., and Hadar, Y., eds., *Iron Nutrition and Interactions in Plants.* Dordrecht: Kluwer Academic Publishers, pp. 213–233.

Dalai, R.C., 1978. Soil Organic phosphorus. *Adv. Agron.*, **29**: 83–117.

Fanning, D.S., Keramidas, V.Z., and El-Desoky, M.A., 1989. Micas. In Dixon, J.B., and Weed, S.B., eds., *Minerals in Soil Environments.* Madison, WI: Soil Sci. Soc. Of America, pp. 551–634.

Feigenbaum, S., Edelstein, R., and Shainberg, I., 1981. Release of potassium and structural cations from micas to ion exchangers in dilute solutions. *Soil Sci. Soc. Am. J.*, **45**: 501–506.

Gardner, W.K., Barber, D.A., and Parbery, D.G., 1983. The acquisition of phosphorus by *Lupinus albus* L. Ill The probable mechanism by which phosphorus movement in the soil/root interface is enhanced. *Plant Soil*, **70**: 107–124.

Gerke, J., Meyer, U., and Romer, W., 1995. Phosphate, Fe and Mn uptake of N_2 fixing red clover and ryegrass. 1. Plant parameters and soil solution composition. *Z. Pflanzenernahr. Bodenk.*, **158**: 261–268.

Gok, M., and Ottow, J.C.G., 1988. Effect of cellulose and straw incorporation in soil on total denitrification and nitrogen immobilization at initially aerobic and permanent anaerobic conditions. *Biol. Fertil. Soils*, **5**: 317–322.

Goldberg, S., and Forster, H.S., 1991. Boron sorption on calcareous soils and reference calcites. *Soil Sci.*, **152**: 304–310.

Goldberg, S., and Glaubig, R.A., 1986. Boron adsorption on California soils. *Soil Sci. Soc. Am. J.*, **50**: 1173–1176.

Grinsted, M.J., Hedley, M.J., White, R.E., and Nye, P.H., 1982. Plant induced changes in the rhizosphere of rape *(Brassica napus var.* Emerald) seedlings. I. pH change and the increase in P concentration in the soil solution. *New Phytol.*, **91**: 19–29.

Groot, J.J.R., and Houba, V.J.G., 1995. A comparison of different indices for nitrogen mineralization. *Biol. Fertil. Soils*, **19**: 1–9.

Helal, H.M., and Dressler, A., 1989. Mobilization and turnover of soil phosphorus in the rhizosphere. *Z. Pflanzenernahr. Bodenk.*, **152**: 175–180.

Henkens, C.H., 1965. Richtlinien fur die Diingung mit Spurenelementen in Holland. *Landw. Forsch.*, **18**: 108–116.

Keita, S., and Steffens, D., 1989. EinfluR des Bodengefuges auf Wurzelwachstum und Phosphataufnahme von Sommerweizen. *Z. Pflanzenernahr. Bodenk.*, **152**: 345–351.

Kingston, F.J., Posner, A.M., and Quirk, J.P., 1972. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *J. Soil Sci.*, **23**: 177–193.

Kosegarten, H., Hoffman, B., Rroco, E., Grolig, F., Glusenkamp, K.H., and Mengal, K., 2004. Apoplastic pH and Fclll reduction in young sunflower (*Helianthus annuus*) roots. *Physiol. Plantarum*, **122**: 95–106.

Lindsay, W.L., 1972. Zinc in soils and plant nutrition. *Adv. Agron.*, **24**: 147–186.

Lindsay, W.L., 1991. Iron oxide solubilization by organic matter and its effect on iron availablitiy. In Chen, Y., and Hadar, Y., eds., *Iron Nutrition and Interactions in Plants.* Dordrecht: Kluwer Academic Publishers, pp. 29–36.

Loeppert, R.H., and Hallmark, C.T., 1985. Indigenous soil properties influencing the availability of iron in calcareous soils. *Soil Sci. Soc. Am. J.*, **49**: 597–603.

Loll, M.J., and Bollag, J.-M., 1983. Protein transformation in soil. *Adv. Agron.*, **36**: 351–382.

Loneragan, J.F., and Snowball, K., 1969. Calcium requirements of plants. *Aust. J. Agric. Res.*, **20**: 465–478.

Maci, A., Rocco, E., Kosegarten, H., and Mengal, K., 2007. Nitrogen turnover in the bare soil planted subsequently with grass as investigated by electro-ultrafiltration (EUF). *J. Plant Nutr. Soil Sci.*, **170**: 81–86.

Mahler, R.L., and McDole, R.E., 1987. Effect of soil pH on crop yield in Nothern Idaho. *Agron, J.*, **79**: 751–755.

Martin, H.W., and Sparks, D.L., 1983. Kinetics of nonexchangeable potassium release from two coastal plain soils. *Soil Sci. Soc. Am. J.*, **47**: 883–887.

Martini, J.A., and Mutters, R.G., 1984. Effect of liming and fertilization on sulfur availability, mobility, and uptake in cultivated soils of South Carolina. *Soil Sci.*, **138**: 403–410.

Mengel, K., 1985. Dynamics and availability of major nutrients in soils. *Adv. Soil Sci.*, **2**: 65–131.

Mengel, K., 1994. Iron availability in plant tissues – iron chlorosis on calcareous soils. *Plant Soil*, **165**: 275–283.

Mengel, K., 1994. Phosphate dynamics in soils and phosphate fertilizer efficiency. Casablanca: World Phosphate Institute, IMPHOS, pp. 504–518.

Mengel, K., 1996. Turnover of organic nitrogen in soils and its availability to crops. *Plant and Soil*, **181**: 83–93.

Mengal, K., Hutsch, B., and Kane, Y., 2006. Nitrogen fertilizer application rates on cereal crops according to available mineral and organic soil nitrogen. *Eur. J. Agron.*, **24**: 343–348.

Mengel, K., and Rahmatullah, 1994. Exploitation of potassium by various crop species from primary minerals in soils rich in micas. *Biol. Fertil. Soils*, **17**: 75–79.

Mengal, K., Schneider, B., and Kosegarten, H., 1999. Nitrogen compounds extracted by electroultrafiltration (EUF) or CaCl2 solution and their relationships to nitrogen mineralization in soils. *J. Plant Nutr. Soil Sci.*, **162**: 139–148.

Mengel, K., and Uhlenbecker, K., 1993. Determination of available interlayer potassium and its uptake by ryegrass. *Soil Sci. Soc. Am. J.*, **57**: 761–766.

Mulvaney, R.L., Khan, S.A., and Ellsworth, T.R., 2006. Need for a soil – based approach in managing nitrogen fertilizers for profitable corn production. *Soil Sci. Soc. Am. J.*, **70**: 172–182.

Nair, K.P.P., 1996. The buffering power of plant nutrients and effects on availability. *Adv. Agron.*, **57**: 237–287.

Nguyen, M.L., and Goh, K.M., 1992. Sulphur mineralization and release of soluble organic sulphur from camp and non-camp soils of grazed pastures receiving long-term superphosphate applications. *Biol. Fertil. Soils*, **14**: 272–279.

Nodvin, S.C., Driscoll, C.T., and Likens, G.E., 1986. The effect of pH on sulfate adsorption by a forest soil. *Soil Sci.*, **142**: 69–75.

Otter-Nacke, S., and Kuhlmann, H., 1991. A comparison of the performance ofN simulation models in the prediction of N-min on farmers' fields in the spring. *Fert Res.*, **27**: 341–347.

Parfitt, R.L., 1978. Anion adsorption by soils and soil materials. *Adv. Agron.*, **30**: 1–50.

Pasricha, N.S., and Fox, R.L., 1993. Plant nutrient sulfur in the tropics and subtropics. *Adv. Agron.*, **50**: 209–269.

Pirela, H.J., and Tabatabai, M.A., 1988. Sulfur mineralization rates and potentials of soils. *Biol. Fertil. Soils*, **6**: 26–32.

Rodenkirchen, H., and Roberts, B.A., 1993. Soils and plant nutrition on a serpentinized ridge in South Germany. II. Foliage macronutrient and heavy metal concentrations. *Z. Pflanzenernahr. Bodenk.*, **156**: 411–413.

Römheld, V., 1991. The role of phytosiderophores in acquisition of iron and other micronutrients in graminaceous species: An ecological approach. In Chen Y., and Hadar, Y., eds., *Iron Nutrition and Interactions in Plants.* Dordrecht: Kluwer Academic Publishers, pp. 159–166.

Römheld, V., and Marschner, H., 1986. Mobilization of iron in the rhizosphere of different plant species. *Adv. Plant Nutr.*, **2**: 155–204.

Sah, R.N., and Mikkelsen, 1986. Transformations of inorganic phosphorus during flooding and draining cycles of soil. *Soil Sci. Soc. Am. J.*, **50**: 62–67.

Savant, N.K., and De Datta, S.K., 1982. Nitrogen transformations in wetland rice soils. *Adv. Agron.*, **35**: 241–302.

Scherer, H.W., 1993. Dynamics and availability of the non-exchangeable NHrN – a review. *Eur. J. Agron.*, **2**: 149–160.

Schnug, E., 1991. Sulphur nutritional status of European crops and consequences for agriculture. *Sulphur in Agric.*, **15**: 7–12.

Schon, H.G., Mengel, K., and De Datta, S.K., 1985. The importance of initial exchangeable ammonium in the nitrogen nutrition of low land rice soil. *Plant Soil*, **86**: 403–413.

Schubert, E., Mengel, K., and Schubert, S., 1990. Soil pH and calcium effect on nitrogen fixation and growth of broad bean. *Agron. J.*, **82**: 969–972.

Schwertmann, U., Susser, P., and Natscher, L., 1987. Protonenpuffersubstanzen in Böden. *Z. Pflanzenernahr. Bodenk.*, **150**: 174–178.

Shainberg, J., Sumner, M.E., Miller, W.P., Farina, M.P.W, Pavan, M.A., and Fey, M.V. 1989. Use of gypsum on soils: a review. *Adv. Soil Sci.*, **9**: 1–111.

Sharpley, A.N., 1990. Reaction of fertilizer potassium in soils of differing mineralogy. *Soil Sci.*, **149**: 44–51.

Silberbush, M., and Barber, S.A., 1983. Sensitivity of simulated phosphorus uptake to parameters used by a mechanistic-mathematical model. *Plant Soil*, **74**: 93–100.

Sparks, D.L., 1987. Potassium dynamics in soils. *Adv. Soil Sci.*, **6**: 1–63.

Stanford, G., and Smith, S.J., 1972. Nitrogen mineralization potentials of soils. *Soil Sci. Soc. Am. J.*, **36**: 465–472.

Steffens, D., 1994. Phosphorus release kinetics and extractable phosphorus after long-term fertilization. *Soil Sci. Soc. Am. J.*, **58**: 1702–1708.

Sturm, H., and Isermann, K., 1978. Überlegungen zur langfristigen Ausnutzung von Mineraldünger-Phosphat auf Ackerboden, *Landw. Forsch. Sonderh.*, **35**: 180–192.

Tabatabai, M.A., and Al-Khafaji, A.A., 1980. Comparison of nitrogen and sulfur mineralization in soils. *Soil Sci. Soc. Am. J.*, **44**: 1000–1006.

Tarafdar, J.C., and Claassen, N., 1988. Organic phosphorus compounds as a source of P for higher plants through phosphatases produced by plant roots and microorganisms. *Biol. Fert. Soils.*, **5**: 308–312.

Tarafdar, J.C., and Jungk, A., 1987. Phosphatase activity in the rhizosphere and its relation to the depletion of soil organic phosphorus. *Biol. Fert. Soils*, **3**: 199–204.

Tributh, H., Boguslawski, E.v., Lieres, A.v., Steffens, D., and Mengel, K., 1987. Effect of potassium removal by crops on transformation of illitic clay minerals. *Soil Sci.*, **145**: 404–409.

Turner, L.J., and Kramer, J.R., 1991. Sulfate ion binding on goethite and hematite. *Soil Sci.*, **152**: 226–230.

Uren, N.C., and Reisenauer, H.M., 1988. The role of root exudates in nutrient acquisition. *Adv. Plant Nutr.*, **3**: 79–114.

Wainwright, M., 1984. Sulfur oxidation in soils. *Adv. Agron.*, **37**: 349–396.

van Wambeke, A., 1994. *Soils of the Tropics.* New York: McGraw-Hill, pp. 139–161.

Werner, W., and Scherer, H.W., 1995. Quantity/intensity relation and phosphorus availability in South Brasilian latosols as affected by form and placement of phosphorus and farmyard manure. In Date et al., eds., *Plant Soil Interactions at Low pH.* Dordrecht: Kluwer Academic Publishers, pp. 129–133.

Zhang, F., Romheld, V., and Marschner, H., 1989. Effect of zinc deficiency in wheat on the release of zinc and iron mobilizing root exudates. *Z. Pflanzenernahr. Bodenk.*, **152**: 205–210.

Cross-references

Macronutrients
Micronutrients
Nitrogen Cycle
Phosphorus Cycle
Plant Nutrients
Potassium Cycle
Sorption Phenomena
Sulfur Transformations and Fluxes
Trace Elements

O

O HORIZON

See *Horizon, Profile, Horizon Designations*.

ORDER

The highest, most generalized category of soil within several soil classifications, and in particular the Soil Taxonomy system of the U.S. Department of Agriculture, where it is further divided into sub-order, great group, sub-group, family and series. Several of the soil units of the WRB classification are equivalent to orders in the USDA system, though others are equivalent to lower categories. See the individual articles on the 32 WRB soil types.

The classic, 1938 Soil Classification used by the U.S. Department of Agriculture, divided soils into three orders:

- *Zonal soil:* soil typical of a large area or zone, with characteristics that reflect the regional variables of climate and vegetation. There were two major types of zonal soil: *(i)* Pedalfer. A group of soils, lacking calcite in the solum, and with a weathering trend typical of humid climates, leading to enrichment in Fe and Al at the expense of Si. In the extreme, this leads to the formation of acid soils of low nutrient status, for example Podzols in cooler regions, and Ferralsols in hotter ones. *(ii)* Pedocal. A group of soils in which calcium carbonate (as calcite) is formed during soil genesis. Characteristic of arid or semi-arid climates and leading at the extreme to the formation of carbonate-cemented horizons as in caliche or calcrete.
- *Intrazonal soil:* soil with more or less well developed soil characteristics that reflect the dominating influence of some local factor of relief, parent material, or age, over the normal effect of climate and vegetation.
- *Azonal soil:* Soils that lack well developed profile characteristics such as distinct genetic horizons.

None of these terms are used in the current American classification, Soil Taxonomy, but they are still found in geological, geomorphological and geographical texts, and in descriptions of Reference Soil Groups in the WRB system of classification.

ORGANAN

See *Cutan*.

ORGANIC FERTILIZERS

See *Fertilizers, Organic*.

ORGANIC MATTER

See *Carbon Cycling and Formation of Soil Organic Matter, Carbon Sequestration in Soil, Humic Substances*.

ORGANIC SOIL

A soil in which the organic component is dominant with respect to the mineral component (in Histosols for example). Compare *Mineral soil*.

ORGANIC WEATHERING

The physical and chemical modification of landscape materials by organisms, especially plants and the acids and complexants that they exude during life, or yield as decay products in death.

ORTSTEIN

A hardpan cemented with iron and organic matter, that forms in acid soils, most commonly in the B horizon of a Podzol, where it tends to form at the top of the water table. The Eh-pH diagram (Figure O1) illustrates the process. Water in the zone of saturation contains ferrous iron in solution. At the water table oxygen becomes available in soil pores and iron is oxidized to the ferric state in which form it precipitates as ferric hydroxide to form a pan. Iron-rich cutans (ferrans) are explainable by the same mechanism acting on the surface of a host mineral. Manganese-rich cutans (mangans) form in an analogous way.

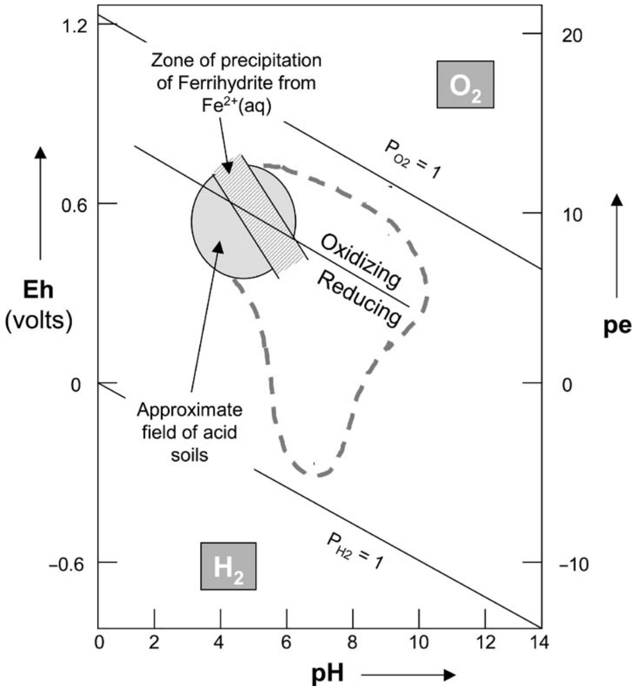


Figure O1 Eh-pH diagram. On the low Eh-pH side of the zone of precipitation, iron is reduced to the ferrous state and ferrihydrite dissolves. On the high Eh-pH side, iron is oxidized to the ferric state and ferrihydrite precipitates. Ferrihydrite is metastable and can be expected to age or ripen to goethite. Fluctuations across the zone of precipitation are also important in causing mottling and nodule formation in gleyic varieties of soil.

Bibliography

Lapen, D.R., and Wang, C., 1999. Placic and ortstein horizon genesis and peatland development, southeastern Newfoundland. *Soil Sci. Soc. Am. J.* **63**: 1472–1482.

Cross-reference

Podzols

OSMOSIS

The process by which molecules of water pass through a semipermeable membrane from a less concentrated aqueous solution into a more concentrated one, in an attempt to equalize concentrations of solute on either side of the membrane. The resulting increase in pressure across the membrane is called the *osmotic pressure*.

Electro-osmosis. Osmosis under the influence of an electric field. The *osmotic potential* is that part of the water potential that results from the combined effect of all solute species in the soil system. When measured in pressure units (e.g., kilopascals) it may be referred to as the osmotic pressure.

Reverse osmosis is a process used in desalinization. A solution of salt water is separated from pure water by a semipermeable membrane, and the pressure on the salt water is raised above the osmotic pressure of the system. This causes water to pass from the salt water to the water.

Bibliography

Drewes, J.E., Reinhard, M., and Fox, P., 2003. Comparing microfiltration-reverse osmosis and soil-aquifer treatment for indirect potable reuse of water. *Water Res.*, **37**: 3612–3621.

Cross-references

Solonchaks
Thermodynamics of Soil Water
Transport Processes
Zeta potential

OUTWASH

A sedimentary deposit laid down more or less as a sheet, by meltwaters from a glacier. The meltwater sorts and redistributes debris originally transported by the ice. The relatively level landform that results is referred to as an outwash plain. The largest active outwash plain is a 1 350 km^2 sandur in southern Iceland, constructed by braided streams issuing from an outlet glacier on the southern edge of the Vatnajökull ice cap (Gomez et al., 2000). Other examples are constructed by the sudden catastrophic floods (jökulhlaups) when ice dams fail, or when volcanoes erupt beneath a glacier. Sands and gravels predominate; clay sized particles are flushed from the system by water or are blown offshore by wind. Analogous deposits in North America, following several thousand years of pedogenesis after the Wisconsinian glaciation, have weathered to Podzols, Cambisols and Luvisols.

Bibliography

Gomez, B., Smith, L.C., Magilligan, F.J., Mertes, L.A.K., and Smith, N.D., 2000. Glacier outburst floods and outwash plain development: Skeiðarársandur, Iceland. *Terra Nova*, **12**: 126–131.

Cross-reference

Ice Erosion

OVERBURDEN

The loose material including soil that overlies bedrock. Also used in mining engineering to refer to all geological materials overlying any deposit of economic value.

P

PADDY SOILS

The soils of rice paddies may be true Gleysols in origin, but are more often anthraquic soil units in some other Reference Soil Group.

However, wet cultivation of the surface soil of paddy soils produces a puddled layer with a thin, compacted and slowly permeable plow pan or sole at the depth of cultivation. The combination of puddled layer and plow pan constitutes an anthraquic horizon and shows redoximorphic characteristics due to seasonal flooding for rice cultivation. Below the puddled layer and the plow pan is a hydragric horizon, which may have indications of reduction in pores and channels, and/or precipitation of Fe and Mn in the soil matrix indicating oxidation. The combination of human induced anthraquic and hydragric horizons is diagnostic for Hydragric Anthrosols, the WRB designation for paddy soils.

An important environmental issue related to paddy soils is the fact that redox potential when the fields are flooded is low enough for the generation of methane (CH_4), one of the greenhouse gases significantly implicated in global warming (Wassman et al., 2000).

Bibliography

Wassman, R., Lantin, R.S., and Neue, H.-U., 2000. *Methane Emissions from Major Rice Ecosystems in Asia*. Dordrecht: Kluwer, 394 pp.

Cross-references

Anthrosols
Puddling
Redox Reactions and Diagrams in Soil

PALEOSOL

An ancient soil in which the soil-forming processes are no longer active, by virtue of the fact that the soil has been buried under a later geological formation such as an eolian sand or a volcanic ash or flow.

Bibliography

Retallack, G.J., 2001. *Soils of the Past: An Introduction to Paleopedology*, 2nd edn. Oxford; Malden, MA: Blackwell Science, pp. 404.

PALLID ZONE

A relatively pale colored unit in a lateritic profile, made up usually of a quartz, kaolinite, iron oxyhydroxide assemblage, and considered to have lost iron by leaching.

According to Tardy (1992, p. 386) it is a term to be avoided, the preferred term being lithomarge: a fine saprolite.

Bibliography

Tardy, Y., 1992. Diversity of terminology of lateritic profiles. (Chap. 15). In Martini, I.P., and Chesworth, W., eds., *Weathering, Soils & Paleosols*. Amsterdam: Elsevier, pp. 379–405.

Cross-references

Duricrusts and Induration
Saprolite, Regolith and Soil

PALUDIFICATION

The accumulation of peat and the formation of peatland by colonization from an existing peat mass, accompanied by a local rise in the water table. A secondary stage of peatland formation in contrast to the primary process of the filling in of a body of surface-water (terrestrialization).

Bibliography

Gorham, E., Lehmana, C., Dykeb, A., Janssensc, J., and Dykeb, L., 2007. Temporal and spatial aspects of peatland initiation following deglaciation in North America. Quat. Sci. Rev., **26**: 300–311.

Cross-references

Mire
Peat

PAN

A hard and typically impermeable subsurface layer in a soil. Hardness may be a function of cementation, compaction or a high clay content of soil. The commonest varieties are iron pan, where the cement is iron carbonate; clay pan, a distinct clay-packed layer within a profile; and plow pan, a compacted layer resulting from repeated plowing and an integral part of the human-induced anthraquic horizon of Hydragric Anthrosols. A less common usage is peat or moor pan for a hard layer sometimes found in moorland at the bottom of a peatbog, see also *Fragipan*.

PARALITHIC

An adjective used in both Soil Taxonomy and WRB to denote a weathered rock contact within a profile. As opposed to a lithic, or continuous rock contact, paralithic implies the presence of breaks and fissures which allow roots to penetrate the underlying rock. The term is synonymous with the original definition of saprolite.

Cross-reference

Saprolite, Regolith and Soil

PARENT MATERIAL

The C horizon of a soil, upon which the solum has developed. Although weathered, it is considered to be below the level at which pedogenic weathering, and other soil-forming processes operate.

The conventional understanding is that the influence of organic components at this depth in a profile is sufficiently attenuated as to be negligible, at least macroscopically. Any weathering that takes place is judged to be geological.

Parent material is one of the major factors in soil formation.

Cross-references

Factors of Soil Formation
Geology and Soils

PARENT ROCK

The solid, continuous bedrock that may become parent material of the parent material of soil, saprolite, regolith, gossan and other products of surficial weathering.

PARTICLE DENSITY

Particle density is the density of the solid particles that collectively make up a soil sample. The value is commonly expressed in grams per cubic centimeter. The common range among soils is 2.55 to 2.70 g cm^{-3}. A value of 2.65 is therefore used generally, exceptions being made where great accuracy is required or where soils are known to depart from the common range.

Particle density of a soil sample is actually a weighted mean value for the various kinds of minerals and humus. The measured density depends on the relative proportions of constituent minerals and humus. Densities of widely occurring minerals in the sand and silt fractions are quartz 2.65, feldspars 2.5 to 2.8, micas 2.7 to 3.3, and apatite 3.1 to 3.3 g cm^{-3} (Kretz, 1974–1975). Densities of clay minerals range from 2 to 3, but many are near 2.65 g cm^{-3}. The density of humus is usually less than 1.5 g cm^{-3}. Particle densities of samples of surface soil containing humus in fair quantities are commonly between 2.5 and 2.6 g cm^{-3}.

Information on particle density is needed for estimates of porosity, air-filled voids, settling rates of particles in fluids, and transport of particles by wind or water. Particle density of a soil sample is measured by first determining its mass after drying to 105 °C and then dividing that mass by the volume of the particles, excluding spaces among them. Rather precise measurements can be made with a good balance and a volumetric flask (Natural Resources Conservation Service, 2004). A specially designed flask, called a *pycnometer*, can be filled to a precise volume because it has a ground-glass stopper pierced by a capillary opening through which water in excess of the volume overflows. Use of an ordinary volumetric flask results in a larger error of estimate.

Four weights are needed: weight of oven-dry flask, W_a; weight of flask filled with distilled water at room temperature, W_w; oven-dry weight of flask plus soil sample, W_s; and weight of flask plus soil plus distilled water needed to fill the flask when it contains the soil sample, W_{sw}. Temperature of the water must be known to find the density of the water ρ_w in standard tables. Particle density (ρ_p) is then given by the equation:

$$\rho_p = \frac{\rho_w (W_s - W_a)}{(W_s - W_a) - (W_{sw} - W_w)}$$

Preboiled, distilled water stored in a stoppered bottle at room temperature is used in the determination. Any entrapped air can be eliminated by first placing the soil sample in the flask or pycnometer, partially filling it with water, gently boiling the contents with agitation, then stoppering and cooling to room temperature. The flask is then completely filled with water before determining W_{sw}.

About 10 g of dry soil are needed if a 50 ml pycnometer is used. When an ordinary volumetric flask is used instead, a larger sample should also be taken to help offset the reduced precision in filling that flask.

An error of 0.0003 g cm^{-3} in the density results from a weighing error of 1 mg on a 10 g soil sample if there is no error in measuring water volume. Greater errors result from inexact measurements of liquid volume in volumetric flasks. If W_{sw} is based on a volume that exceeds the flask volume by 0.2 ml and W_w on a volume 0.2 ml less than the mark on the flask, the compounded particle density error is 0.07 g cm^{-3} on a 40 g soil sample.

George R. Blake

Bibliography

Kretz, R., (compiler), 1974–1975. Physical constants of minerals. In Weast, R.C., ed., *Handbook of Chemistry and Physics*, 55th edn. Cleveland, OH: Chemical Rubber Co., pp. B193–B197 (any recent edition).

Natural Resources Conservation Service, 2004. *Soil Survey Laboratory Methods Manual*. Soil Survey Investigations Report No. 42 Version 4.0 (edited by Burt, R.) Washington, D.C.: United States Department of Agriculture Natural Resources Conservation Service. 700 pp.

Cross-references

Bulk Density
Soil Engineering

PARTICLE-SIZE DISTRIBUTION

Particle-size distribution of soils and sediments is important to many of their properties. Whether soils consist of sand, clay, silt or some mixture of those and silt, the size distribution affects the movement and retention of water, consistency tilth, and capacity to shrink and swell to name but a few properties. Moreover, particle-size distribution is influenced little by tillage or other manipulation unless it is drastic. Most soil classification systems therefore use particle-size distribution as one criterion.

Early work in particle-size analysis

Attempts to measure particle-size distribution of soils date back to the seventeenth century. Keen (1931) mentions the investigations by Houghton reported in "*A Collection of Letters for the Improvement of Husbandry and Trade*" dated 1681. He mixed known weights of soil and water and then decanted the suspension into a second container. After materials in the two containers had dried, he weighed them and compared relative amounts of coarse and fine materials. Additional studies showed that the fine materials held more water than the coarse ones. Sir Humphrey Davy of England standardized Houghton's method and described it in "*Elements of Agriculture*," published in 1813 (Keen, 1931). Davy also realized that particle-size distribution affected the chemical properties of soils. Oddly enough, sieves were not used in these early investigations, although the Greeks and Romans had used them in mining operations from about 150 B.C. From these early beginnings of measuring particle-size distribution, many systems of size limits have been developed, eleven of which are shown in Figure P1.

Particle-size limits in American soil science

The U.S. Department of Agriculture (USDA) system (Soil Survey Staff, 1993) is the standard for the National Cooperative Soil Survey and is used in all soil science related to agriculture in the United States. The system is based on the fine earth (less than 2.0 mm in diameter) and divides that into seven size classes. These classes are actually subdivisions of a continuum, and the changes in characteristics are therefore gradual across the full range. Subdividing the continuum is necessary,

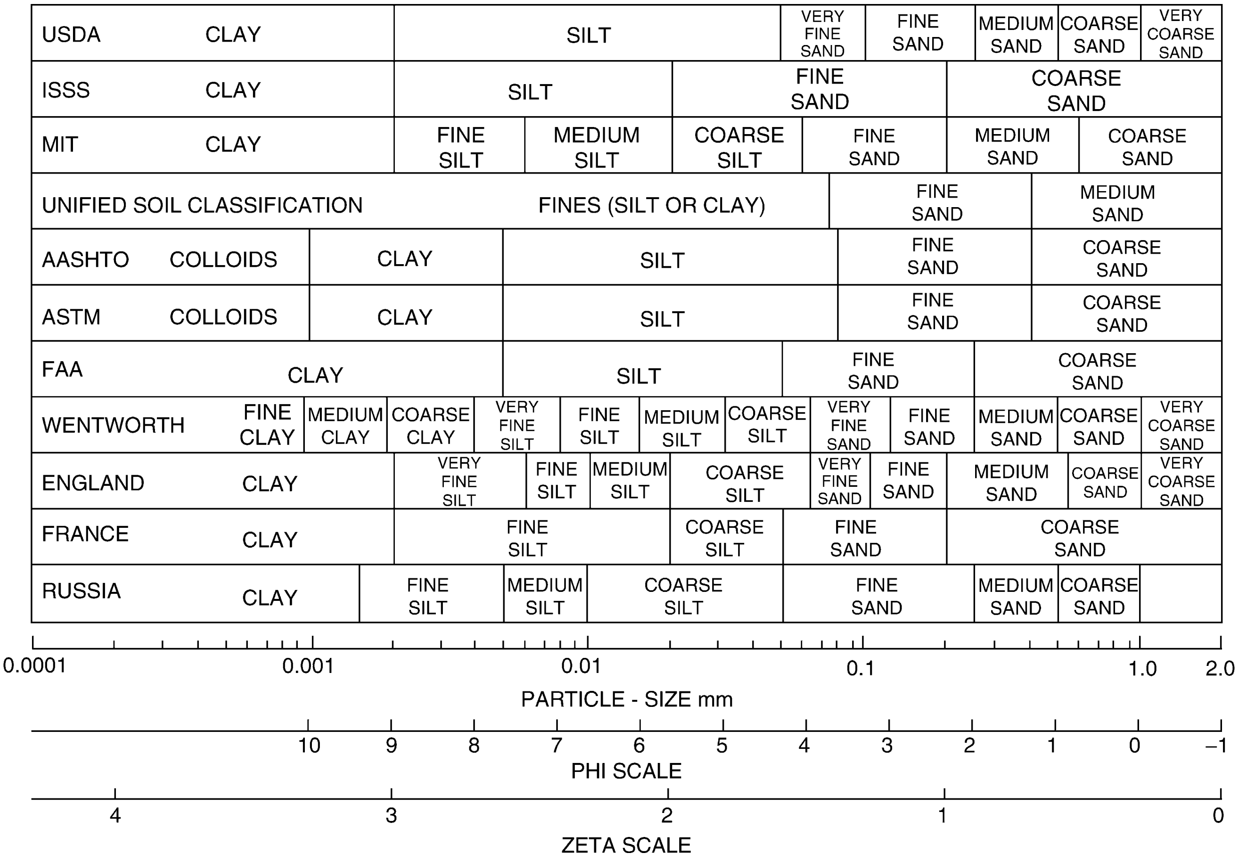


Figure P1 Particle-size class limits in several systems.

however, to permit the identification and description of soil materials. The current size limits in the USDA system are given as the first line in Figure P1.

The seven classes in the system evolved partly by accident. Thus, for example, the size limits for the subdivisions of sand were originally used by Osborne (1887) because they fit his eyepiece micrometer (Hopkins, 1899). The early upper limit of 0.005 mm for clay was set for a similar reason; measuring diameters of smaller particles was troublesome. The limit of 0.005 mm was replaced by 0.002 mm 40 years ago (Shaw and Alexander, 1936). Dispersing of samples was then more complete, and it had also been learned that proportions of primary minerals such as feldspars dropped off in soil materials finer than 0.002 mm. Moreover, that limit had been adopted earlier by the International Society of Soil Science. The agricultural significance of particle-size limits in the USDA system, as well as those in some other systems, had been discussed in a report of a Committee on Particle Size and Distribution (1967) of the Soil Science Society of America.

Particle-size limits of the International Society of Soil Science

The size limits adopted by the International Society of Soil Science in 1913 are shown as the second line in Figure P1. These limits were proposed by Atterberg (1905) on the basis of studies in southern Sweden. He first examined the behavior of many soil separates with narrow size ranges, e.g., 1–2 mm, 0.1–0.2 mm, 0.02–0.05 mm, and 0.001–0.002 mm. Measurements were made of water-holding capacity, rate of capillary rise, tendency to coagulate in suspension, and Brownian movement. From these studies, Atterberg concluded that four size classes for fine earth less than 2.0 mm in diameter would be adequate. Further, he proposed that the class intervals could be two times powers of 10. He also suggested that particles coarser than 2.0 mm could be described by the same approach; however, that part of his proposal was not adopted.

Summarizing his observations, Atterberg (1908) reported that 0.2–2.0 mm separate had little water-holding capacity and that capillary rise was both slow and small. Soil materials of that size would not hold enough water to sustain a crop in southern Sweden for a week. In contrast, the 0.02–0.2 mm separate would hold an amount of water equivalent to the highest average rainfall of any month in Sweden. Capillary rise within 24 h was most rapid in that separate; water removed by growing plants during the day could be replaced the subsequent night. Particles of the 0.02–0.002 mm separate were no longer visible to the naked eye, and suspensions could be coagulated by salts. Capillary rise was much slower but greater over a long period of time. Interstices among particles of this separate were too small for entry by root hairs. Particles finer than 0.002 were the largest to exhibit active Brownian movement. A suspension of that separate was readily coagulated by salt solutions, and capillary rise was very slow.

Atterberg (1908) also proposed that each of the four size classes of soil particles could be subdivided if necessary, suggesting that limits of six as well as two times powers of 10 would be suitable. This proposal was not adopted by the International Society of Soil Science, but it has been revived by (Terzaghi and Peck, 1948) and is now part of the MIT classification of particle sizes. This is shown as the third line in Figure P1. The ISSS and MIT systems have size classes that can be represented conveniently in logarithmic graphs, which are useful for some purposes.

Particle-size limits in civil engineering and geology

The American Association of State Highway and Transportation Officials (AASHTO) had long used particle-size distribution in designing subgrades for roads and highways (Highway Research Board, 1945; AASHTO, 2004). Size limits in the AASHTO system, shown as the fifth line in Figure P1, were adapted from those of the USDA system many years ago. The upper size limit of 0.001 mm for colloids goes back to a subdivision of the clay fraction when its upper size limit was 0.005 mm in the USDA system. Several subdivisions of the gravel fraction (>2.0 mm) are made in the AASHTO system to aid in evaluating aggregate for construction.

The particle-size limits of the AASHTO system have been adopted by the American Society for Testing and Materials (ASTM, 2002), as shown in the sixth line in Figure P1. The system shared by the two organizations is used in construction of highways and other earth structures.

The size limits and nomenclature in the system of the Federal Aviation Agency (U.S. Department of Commerce, 1962) differ slightly from those of the AASHTO and ASTM systems, as shown in the seventh line in Figure P1. The upper size limit of the clay fraction is the same in the three systems, but other limits differ. The FAA system was designed to evaluate soils and sediments for airport construction.

A fourth system originally developed to evaluate soils and sediments for construction of both roads and airfields is known as the Unified Soil Classification (ASTM, 2002). This system was developed by Casagrande for the U.S. Corps of Engineers during World War II. Subsequently the system was adopted by the Bureau of Reclamation, U.S. Department of Interior, and the criteria were modified somewhat to cover construction of earth dams. The particle-size limits in this system are much the same as those of the AASHTO, ASTM, and FAA systems for the coarser fractions, but the finer fractions are lumped together, as shown in the fourth line in Figure P1. The silt and clay fractions are not separated. Furthermore, a diameter of 0.074 mm was set as the upper limit for fine-grained materials with undesirable engineering properties (ASTM, 2002; U.S. Department of Interior, 1998).

The Wentworth particle-size classification is used primarily in sedimentology. The size limits are shown as the eighth line in Figure P1. Introduced originally by Udden and modified by Wentworth (Pettijohn, 1975), the system has a logarithmic scale with one limit set at 1 mm and others successively halved or doubled. A logarithmic scale facilitates certain analyses of data.

Krumbein (1936) represented the geometric intervals of the Wentworth scale on an arithmetic scale by means of the relationship:

$$\text{Phi scale number} = -\log_2(\text{particle-size limit in mm})$$

The resulting scale is shown near the bottom of Figure P1. Krumbein also recommended a change in the ISSS system to what he called the Zeta scale to represent geometric intervals on an arithmetic scale:

$$\begin{aligned}&\text{Zeta scale number}\\&\quad = 0.301 - \log_{10}(\text{particle-size limit in mm})\end{aligned}$$

The Zeta scale is shown at the bottom of Figure P1. The transformations provide a better framework for statistical analysis.

Particle-size limits used in Europe

West-European soil scientists use several systems of particle-size limits. A discussion of these systems is given in a report compiled by the West-European Working Group on Soil Structure (1967), International Society of Soil Science. Although the report deals primarily with methods for measuring other physical and chemical and mineralogical properties of soils, particle-size limits are given in many cases. Figure P1 shows three sets of particle-size limits used in Europe to indicate differences from the USDA and ISSS systems.

The Soil Survey of England and Wales uses particle-size limits that include those of the ISSS system and provides additional subdivisions (Hodgson, 1974). A coarser upper limit is also used for the silt fraction (0.06 rather than 0.02 mm). These size limits are shown as the ninth line in Figure P1. The spans of particle size classes in England and Wales provide almost equal divisions on a logarithmic scale.

Like the system in England and Wales, the Soil Science Laboratory in Versailles, France, uses particle-size limits that include those of the ISSS system but provide additional subdivisions, as shown in the tenth line in Figure P1. The upper size of silt is set at 0.05 rather than at 0.02 mm limit of the ISSS system. In this respect, the French and USDA systems are the same.

Several systems of particle-size limits used in the former Soviet Union were reported by Kachinskii (1958). The system most commonly used between 1937 and 1957 is shown as the eleventh line in Figure P1. The total number of size classes in that system matches the one of the USDA, but the size limits themselves differ. Kachinskii (1958) considered size fractions arbitrary separations for convenience rather than direct reflections of geologic processes or direct indicators of other soil properties. He also thought that the ISSS system did not have enough classes to give a good picture of particle-size distribution in soils.

Soil texture classes in the United States

Most soils and sediments are mixtures of particles of various sizes. To facilitate the description of these mixtures, classes have been defined according to relative proportions of sand, silt, and clay. The most common set of classes used by American soil scientists are given by the USDA *texture triangle* (Soil Survey Staff, 1993), shown in Figure P2. These classes were defined for their practical value in agriculture. Thus, for example, sands and sandy loams are set apart because the latter retain more water and are less droughty than the former. Clays are more difficult to plow and prepare for crops than loams. Parallel distinctions apply generally. Names for the texture classes other than subdivisions of sands and sandy loams are given in Figure P2. One texture class in the system is called *loam*, which refers to soil material with certain proportions of sand, silt, and clay. That meaning is much different from the one that was long popular in English, namely, a dark, well-structured, and humus-rich soil. Texture class subdivisions have been devised for sands and sandy loams in addition to those that can be shown in the triangle. The names and definitions of these additional texture classes are given in Table P1.

Field estimates of texture are related to laboratory determinations of particle-size distribution by means of the texture triangle. Field soil scientists estimate the textures of soil materials by working them between their fingers. Accurate estimates require practice and periodic checks on samples of known texture. General descriptions of the field characteristics of soil materials of major texture classes, from the *Soil Survey Manual* (Soil Survey Staff, 1993), are given below:

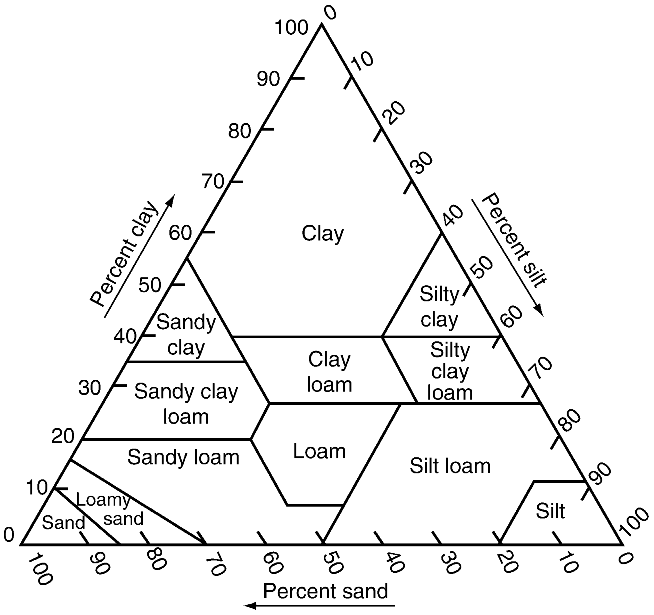


Figure P2 U.S. Department of Agriculture textural classification chart for soil material <2 mm.

- *Sand:* Sand is loose and single grained. The individual grains can be readily seen or felt. Squeezed in the hand when dry, it will fall apart when the pressure is released. Squeezed when moist, it will form a cast but will crumble when touched.
- *Sandy loam:* A sandy loam is a soil containing much sand but which has enough silt and clay to make it somewhat coherent. The individual sand grains can readily be seen and felt. Squeezed when dry, it will form a cast that will readily fall apart, but squeezed when moist, it will form a cast that will bear careful handling without breaking.
- *Loam:* A loam is a soil having a relatively even mixture of different grades of sand and of silt and clay. It is mellow with a somewhat gritty feel yet fairly smooth and slightly plastic. Squeezed when dry, it will form a cast that will bear careful handling, while the cast formed by squeezing the moist soil can be handled quite freely without breaking.
- *Silt loam*: A silt loam is a soil having a moderate amount of the fine grades of sand and only a small amount of clay, over half the particles being of the size called "silt." When dry, it may appear cloddy, but the lumps can be readily broken, and when pulverized it feels soft and floury. When wet, the soil readily runs together and puddles. Either dry or moist, it will form casts that can be handled freely without breaking, but when moistened and worked between thumb and finger, it will not "ribbon" and will give a broken appearance.
- *Clay loam:* A clay loam is a fine-textured soil that usually breaks into clods or lumps that are hard when dry. When the moist soil is worked between the thumb and finger, it will form a thin "ribbon" that will break readily, barely sustaining its own weight. The moist soil is plastic and will form a cast that will bear much handling. When kneaded

Table P1 Percentage of sand sizes in subclasses of sand, loamy sand, and sandy loam basic textural classes as defined by the U.S. Department of Agriculture

Basic soil class	Subclass	Soil separates				
		Very coarse sand, 2.0–1.0 mm	Coarse sand, 1.0–0.5 mm	Medium sand, 0.5–0.25 mm	Fine sand, 0.25–0.1 mm	Very fine sand, 0.1–0.05 mm
Sands	Coarse sand	25% or more		Less than 50%	Less than 50%	Less than 50%
	Sand	25% or more			Less than 50%	Less than 50%
	Fine sand		Less than 25%		50% or more	Less than 50%
	Very fine sand					50% or more
Loamy sands	Loamy coarse sand	25% or more		Less than 50%	Less than 50%	Less than 50%
	Loamy sand		25% or more		Less than 50%	Less than 50%
	Loamy fine sand		Less than 25%		50% or more	Less than 50%
	Loamy very fine sand					50% or more
Sandy loams	Coarse sandy loam	25% or more		Less than 50%	Less than 50%	Less than 50%
	Sandy loam		30% or more		Less than 30%	Less than 30%
		Less than 25%			Less than 30%	Less than 30%
	Fine sandy loam				30% or more	Less than 30%
				-or-		
			Between 15 and 30%			30% or more
	Very fine sandy loam		Less than 15%		More than 40%[a]	

[a] Half of fine sand and very fine sand must be very fine sand.

in the hand, it does not crumble readily but tends to work into a heavy compact mass.

- *Clay:* A clay is a fine-textured soil that usually forms very hard lumps or clods when dry and is quite plastic and usually sticky when wet. When the moist soil is worked between the thumb and fingers, it will form a long, flexible "ribbon." Some fine clays very high in colloids are friable and lack plasticity in all conditions of moisture.

Not all the texture classes used in the United States are covered by the preceding descriptions. The nature of the undescribed classes can be inferred, however, from their names, e.g., sandy clay loam. That class is a clay loam containing more sand than normal for clay loams.

The boundaries between adjoining soil texture classes are limits in a continuum. Some soil materials consequently have textures that are at or near the shared limit of two classes. Practice plus continuing evaluation of field estimates are necessary for determination of the textures of such soil materials. Even then, errors are possible, but fortunately placing a given specimen in one or the other of adjacent classes is not a serious error.

Particle-size classes at the family level in soil taxonomy

In the USDA soil classification system (Soil Survey Staff, 1999), efforts were made to define the family classes so that they would have meaning to both plant growth and engineering. The principal criteria for family classes are: particle size, mineralogy, reaction, soil temperature, and soil depth. Other characteristics are used as criteria in some subgroups.

The particle-size classes at the family level differ from soil texture classes for several reasons. The objectives to be served by the two systems are not the same. Furthermore, particle-size classes for families center on the deeper profile, a specified vertical thickness called the *control section*, rather than on any sample of soil material. Another distinction follows from consideration of particles of all sizes rather than the fine earth below a diameter of 2.0 mm, as is done in soil texture classes. The control section, as defined for the sub-orders and great groups in the classification system, is not uniform across the board. Most commonly, the control section is that part of the profile between depths of approximately 25 and 100 cm (10 and 40 inch).

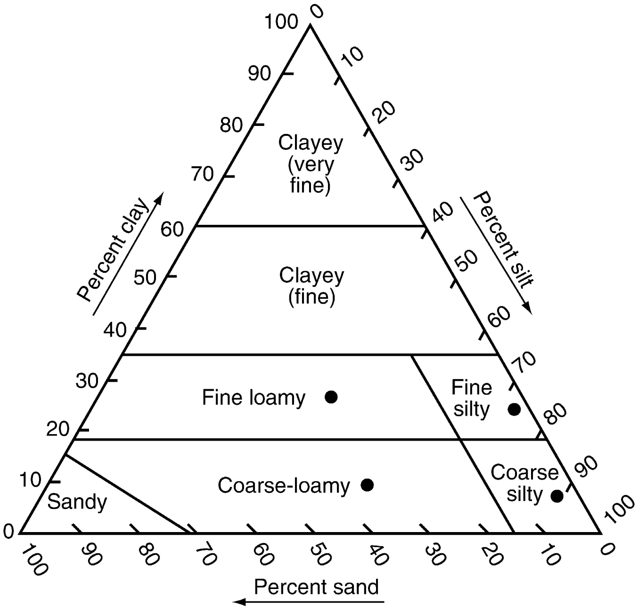
A further difference between the particle-size classes for families and the soil texture classes is the disposition of the very fine sand fraction. Franzmeier et al. (1960) found that soil materials with an upper limit of 0.1 mm, which include the very fine sand separate, would hold water at tensions usable by plants. Coarser separates would have pores too large to hold usable water. Consequently, the very fine sand fraction is included with coarser separates in the fine sand, loamy fine sand, and coarser textured classes. The very fine sand separate is included with silt in very fine sand, loamy very fine sand, sandy loam, silt loam, and finer textured classes. The application of these conventions makes the effective particle-size limit between sand and silt for the family classes much more nearly the same as that of 0.074 mm widely used by civil engineers. Definitions of the particle-size classes are as follows:

- *Fragmental:* Stones, cobbles, gravel, and very coarse sand particles; too little fine earth to fill interstices larger than 1 mm in diameter.
- *Sandy-skeletal:* Rock fragments 2 mm in diameter or larger make up 35% or more by volume; enough fine earth to fill interstices larger than 1 mm; the fraction finer than 2 mm is sandy as defined for the sandy particle-size class.
- *Loamy-skeletal:* Rock fragments make up 35% or more by volume; enough fine earth to fill interstices larger than 1 mm; the fraction finer than 2 mm is loamy as defined for the loamy particle-size class.
- *Clayey-skeletal:* Rock fragments make up 35% or more by volume; enough fine earth to fill interstices larger than 1 mm; the fraction finer than 2 mm is clayey as defined for the clayey particle-size class.
- *Sandy:* The texture of the fine earth is sand or loamy sand but not loamy very fine sand or very fine sand; rock fragments make up <35% by volume.
- *Loamy:* The texture of the fine earth is loamy very fine sand, very fine sand, or finer, but the amount of clay is <35%; rock fragments are <35% by volume.

- *Coarse-silty:* By weight, 15% or more of the particles are fine sand (diameter 0.25–0.1 mm) or coarser, including fragments up to 7.5 cm in diameter; <18% clay in the fine-earth fraction.
- *Fine-loamy:* By weight, 15% or more of the particles are fine sand or coarser; including fragments up to 7.5 cm in diameter; 18 through 35% clay in the fine-earth fraction (<30% in vertisols).
- *Coarse-silty:* By weight, <15% of the particles are fine sand or coarser, including fragments up to 7.5 cm in diameter; <18% clay in the fine-earth fraction.
- *Fine-silty:* By weight, <15% of the particles are fine sand or coarser, including fragments up to 7.5 cm in diameter; 18 through 34% clay in the fine-earth fraction (<30% in vertisols).
- *Clayey:* The fine earth contains 35% or more clay by weight, and rock fragments are <35% by volume.
- *Fine:* A clayey particle-size class that has 35 through 59% clay in the fine-earth fraction (30 through 59% in vertisols).
- *Very fine:* A clayey particle-size class that has 60% or more clay in the fine-earth fraction.

The class limits and names for the particle-size classes at the family level are shown by a triangular graph in Figure P3. The system provides for either seven or eleven classes, the choice depending on which better sets apart families that differ in usefulness to one or both of agriculture and engineering. Certain classes such as coarse-loamy, fine-loamy, coarse-silty, and fine-silty are optional in some subgroups. Full definitions and guides for use of the family classes are given in the monograph (Soil Survey Staff, 1993).

A set of modifiers can be used with the names of some great groups and subgroups to eliminate the need for particle-size classes at the family level. The mineralogy is also a criterion in classes above the family level for soils derived from volcanic ash.



● Very fine sand (0.05–0.01 mm) is treated as silt

Figure P3 U.S. Department of Agriculture particle-size classes for the fine-earth fraction at the family level.

Because of their effects on moisture relationships, strongly contrasting particle-size classes within the control section form bases for family distinctions. The break in materials introduces differences in pore sizes, which in turn alter water movement and retention. At present, 40 combinations of contrasting materials within the control section are used in setting apart families within the United States. This total consists of combinations that have been found; others are possibilities.

Soil texture classes in other systems

Various texture classes differing from those used in soil science in the United States are used in engineering operations and in other countries. The AASHTO, ASTM, and FAA systems and the Unified Soil Classification, applied in the design and construction of one or more of roads, airports, and earth dams, group soils partly on the basis of particle-size distribution and partly on the basis of the Atterberg plastic and liquid limits.

Additional and different systems of texture classes are used in soil science in other countries. Names much like those in the United States are used in Australia, England and Wales, and New Zealand, but each country has its own set of definitions. Australia and New Zealand use the ISSS size limits in defining texture classes (McKenzie, 2004; Hewitt, 1998). The Soil Survey of England and Wales includes the ISSS size limits but adds others for defining texture classes (Hodgson, 1974). Several systems of texture classes have been used in the Soviet Union (Kachinskii, 1958; Stolbovoi, 2000). More examples of differing systems could be included, but these four indicate the current variety in soil texture classes throughout the world.

Particle-size analyses

Particle-size distribution of soil samples is determined partly by sieving and partly by sedimentation. The sand fractions are separated from the silt and clay by sieving, which is also used to determine proportions of the size fractions of sand. The silt and clay fractions are determined by sedimentation, measurements being made with either a pipette or hydrometer Gee and Or (2002). Separation of the sand from the silt and clay may be done either before or after determination of the two latter fractions.

One or more pretreatments are normally used for particle-size analyses, also known as *mechanical analyses*. For samples containing organic matter, some treatment to destroy it is usually a first step. Samples must also be treated with compounds such as sodium metaphosphate to effect dispersion.

Dry sieving of sand to determine the proportions of the different size fractions is done with a nest of sieves having the proper openings. The National Bureau of Standards and the American Society for Testing and Materials have adopted specifications that ensure consistency among sieves, but careful measurement and periodic inspection of sieve openings are still desirable. Difficulties due to shapes of sieve openings and soil particles and to time of shaking cannot be eliminated. Consequently, a standard procedure must be followed to obtain comparable results. Specific techniques are given by Gee and Or (2002) and the Natural Resources Conservation Service (1996).

Pipette and hydrometer methods

The pipette technique was introduced in the early 1920s by Jennings and Robinson (Gee and Or, 2002). The method involves extracting a known volume of a suspension and dispersing solution to measure density of the suspension at a specific depth after the critical particle-size fraction has settled to that depth according to *Stokes Law*. Stokes Law is an equation that relates the velocity at which a spherical particle of a particular diameter falls in a medium. The equation is given in this form:

$$V = \frac{2}{9}\frac{(d_p - d_1)gr^2}{\mu}$$

where V is velocity of fall in cm s^{-1}, d_p is the density of the particles (usually assumed to be about 2.6 g cm^{-3} for soils), d_1 is the density of the liquid, g is the constant of gravity, r is the radius of the particle, and μ is the viscosity of the liquid. The material extracted in the pipette is weighed, corrected for the weight of the dispersing reagent, and the total weight of clay is calculated from the amount in the aliquot. Specific techniques are given by Gee and Or (2002) and the Natural Resources Conservation Service (1996). The pipette method is the standard technique used to characterize soils.

The hydrometer method is also an attempt to measure density of a suspension at a particular depth. To do this requires a hydrometer of a particular design and a controlled laboratory procedure that takes into account the temperature and time of sedimentation. This method also depends on Stokes Law. Procedures for the hydrometer method are given by Gee and Or (2002) Natural Resources Conservation Service (1996). The hydrometer method is used mostly by engineers to determine particle-size distribution.

Neither method is completely free of difficulties, but they are the best developed so far to measure particle-size distribution. A comparison of the two methods by Liu et al. (1966) showed that with few exceptions, similar data were obtained by the two methods. In general, the hydrometer analyses showed slightly higher clay contents than the pipette analyses. The traditional techniques have not yet been replaced in routine soil testing by any of the new instrumental techniques that have been developed for industrial purposes, though particle size by image analysis is now an accepted research technique. Allen (1996) reviews the state of the art.

Gary C. Steinhardt

Bibliography

Allen, T., 1996. *Particle Size Measurement*, 5th edn, Vol. I. Berlin Heidelberg New York: Springer, 552 pp.

American Association of State Highway and Transportation Officials, 2004. Terms relating to subgrade, soil aggregate, and fill materials. AASHTO Designation: M146-91. In *Standard Specifications for Transportation Materials and Methods of Sampling and Testing*, Part 1, 685 pp.

ASTM (American Society for Testing and Materials), 2002. ASTM standards relating to environmental site characterization. West Conshohocken, PA: ASTM International, 2074 pp.

Atterberg, A., 1905. Die rationelle klassifikation der sande und kiese. *Chemiker Zeitung*, **29**: 195–198.

Atterberg, A., 1908. Studien auf dem Gebiete der Bodenkunde, *Landwirtschaftliche Versuchs-Stationen*, **69**: 93–143.

Committee on Particle Size and Distribution, 1967. Considerations relative to a common particle-size scale of earthy materials, *Soil Sci. Soc. Am. Proc.*, **31**: 579–584.

Franzmeier, D.P., Whiteside, E.P., and Erickson, A.E., 1960. Relationship of texture classes of fine earth to readily available water, *Proc. Seventh Int. Cong. Soil Sci.* (*USA*), **1**: 354–363.

Gee, G.W., and Or, D., 2002. Particle-size analysis. In Dane, J.H., and Topp, G.C., co-eds., *Methods of Soil Analysis. Part 4, Physical Methods*. Madison, WI: Soil Science Society of America, pp. 255–293.

Hewitt, A.E., 1998. *New Zealand Soil Classification.* Lincln, NZ: Manaaki Whenua Press, 133 pp.

Highway Research Board, 1945. Classification of soils and sub-grade materials for highway construction, *Proc. 25th Annu. Meet. Highway Res. Board*, 376–382.

Hodgson, J.M., ed., 1974. *Soil Survey Field Hand-book: Describing and Sampling Soil Profiles*, Soil Survey of England and Wales Tech. Mon. No. 5, pp. 22–25.

Hopkins, C.G., 1899. *A plea for Scientific Basis for the Division of Soil Particles in Mechanical Analysis. U.S. Depart. Agric.*, Div. Chem. Bull. No. 56, pp. 64–66.

Kachinskii, N.A., 1958. *Mechanical and Microaggregate Composition of Soils: Methods of Investigation*, translated from Russian, 1966. Jerusalem: Israel Program for Scientific Translations, 134 pp.

Keen, B.A., 1931. *The Physical Properties of the Soil.* London: Longmans, 381 pp.

Krumbein, W.C., 1936. The application of logarithmic moments to size frequency distribution of sediments, *J. Sed. Petrol.*, **6**: 35–47.

Liu, T.K., Odell, R.T., Etter, W.C., and Thornburn, T.H., 1966. A comparison of clay contents determined by hydrometer and pipette methods using reduced major axis analysis. *Soil Sci. Soc. Am. Proc.*, **30**: 665–669.

McKenzie, N., 2004. *Soils, an Australian Viewpoint.* Collingwood, VIC: CSIRO. 416 pp.

Natural Resources Conservation Service, National Soil Survey Center, 1996. *Soil Survey Laboratory Methods Manual*. Washington, DC, 693 pp.

Nimmo, J.R., 2002. Aggregate stability and size distribution. In Dane, J.H., and Topp, G.C., co-eds., *Methods of Soil Analysis. Part 4, Physical Methods.* Madison, WI: Soil Science Society of America, pp. 317–361.

Osborne, T.B., 1887. The methods of mechanical soil analysis, Conn. Agric. Exp. Sta. Ann. Rept., 1887, pp. 141–158.

Pettijohn, F.J., 1975. *Sedimentary Rocks*, 3rd edn. New York: Harper, 27–31.

Shaw, T.M., and Alexander, L.T., 1936. A note on mechanical analysis and soil textures. *Soil Sci. Soc. Am. Proc.*, **1**: 303–304.

Soil Survey Staff, 1993. *Soil Survey Manual*. Washington DC: USDA, 437 pp.

Soil Survey Staff, 1999. *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys*. Washington, DC: USDA, 869 pp.

Stolbovoi, V., 2000. *Soils of Russia: Correlated with the Revised Legend of the FAO Soil Map of the World and World Reference Base for Soil Resources*. RR-00-13. Laxenburg, Austria: International Institute for Applied Systems Analysis (IIASA), 111 pp.

Terzaghi, K., and Peck, R.B., 1948. *Soil Mechanics in Engineering Practice.* New York: Wiley, 566 pp.

U.S. Department of Commerce, Federal Aviation Agency, 1962. *Airport Paving*. Washington, DC: U.S. Government Printing Office, 187 pp.

U.S. Department of Interior, Bureau of Reclamation, 1998. *Earth Manual*, 3rd edn. Washington, DC: U.S. Government Printing Office, 329 pp.

West-European Working Group on Soil Structure, Int. Soc. Soil Sci., 1967. *West-European Methods for Soil Structure Determination*. Ghent, Belgium: Faculty of Agricultural Sciences, State University, 529 pp.

Cross-references

Mineral Analysis (Geochemistry Volume)
Soil Engineering
Soil Pores

PASTURE

An area of the land surface covered principally by grasses, set aside for the grazing of farm animals. (see *Rangeland*).

PEAT

The classic definition of peat is an organic sediment, pale brown to black in color, formed under waterlogged conditions from plant (mosses, briophites, grasses, sedges, bushes and trees) and animal remains. Peat has a fibric or amorphous structure and variable amounts of C, N, H and O. Nevertheless, this description does not reflect its ecological relevance, which arises from the fact that it is the main component of peatlands (see *Mire*). Consequently, more dynamic definitions based on pedogenetic properties are currently preferred.

The Irish Peatland Conservation Council (2001) defines peat as:

> "*a soil that is made up of the partially decomposed remains of dead plants which have accumulated on top of each other in waterlogged places for thousands of years. Areas where peat accumulates are called peatlands. Peat is brownish-black in color and in its natural state is composed of 90% water and 10% solid material*".

However, only a small proportion of the biomass production of a peatland actually accumulates as peat (approximately 20%). Plant remains decompose while they are in the superficial layers of the soil (acrotelm, see *Mire*) but as the accumulation of organic matter increases peat decomposition decreases. This is due to a decrease in the efficiency of the microorganisms to degrade the organic matter under high acidity, low oxygen availability and the inhibitory effect of the high concentration of alelopathic substances typical of deeper peat layers (catotelm, see *Mire*).

With its low bulk density and very high porosity, peat normally contains large amounts of water, outweighing in fact, the solid component. The solid phase is mainly comprised of organic matter with very small amounts of inorganic material. The organic fraction is made up of 36 to 59% of lignins and similar compounds, their concentration increasing with the degree of decomposition. Carbohydrates vary between 10 and 31%, with a mean value of 20.5%, and in general progressively decrease with the age of the peat. The average composition of the carbohydrate varies with the source of the plant remains, but glucose is by far the most abundant sugar (30–70%). Peats also contain bitumen, a recalcitrant material that is a complex mixture of waxes, asphalt and resins. Its content increases with the age of the peat, that is to say, with humification.

The inorganic fraction depends on the evolution of the organic components, botanical composition, source and nature of the water and the geology of the area. In Sphagnum peats the ash content usually ranges between 1 and 15%. The most abundant elements in minerogenic peat (see *Mire*) are Si, Ca, Fe and Al; followed by Mg, K, P, Na, S, V, Ni, Pb, Mn and Cu. The composition of ombrogenic peat (see *Mire*) is comparable but the concentrations are quite different, since elements with an atmospheric origin (particularly Mg) are more abundant.

The ash content has been a key, though controversial parameter for the identification of peat. For instance, the Canada Soil Survey Committee (1979) establishes the ash content for peats in a 75%, the International Peat Society (1981) considers as peat any soil material or sediment with less than 80% ash content, while the American Association for Testing and Materials (1982) limits the term peat to those substrates with less than a 25% ash content.

Discrepancies may sometimes be resolved by using additional properties, like botanical composition, hydrology, relief, degree of decomposition of organic matter, color and composition of the pore waters, and so on. However, the problem remains.

Given its very high total porosity, peat is one of the most compressible of materials at the surface of the Earth. When it is water saturated, reduced forms of Fe and Mn are present in solution, and if S is present, sulfides, especially pyrite, may precipitate under the influence of sulfur-reducing bacteria. Under extreme reduction, methanogenic bacteria may reduce carbonate C to methane.

Peat as a resource

Peat deposits currently cover about 3% of the total continental surface of the Earth, with an average thickness of 1.3 to 1.4 m. This amounts to between 5000 and 6000 Gm^3 of global peat resource. The structure and biogeochemical properties of peat make it potentially useful in energy production, agriculture, forestry, construction, pharmacology, medicine and even environmental engineering.

For thousands of years peat has been extracted, dried and used as fuel and as construction material. Peatlands were at least partially drained by the Romans at various places in the Empire, the Pevensey and Somerset Levels in Britain for example. Large scale draining programs using wind technology began to transform peatlands into pasture in The Netherlands in the 16th century. Drainage works in the East Anglian Fens, under the direction of Dutch engineers date from the 17th century in Great Britain. In Poland, in the Notec Valley, drainage operations date from the 18th century. In Norway and Germany agriculture on peatlands became general in the mid 19th century, while draining in Russia intensified towards the end of the 19th century. In North America the oldest draining operations seem to date back to the 18th century on the coasts of Virginia, but extensive draining only began in the second half of the 19th century.

The greatest losses of peat deposits have occurred in the temperate areas of the world, where some 25 million ha have been drained or transformed for agricultural and forestry use. New uses of peat in more recent times have had a dramatic and negative impact on peatlands. Particularly in Europe peatlands have been reduced to very small and isolated fragments.

Peat deposits represent a large reservoir of carbon estimated at 329 to 528 Gt – that is approximately 20% of the total carbon content in soils. With its slow rate of decomposition, it is one of the most significant ecosystems in the sequestration of carbon at the surface of the Earth. Human exploitation, mainly through agriculture, currently causes CO_2 emission at a rate of about 426 Mt per year. Total emission since the beginnings of the Industrial Revolution in the 18th century amount to 30 000 Mt of CO_2. This essentially irreversible addition of greenhouse gases to the atmosphere is of great importance in the current debate about global warming.

X. Pontevedra Pombal, J. C. Nóvoa Muñoz,
and A. Martínez Cortizas

Bibliography

American Association for Testing and Materials (ASTM), 1982. *Annual Book of ASTM Standards*. Test. D 2979. Philadelphia: American Society for testing and materials.

Canada Soil Survey Committee (CSSC), 1979. *The system of soil classification for Canadian*. Ottawa: Canada Soil Survey Committee, Pub. 1646, Canadian Department of Agriculture, 83 pp.

International Peat Society (IPS), 1981. *Glossary of Peat and Peatland Terminology.* Finland: International Peat Society.

Irish Peatland Conservation Council (IPCC), 2001. *Action for bogs and wildlife. Irish Peatland Conservation Council.* Accessed at http://www.ipcc.ie.

Cross-references

Mire
Wetland

PED

An individual aggregate or structural unit within an undisturbed soil, as opposed to a clod, which is formed by disturbance (e.g., cultivation).

Cross-reference

Micromorphology

PEDALFER

See *Order*.

PEDOCAL

See *Order*.

PEDOGENIC GRID

See *Redox Reactions and Diagrams in Soil*.

PEDOLOGY AND PEDOGENESIS

Pedology is "*the study of soils that integrates their distribution, formation, morphology, and classification as natural landscape bodies*" (Gregorich et al., 2001). Pedogenesis or soil genesis, as the story of soils and how they have developed, essentially calls upon the whole of pedology in telling the story. An article on pedogenesis therefore, inevitably contains pedology as its subtext. Consequently, in this account, Pedology is introduced through the prism of Pedogenesis.

Pedogenesis includes the events and processes that have occurred, both in the landscape and in the soil profiles themselves. In our global system the pedosphere is an important reactor within the complex of atmosphere, biosphere, hydrosphere and lithosphere. Increasingly important are the interactions with humans. The formation of pedosphere properties results from processes that are conditioned by environmental factors and those of man. Transformations of soil parent materials and biota into mineral and organic components involve disintegration and integration processes of weathering, decomposition, neoformation and transformation. The development of soil structure is often a combination of aggregation and segregation processes. Translocation processes, that is, mobilization, transport, and immobilization of organic and inorganic components adjust to changing external and internal environmental conditions. Collectively the results of the events and processes throughout the history of a soil are its genesis. Soil genesis has been referred to as the heart of pedology because it keeps the vital information flowing and without it the discipline would die.

Soil properties vary widely in their rates of formation and differ significantly in the duration of time for their formation. The characteristic times in Tables P2 and P3 refer to how rapidly a property or regime in a soil may change to attain a state of quasi-equilibrium with changes of its environment, whether natural or human-induced. For example, the composition of air in pores near the soil surface may change considerably in the matter of a few minutes, whereas the chemical destruction of minerals and the neoformation of secondary clay minerals such as kaolinite may take several millions of years. Soil genesis processes include dissolution at the surface of a carbonate concretion as well as the erosional stripping and redeposition of sediments in a stepped landscape of several thousand square kilometers.

There are several schools of thought about soil genesis in the U.S. The earlier school deals mainly with how parent materials accumulate and are exposed to the soil forming processes and the overview of events that give rise to the more stable features. This school of soil genesis is similar to descriptive geography as it relates mainly to the integration of landscape components.

The later school deals mainly with the sophisticated biogeochemical processes that have interacted to give rise to the unique physical, chemical, and biological properties observed in soils today. These schools exist, in large part, due to the improved techniques and tools of technology that enable the

Table P2 Daily to annual characteristic times of soil regimes and selected soil properties

CT (yr)	Regimes	Soil parameters
$<10^{-1}$	Aeration Temperature	Air composition Nitrate composition Near surface porosity and infiltration
10^{-1}–10^{0}	Microbial Managed plant nutrients	General microbiological activity Water capacity pH Solution composition
10^{0}–10^{1}	Moisture Natural fertility Salinity-alkalinity Permafrost	Exchange capacity Acidity Exchangeable cations Extract composition

Table P3 Decadal to millennia characteristic times of some soil features

CT (yr)	Soil features
10^{1}–10^{2}	Organic matter content and composition Clay mineral associations Translocation of soluble mineral components
10^{2}–10^{3}	Primary mineral transformations Chemical composition of mineral components Additional translocations of transformed components
$>10^{3}$	Textural components Particle size distributions Translocation of transformed mineral components

examination of events and processes of short time scales in small spaces in more detail and with greater precision.

A goal of the earlier school was to describe the events and resulting soils with special emphasis on those things that enabled one to classify the soils into a hierarchy of relational information. An interpretation of horizons and features of Soil Taxonomy, the U.S. system of soil classification, according to their assumed persistence is such an example (Table P4). The current school has an important goal of describing microprocesses and events that explain the complexity of morphological and chemical features that are measurable in soils.

Changing technology has permitted scientists to deal more effectively with a broader spectrum of the time and space scales of soil genesis. Mathematical models are more amenable to the data of the current school and descriptive models of relationships are more amenable to the old school. It is artificial, of course, to partition the skill and innovativeness of soil scientists into schools when the blending and merging of ideas are what give rise to the meaningful Earth system histories that are referred to as soil genesis.

Characteristics of a good story

A quality story results from quality science, thus attention to the investigative nature of the scientific method is requisite. Related phenomena, either observed or measured, are suggested as a hypothesis. Alternative explanations of how the relationship developed lead to systematic experiments and measurements that refute or strengthen the proposal. The cycling and interactions of ideas and testing of their validity commonly modify the original hypothesis. The new improved hypothesis needs to be evaluated in other locations and situations. It is unfortunate that most soil genesis stops before this final testing and evaluation leaving behind a fragmented set of non-integrated stories of soil genesis.

The pedological concept of soil genesis involves the accumulation or preservation of unconsolidated earthy materials, called soil parent materials, at or near the Earth's surface where physical, chemical, and biological processes modify and alter the parent material into recognizable soil horizons and features.

Soil parent material is a stratigraphic entity that has either not yet been sufficiently altered to be recognized as distinct soil horizons, or is a prior soil whose initial state (parent material) has been or can be assumed.

In a stratigraphic sense there are two characteristics of importance to understanding the genesis of a soil pedon or set of associated soil pedons.

1. Unity of the soil system. This asks the question of how many unique layers are present in the observed system? Are they functionally related or are they independent segments belonging to prior systems that are now superposed?
2. Uniformity within the soil parent materials. Evidence indicates that in the upper 1 to 2 meters of the soil mantle there are multiple layers, or sediments, that may represent different parent materials. Increasing or decreasing trends or existing properties are often used to estimate the initial state of the layers. These estimates of properties of an initial state are the assumed properties of the parent material at time zero for the pedological properties of interest.

Table P4 Relative persistence of soil horizons and features

Easily altered	Relatively persistent	Persistent
Mollic epipedon	Histic epipedon	Oxic horizon
Ochric epipedon	Umbric epipedon	Kandic horizon
Salic horizon	Albic horizon	Argillic horizon
Gypsic horizon	Cambic horizon	Natric horizon
	Argillic horizon	Petrocalcic horizon
	Spodic horizon	Plinthite
	Calcic horizon	Duripan
	Fragipan	

The properties and patterns of pedological features, which are studied, depend, in great part, on the interest of the investigator, however, as a starting point it is desirable to at least explain those features that are observed in thin sections. These properties and features reflect different characteristic time and space scales, which have influenced a soil's genesis. They are the record of events and processes that still remain evident in the soil and represent a minimum amount of development.

A quality soil genesis story, therefore, includes information about: the unity of the system, the number and nature of parent materials including information about their accumulation or exposure, the estimated initial state of each, the features that are believed to be associated with pedological changes, the processes and sequence of events of how the features have developed, the extent or limits of the proposed genesis, and a proposal for validation or further testing of the hypotheses. In short, soil genesis is the model that is built and developed to explain and understand a particular soil system.

The unity of a soil system

The importance of establishing the unity of a system or the separateness of adjoining layers is that it reveals the sequence of events of landscape history and the complexity of soil genesis.

a. The lateral stratigraphic tracing of soil horizons and/or sediment bodies uses superpositioning and random association to determine the unity or lack of it in a soil profile. In essence if a layer, or set of layers, occurs over different substrata then they are independent of each other. That is, the properties of one are not the direct result of being associated with the other.

   Recognition of erosional and depositional surfaces is crucial to explaining the lack of unity in many soil profiles. If extenuating circumstances exist, such as the presence of discontinuous bedrock that limits the expression of soil horizons relative to those in adjacent unconsolidated materials, then the exception to the random association is understood and waived. Australian and French soil scientists have made remarkable use of this method. The properties of most importance are those with morphological expression in the field.
b. The more commonly used technique to determine unity of a soil system is by evaluating depth functions of selected features. Changes are detected as significant variations in the vertical trends of properties and features. There are many features used to detect changes including particle sizes, soluble salts, carbonates, organic matter, structure, consistence, colors, rooting patterns, coarse fragments, and artifacts.

   Changes in the trends of properties that are suspected to be associated with separate layers can be investigated for spatial extent. Seemingly random, non-repeatable, small-scale features are handled as local variations and may constitute noise in the system being studied. For example, if one were studying the genesis of an argillic horizon on an alluvial fan then disruptions due to fence post holes would be discarded for that particular evaluation. Usually systematic, repeatable variations can be recognized by the trends and patterns that they exhibit.

Uniformity of parent material

Because parent material is an assumed prior state of soil horizons, or it's initial state according to Jenny, pedologists look for features that would only have been minimally changed by pedogenic processes. Unity, or lack of it, in soil depth functions does not necessarily establish the uniformity of an assumed parent material within a layer already proven to be separate.

a. Trends of stable components such as zirconium in sands, dominant sand fractions when dominated by quartz, and bulk density are used to detect changes from an expected distribution. Ratios of resistant minerals have been used however they may not be sensitive indicators in incomplete soils caused by erosion, nor to a time break between sediments derived from the same source. Complementary trends of a number of mobile and immobile constituents provide a degree of reliability of selected indicators of uniformity.

   In sedimentary environments it is common to observe fining upward trends within a sedimentary unit. Coarsening upward trends are also evident in certain circumstances. In general, simple linear trends of small increment sample data are used to anticipate potential breaks or changes in the uniformity of the parent material.

   When in situ alteration has been strong the estimates of properties for the parent material are more uncertain. Soil properties associated with erosional processes, such as lag deposits of gravel or sand, assist in understanding truncated or incomplete profiles. Complementary decreasing and increasing trends associated with eluviation and illuviation of mobile constituents can be altered by the deposition of new sediments or by the stripping off of overlying materials. At present, there is very little information available that adequately describes common trends of pedological phenomena and how they relate to trends in sedimentary environments.
b. Estimating the initial state or time zero for soil development, is always uncertain because the material had to be modified to form the morphological features recognized as soil horizons. When an unconsolidated material is available, either by weathering or by deposition, it is important to decide whether the pedogenic changes occur isovolumetrically. As some components are weathered and removed from a microsite there may be additional hydration and the formation of pore space with very little change in the volume of the soil material although there may be important weight changes. If there has been volumetric parity then index indicators can be expressed in units of weight per unit volume. For example, the weight percent of a medium sand fraction used as an indicator of uniformity can be converted to milligrams per cubic centimeter as an improved indicator of change. Bulk density may also change with some processes; therefore, assumptions about the initial trends are needed to better estimate the changes that may have taken place during pedogenesis.

   Because of trends in bulk density, particle size fractions, and other components it is possible to consider that slightly different parent material existed for each small depth increment throughout a soil profile. To estimate the original state it is necessary to assume a trend (usually linear) within each parent material. A reference index also needs to be selected, such as a sand fraction, quartz, a heavy mineral, or even ratios of resistant components. In an increment that is minimally altered the weight percent of the index material is assumed to have been reasonably stable. The index component for all other increments is assumed to have had a similar weight percent and its distributions would vary with the estimated original bulk density. With an assumed trend of the original bulk density and of the amount of the reference index at each depth, the initial condition is estimated. By comparing the present values of the components with those in the initial state the differences are attributed to pedogenesis and should be consistent with other features, including those observed in thin sections.

   Quantitative comparisons have been made of mobile constituents like carbonates, iron, aluminum, manganese, bases, organic matter and clay. Mineralogical comparisons and alterations have also been estimated for some soil profiles.

Explanations of change

The changes of the components of interest in a soil are related to processes that may have occurred. Soil genesis is the development of functional relationships between observed and measured soil properties and processes and events that could account for the current phenomena.

Processes may be physical, chemical, biological or more likely some interacting combination. Whenever possible it is valuable to have estimated dates or time markers so that rates of processes may be estimated. From the time sequences and by comparing with other studies it is sometimes possible to infer the rate and duration of the processes that have produced the soil features. All of this is uncertain and leads to additional working hypotheses, which may assist other researchers in their quest for understanding.

Conclusion

Soil genesis is the story of how a soil comes into being and attains its current properties. The mysteries of soil evolution are still mainly conveyed in models. Most models are qualitative although more and more contain quantitative elements where knowledge is increasing.

New instrumentation and improved computer systems enable scientific disciplines to delve farther and deeper into the mechanisms and periods when changes occurred in the Earth's history. Pedology has been undergoing the same changes. Linking the models of today, extending the evidence at points to larger areas, and developing scenarios to integrate time and space are still very real challenges.

Details of the distribution, formation, morphology, and classification of individual soil types will be found elsewhere in this volume, particularly in the cross-references at the end of this article.

R. W. Arnold

Bibliography

First, a comprehensive and up-to-date dictionary

Gregorich, E.G., Turchenek, L.W., Carter, M.R., and Angers, D.A., 2001. Soil and Environmental Science Dictionary. Boca Raton, FL: CRC Press. 577 pp.

An excellent summary of the old school and the beginning of the new school of soil genesis is available in the two volume set

Wilding, L.P., Smeck, N.E., and Hall, G.F., eds., 1983. *Pedogenesis and soil Taxonomy. I: Concepts and Interactions. II. The Soil Orders*. Elsevier. (Of particular interest are the chapters: Dynamic and genetic modeling of soil systems, Vol. 1, pp. 51–81, and Pedology and geomorphology, Vol. 1, pp. 117–140.)

An overview of the new school of soil genesis

Bryant, R.B., and Arnold, R.W. eds., 1994. Quantitative Modeling of Soil Genesis Processes. *Soil Sci. Soc. Am. Spec. Publ.* 39.

Individual papers referenced in the Elsevier volumes that highlight the U.S. approach to soil genesis include the following (listed alphabetically in each section)

General concepts

Arnold, R.W., 1965. Multiple working hypotheses in soil genesis. *Soil Sci. Soc. Am. Proc.* **29**: 717–724.

Cline, M.G., 1961. The changing model of soil. *Soil Sci. Soc. Am. Proc.* **25**: 442–446.

Dijkerman, J.C., 1974. Pedology as a science; the role of data, models, and theories in the study of natural systems. *Geoderma*, **11**: 73–93.

Jenny. H., 1941. Factors of Soil formation. New York: McGraw-Hill, 281 pp.

Jenny, H., 1961. Derivation of state factor equations of soils and ecosystems. *Soil Sci. Soc. Am. Proc.*, **25**: 385–388.

Runge, E.C.A., 1973. Soil development sequences and energy models. *Soil Sci.*, **115**: 183–193.

Schelling, J., 1970. Soil genesis, soil classification and soil survey. *Geoderma*, **4**: 165–193.

Simonson, R.W., 1959. Outline of a generalized theory of soil genesis. *Soil Sci. Soc. Am. Proc* **23**: 152–156.

Yaalon, D.H., 1971. Soil development processes in time and space. In Yaalon, D.H. ed., *Paleopedology.* Israel: Israel University Publication, 29–39.

Parent material accumulation and geomorphology

Beckett, P.H.T., 1968. Soil formation and soil development. *Z. Geomorphol.*, **12**: 1–24.

Butler, B.E., 1959. Periodic phenomena in landscapes as a basis for soil studies. *CSIRO Soil Pub. No. 14*, 20 pp.

Daniels, R.B., Gamble, E.E., and Cady, J.G., 1971. The relation between geomorphology and soil morphology and genesis. *Adv. Agron.*, **23**: 51–88.

Gile, L.H., and Hawley, J.W., 1966. Periodic sedimentation and soil formation on an alluvial-fan piedmont of southern New Mexico. *Soil Sci. Soc. Am. Proc.*, **30**: 261–268.

Huggett, R.J., 1975. Soil landscape systems; a model of soil genesis. *Geoderma*, **13**: 1–22.

Mulcahy, M.J., 1961. Soil distribution in relation to landscape development. *Z. Geomorphol.*, **5**: 211–225.

Ruhe, R.V., 1956. Geomorphic surfaces and the nature of soils. *Soil Sci.*, **82**: 441–445.

Ruhe, R.V., and Walker, P.H., 1968. Hillslope models and soil formation. 1. Open systems. *Trans. 9th Intl., Cong., Soil Sci., Adelaide.*, **4**: 551–560.

Stevens, and P.R., Walker, T.W., 1970. The chronosequence concepts and soil formation. *Q. Rev., Biol.*, **45**: 333–350.

Unity and uniformity

Arnold, R.W., 1968. Pedological significance of lithologic discontinuities. *Trans. 9th Int. Congr. Soil Science, Adelaide.*, **4**: 595–603.

Brewer, R., 1955. Mineralogical examination of a yellow podzolic soil formed on granodiorite. *CSIRO Soil Pub., No. 5*. 28 pp.

Churchward, A.M., 1961. Soil studies at Swan Hill, Victoria, Australia. 1. Soil laying. *J. Soil Sci.*, **12**: 73–86.

Evaluation of changes

Barshad, L., 1955. Soil development. In Bear, F.E., ed., *Chemistry of the Soil.* New York: Reinhold, 373 pp.

Franzmeier, D.P., Whiteside, E.P., and Mortland, M.M., 1963. A chronosequence of Podzols in northern Michigan 111. Mineralogy, micromorphology, and net changes occurring during formation. *Michigan Agric. Expt. Sta. Q. Bull.*, **46**: 37–57.

Marshall, C.E., and Haseman, J.F., 1942. The quantitative evaluation of soil formation and development by heavy mineral studies: a Grundy silt loam profile. *Soil Sci. Soc. Am. Proc.*, **7**: 448–453.

Miller, F.P., Holowaychuk, N., and Wilding, L.P., 1971. Canfield silt loam, a Fragiudalf: II. Macromorphological, physical, and chemical properties. *Soil Sci. Soc. Am. Proc.*, **35**: 319–324.

Nikiforoff, C.C., and Drosdoff, M., 1943. Genesis of clay pan soil. *Soil Sci.*, **55**: 459–482.

Smeck, N.E., and Wilding, L.P., 1980. Quantitative evaluation of pedon formation in calcareous glacial deposits in Ohio. *Geoderma.* **24**: 1–16.

Wang, C., and Arnold, R.W., 1973. Quantifying pedogenesis for soils with discontinuities. *Soil Sci. Soc. Am. Proc.* **37**: 271–278.

Interesting examples of the transition from old to new are:

Global Soil Change, 1990. Report of an IIASA-ISSS-UNEP Task Force on the Role of Soil in Global change. In Arnold, R.W., Szabolcs, I., and Targulian, V.O., eds., Laxenburg, Austria: International Institute for Applied Systems Analysis.

Targulian, V.O., Sokolova, T.A., Brina, A.G., Kulikov, A.V., and Tselishcheva, L.K., 1974. Arrangement, composition and genesis of Sod-pale-podzolic soil derived from nantle loams. *10th Int. Congr. Soil Sci., Moscow.*

Some examples of literature associated with the current school of soil genesis

Amba, E.S., Smeck, N.E., Hall, G.F., and Bigham, J.M., 1990. Geomorphic and pedogenic processes operative in soils of a hillslope in the unglaciated region of Ohio. *Ohio J. Sci.*, **90**(1): 4–12.

Baham, J., 1984. Prediction of ion activities in soil solution: computer equilibrium modeling. *Soil Sci. Soc. Am. J.*, **48**: 525–531.

Bui, E.N., Dixon, J.B., Sh adfan, H., and Wilding, L.P., 1990. Geomorphic features and associated iron oxides of the Dallol Bosso of Niger (West Africa). *Catena* **17**: 41–54.

Chadwick, O.A., Brimhall G.H., and Hendricks. D.M., 1990. From a black to a gray box – a mass balance interpretation of pedogenesis. *Geomorphology* **3**: 369–390.

Hoosbeek, M.R., and Bryant, R.B., 1992. Towards the quantitative modelling of pedogenesis – a review. *Geoderma*, **55**: 183–210.

Levine, E.R., and Ciolkosz, E.J., 1986. A computer simulation model for soil genesis applications. *Soil Sci. Soc. Am. J.*, **145**: 111–125.

Parton, W.J., Schimel, D.S., Cole, C.V., and Ojima, D.S., 1987. Analysis of factors controlling soil organic matter levels in Great Plains grasslands. *Soil Sci. Soc. Am. J.*, **51**: 1173–1179.

Rabenhorst, M.C., and Wilding, L.P., 1986. Pedogenesis on the Edwards Plateau, Texas. III. New model for the formation of petrocalcic horizons. *Soil Sci. Soc. Am. J.*, **50**: 693–699.

Richter, J., 1987. *The Soil as a Reactor.* Cremlingen, Germany: Catena Verlag.

Ugolini, F.C., Dahlgren, R., Shoji, S., and Ito, T., 1988. An example of osolization and podzolization as revealed by soil solution studies, southern Hakkoda, northeastern Japan. *Soil Sci.*, **145**: 111–125.

Articles from the Spec. Publ. 39, SSSA, Quantitative modeling of soil forming processes, 1994

Addiscott, T.M., Simulation, prediction, foretelling or prophecy? Some thoughts on pedogenetic modeling, 1–16.

Hoosbeek, M.R., and Bryant, R.B. Developing and adapting soil process submodels for use in the pedodynamic Orthod model. 111–128.

Levine, E.R., and Knox, R.G. A comprehensive framework for modeling soil genesis. 77–90.

Marion, G.M., and Schlesinger, W.H. Quantitative modeling of soil forming process is in deserts: the CALDEP and CALGYP models, 129–146.

Parton, W.J., Shimel, D.S., Ojima, D.S., and Cole, C.V. A general model for soil organic matter dynamics; sensitivity to litter chemnistry, texture and management. 147–168.

Slater, B.K., McSweeney, K., McBratney, A.B., Ventura, S.J., and Irvin, B.J. A spatial framework for integrating soil-landscape and pedogenic models. 169–185.

Suarez, D.L., and Goldberg, S. Modeling soil solution, mineral formation and weathering. 37–60.

Wagenet, R.J., Bouma, J., and Hutson, J.L. Modeling water and chemical fluxes as driving forces of pedogenesis. 17–36.

Wesselink, L.G., van Grinsven, J.J.M., and Grosskurth, G. Measuring and modeling mineral weathering in an acid forest soil, solling, Germany, 91–110.

Wilding, L.P., Bouma, J., and Goss, D.W. Impact of spatial variability on interpretive modeling. 61–76.

Cross-references

Classification of soils: Soil Taxonomy
Classification of soils: World Reference Base (WRB) for soil resources
Individual articles on the WRB taxons.

PEDON

The basic soil unit considered necessary for the purposes of classification, consisting of a sufficiently large volume of soil to include all significant features, including the full solum and the uppermost part of the parent material. It is usually less than 2 meters in depth (or as deep as roots grow) and has a circular or hexagonal cross section some 1 to 10 square meters in size. (From Miller and Donahue, 1990, p. 578).

Bibliography

Miller, R.W., and Donahue, R.L., 1990. *Soils: An Introduction to Soils and Plant Growth*, 6th edn. Englewood Cliffs, NJ: Prentice-Hall, 768 pp.

PEDOSPHERE

The zone of interaction of lithosphere, hydrosphere, atmosphere and biosphere on the Earth's land surface where soils form. Coined by the Swedish pedologist, Svente Mattson, in the 1930s who considered it to be the "sphere of spheres". (From Miller and Donahue, 1990, p. 578).

Bibliography

Miller, R.W., and Donahue, R.L., 1990. *Soils: An Introduction to Soils and Plant Growth*, 6th edn. Englewood Cliffs, NJ: Prentice-Hall, 768 pp.

Cross-references

Geology and Soils
Pedology and Pedogenesis
Periodic Table in Soil Science
Water Budget in Soil

PEDOTURBATION

Pedoturbation is synonymous with soil mixing and leads to a homogenization of the solum to various degrees (Gregorich, 2001). The mechanisms and vectors by which this mixing is accomplished are many. The implications and impacts of pedoturbation affect soil genesis as well as cultural and physical interpretations made from soils.

The sciences of pedology and geomorphology are replete with studies that have examined how *pedologic order* (anisotropy, soil horizonation) is produced from sediments with (1) inherited, geologic disorder (isotropic parent materials such as loess or dune sand) or (2) inherited *geologic order,* such as stratified alluvium or saprolite. Comparatively few studies have stressed or examined the converse: the formation of disorder from an otherwise pedologically-ordered soil, or the preservation of disorder, by pedoturbative processes. Still fewer observe that pedoturbation can actually create, or preserve at best, the soil anisotropy that is a result of the long-term actions of many types of pedologic processes.

Any mixing that occurs in the upper few meters of the Earth's surface could be equated with pedoturbation. This type of mixing has implications for persons who study preexisting stratification, such as archeologists (Wood and Johnson, 1978; Stein, 1983; Goodyear et al., 1997) or sedimentologists, or for those who study pedologic stratification, such as soil scientists or geomorphologists (Johnson et al., 1987). Pedoturbation is in large part responsible for maintaining macroporosity in soils, which in turn aids in infiltration and retards runoff and erosion. Physical mixing of organic matter into soils by, for example, biota is the primary mechanism involved in the formation of A horizons, and is an important precursor to many other pedogenic and surficial processes.

Expressions and vectors of pedoturbation

Pedoturbation is studied either by observing the process, such as ants or ice crystals moving/heaving soil particles (Perez, 1987), or by examining and interpreting the end products of such processes (Baxter and Hole, 1967; Schaetzl, 1986; Cox et al., 1987). It can be examined in two major contexts: (1) the vector of mixing (e.g., was the vector animals, plants, shrink-swell clays, or something else?) or (2) the end results of the pedoturbation, as per its effects on soil horizonation (has the mixing resulted in greater or lesser isotropy of the soil?). Because it is conceptually simpler, the former context will be examined first.

Francis Doan Hole (1961) was one of the first persons to draw attention to pedoturbation. He outlined nine different types of pedoturbation, based on the vectors of mixing: (1) animals, (2) plants, (3) ice, (4) shrink-swell clays, (5) gravity, (6) gases, (7) water or liquids, (8) crystals, such as NaCl or $CaSO_4 \cdot H_2O$, and (9) seismic activity. Hole coined names for each of these particular "types" of pedoturbation, which were then modified by Johnson et al. (1987) and are reported below. Johnson and coworkers also added a tenth vector of soil mixing: impacts from celestial bodies such as comets or meteoroids. Paton et al. (1995) provide a thorough review of pedoturbation in their recent text.

Faunalturbation (soil mixing by animals)

Animals are probably the most commonly observed, frequently mentioned, and intensively studied agents of pedoturbation (Thorp, 1949; Heath, 1965; Hole, 1981; Stein, 1983). Earthworms, mammals such as wombats, badgers, gophers and moles, and many species of insects such as ants and termites burrow in the soil as a means of finding food or providing for shelter, hibernation, estivation, or reproduction (Carpenter, 1953). Such fauna are responsible for mixing surface litter into the upper mineral soil, thereby assisting in the formation of A horizons.

Earthworms are, worldwide, a very important grouping of soil animals, due to their feeding, casting and burrowing activities. They are important in the production of soil structure (by casts) and macroporosity (by biopores), and the mixing of organic materials into the mineral soil (Kaldivko and

Timmenga, 1990). Their mixing activities have been shown to be beneficial to crops (Mackay et al., 1982; Stockdill, 1982). Vermudolls and vermustolls arc taxonomic Great Groups of soils that have an A horizon that is dominated by "*wormholes, wormcasts, or filled animal burrows and that either rests on a lithic contact or has a transition to an underlying horizon* ..." with evidence of the same (Soil Survey Staff, 2003). Many other types of mollisols that lack discrete horizon boundaries often have obtained such morphologies because of long-term mixing of their upper layers by soil fauna (see also Langmaid, 1964). Ants (Levan and Stone, 1983) and termites are found worldwide and everywhere are known to move vast amounts of soil material both upwards and downwards within the soil mantle (Figure P4).

Generally, one envisions soil fauna as mixing and homogenizing the soil to some depth, usually to the mean or maximum depth of burrowing. This assumption will hold only if the largest clasts in the soil are smaller than the maximum clasts that the soil animals are capable of moving. For example, Johnson (1989) has shown that a certain species of pocket gopher in California does not transport stones that are larger than about 6–7 cm in diameter. Thus, the stones, which are not carried upward by the gophers, slowly subside to the maximum depth of burrowing, producing a distinct *stone zone* at depth in the soils (Figure P5). Horizons within and above the stone zone are thoroughly mixed, and constitute an excellent example of a biomantle: a layer of "*materials sorted and brought to the surface by animals*" (Soil Survey Staff, 1975, p. 21; Humphreys, 1994; Figure P4). Fine materials may be concentrated in the bioturbated regions (Baxter and Hole, 1967; Salem and Hole, 1968). In other instances, coarse fragments are concentrated at the surface by fauna. This type of activity can have marked effects on the redistribution of archeological artifact layers (Erlandson, 1984; Bocek, 1986), and is not restricted to mammals.

The influence of animal activity on soils and various soil components could fill volumes. Only a few examples have been provided here. Other include changes in nutrient content, pH, organic matter (Levan and Stone, 1983; Mandel and Sorenson, 1982; Litaor et al., 1996). Additionally, those activities may indirectly result in changes in the flora (e.g., King, 1977; Mandel and Sorenson, 1982). Last, the effects of faunalturbation on the formation and maintenance of favorable soil porosity and structure cannot be overestimated, as the burrows formed provide rapid conduits for infiltrating water (Green and Askew, 1965; Stone, 1993). Infilled animal burrows, termed krotovinas, are often the end result of such activities.

Figure P4 Ant activity in a cemetery in Athens, Georgia. Ants continually bring small particles to the surface, creating a biomantle, which may eventually bury the headstone markers.

Floralturbation (soil mixing by plants)

Floralturbation is the mixing of soil by the action of plants. In general, there are four mechanisms by which plants disturb and/or mix the soil: (1) expansion of roots during growth; (2) decay and infilling of root channels; (3) root movement caused by agitation of the plant by wind (Hintikka, 1972); and (4) uprooting, especially of larger plants such as trees. Uprooting is the most visibly important form of floralturbation in forested areas (Schaetzl et al., 1990), the effects of which may be difficult to notice subsequent to cultivation (Figure P6; especially P6c).

Root expansion may cause upward expansion of the soil surface. Later, as the roots die and decay, the infilling of the root channels may allow materials from upper horizons to penetrate deeply into the subsoil (Roberts, 1961). Agitation of roots has been studied theoretically (Hole, 1988) but little work has been done on the field measurement of this process, or its implications for soil mixing (see, however, Stone, 1977).

The term *uprooting* implies that a tree has fallen with most of its larger roots intact. Brown (1979) used the term *arbokturbation*. "Treefall", "tree throw" or "tree-tip" are terms which can be synonymous with uprooting, but which may also refer to trees whose trunks arc broken near the base, with little or no soil disruption. Uprooting may disrupt considerable amounts of soil and often results in the formation of a pit (where the roots once were) and an adjacent mound, where soil slumps off the roots (Figure P6b).

Uprooting contorts, mixes and overturns soil horizons. Floralturbated soil slumps off deteriorating root plates and tends to create irregular patches of mixed and discontinuous horizons in the mound (Pawluk and Dudas, 1982). Intact masses of soil may slump off the root plate and horizons may "fold over" each other, thus doubling their thickness (Veneman et al., 1984, Schaetzl, 1986). Schenck (1924) likened this process to natural plowing of the soil. Certain pedogenic characteristics, such as the interrupted and cyclic horizon character of many spodosols and alfisols, imply past floralturbation. E/B and B/E horizons, common to many forest soils, may be a direct result of floralturbation.

Treethrow initially regresses well-horizonated forest soils such as spodosols or alfisols to lesser-developed orders such as inceptisols or entisols. Soil development subsequent to uprooting seems to be favored more in pits than mounds (Schaetzl, 1990), because the treethrow pit is a zone of stronger leaching (Veneman et al., 1984; Price and Bauer, 1984), presumably enhancing pedogenesis if infiltration is not inhibited. Coarse clasts are readily brought to the surface by uprooting, and gravelly biomantles or lag concentrates may be formed on uprooting mounds (Small et al., 1990). In part because uprooting creates spatial distortion of simple horizonation, and because pit pedons usually classify as different series than mound soils, forest soils are difficult to map at small scales (Alban, 1974).

Cryoturbation (soil mixing by ice)

Many millions of hectares of soils beneath tundra and coniferous forest vegetation undergo annual or less frequent freeze-thaw cycles. These areas are underlain by permafrost but have near-surface "active zones" that melt each summer. Soils that

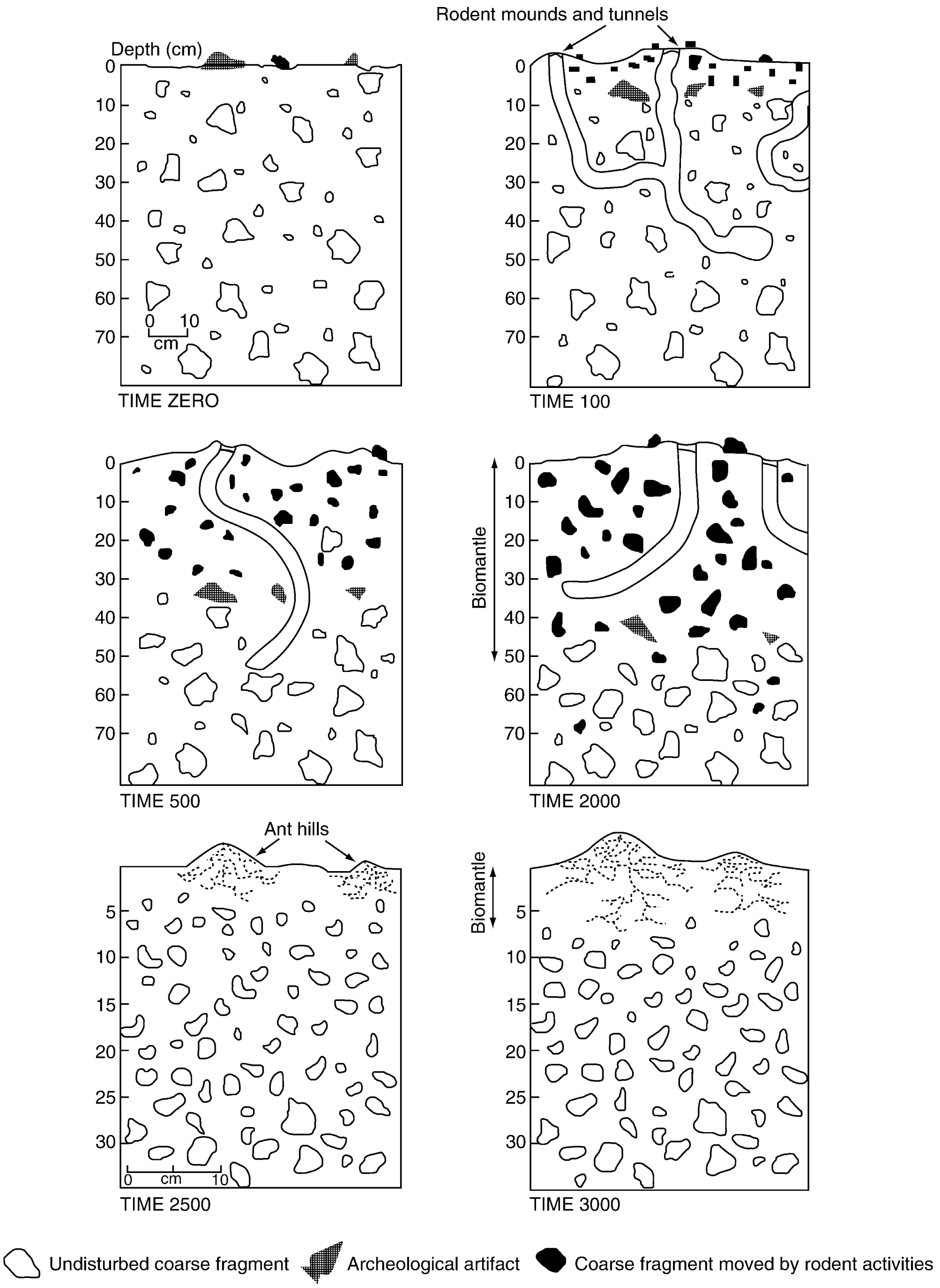


Figure P5 Lowering of stones and coarse fragments by rodents (first 2000 years) and ants (next 1000 years) tunneling activities (in part, after Johnson, 1989, Figure 8, p. 381).

undergo occasional diurnal freezing and thawing comprise an even larger part of the globe (Isard and Schaetzl, 1995). Water expands about 9% in volume upon freezing; this expansion can create significant amounts of heaving, downslope transport, and mixing in soils if repeated frequently (see section on *graviturbation* below). In some areas, the wintertime freezing of soils is vital, as it creates voids that enhance infiltration and hydraulic conductivities.

The primary effect of periglacial and/or intense frost action on soils is one of sorting: coarse fragments may become concentrated at the surface, and eventually form patterned ground (Fitzpatrick, 1975; Thorn, 1976; Washburn, 1980). Frost wedges may form and infill with finer sediments as the ice in the wedge melts. On smaller scales, needle-ice formation may cause significant heaving and mixing in the uppermost O and A horizons.

Argilliturbation (soil mixing by shrink-swell clays)

Shrink-swell, 2:1 silicate clays generally have a high *COLE* (*coefficient of linear extensibility*). They expand upon wetting and shrink when dry. Soils dominated by these types of clays

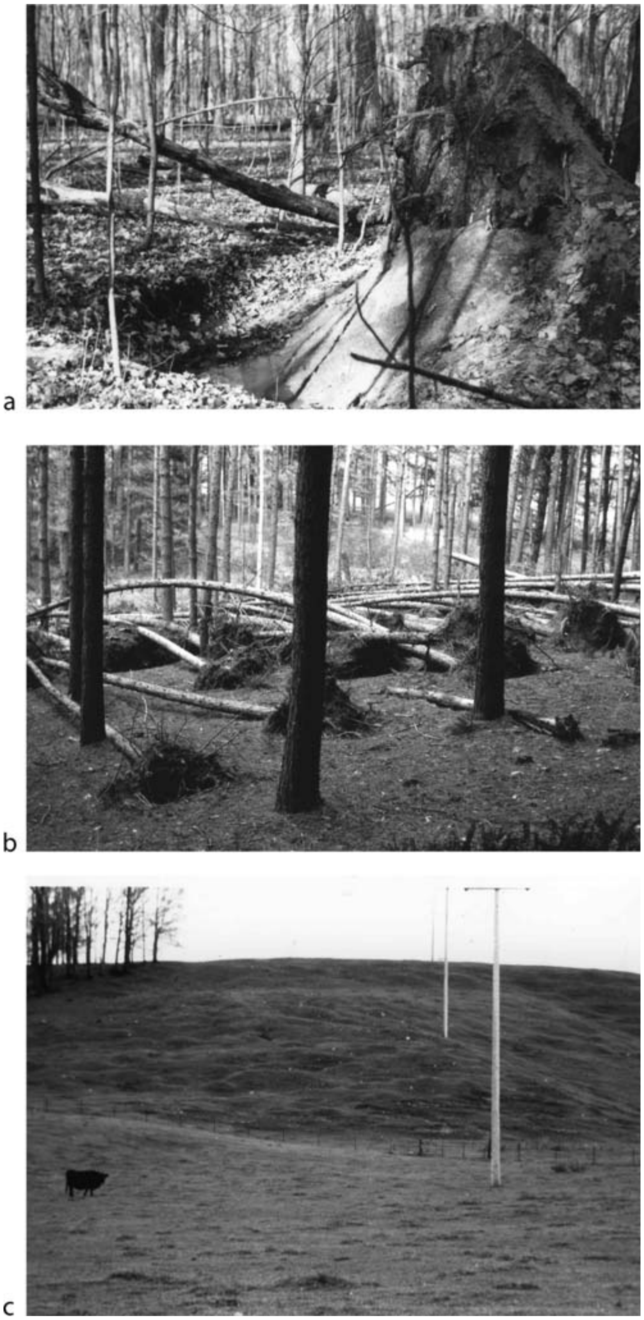


Figure P6 The tree uprooting process, showing; (**a**) slump from root plate, Brownfield Woods, Urbana, Illinois; (**b**) uprooted trees in *Pinus resinosa* plantation, eastern Pennsylvania; (**c**) pit/mound topography in a pasture near East Jordan, Michigan. Note the pastured area (foreground) that has been plowed and thus lost its microtopography. The *black cow* is provided for scale.

(smectites) will undergo volume changes as their water contents fluctuate (Jayawardane and Greacen, 1987). Because the formation and preservation of these clays is exacerbated by dry climates, many such soils are in semi-arid climates that have distinct dry and wet seasons. Thus, a climatic "forcing mechanism" is put in place to provide for the maximum volume changes in these soils, called vertisols.

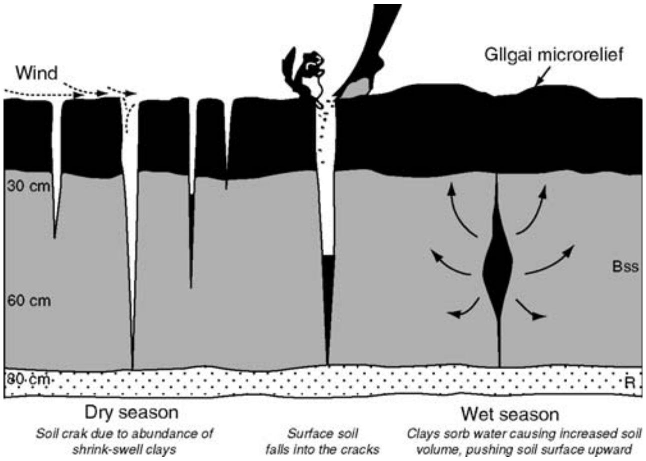


Figure P7 Vertisol horizonation and genesis (after Buol et al., 2003).

The name vertisols comes from "invert", because as these soils shrink when dry, large vertical cracks open up from the surface down to depths as great as a meter or more (Ahmad, 1983; Southard and Graham, 1992; Buol et al., 2003), Surficial materials fall into the cracks and, as the clays hydrate and expand during the wet season, the volume differences caused by the added materials at depth causes the soil material to compress against itself (Bronswijk, 1991; Figure P7). Soil aggregates slide past each other and generally push upward, thereby churning the soil. It is easy to understand why these soils are often referred to as "self-swallowing" or "self-mulching". Due to this annual cycle of argilliturbation, organic matter is incorporated to great depths in these soils, and upper horizon boundaries can become indistinct and blurred. The extreme cracking observed in most vertisols, as well as their fine textures, have widespread implications for management (Garver and Raj, 1989).

Gilgai are a type of hummocky soil microrelief, usually on the order of a few cm in height, formed by repeated episodes of upheaval (Hallsworth et al., 1955). Horizons dominated by argilliturbation often have angularly-shaped peds with polished and grooved surfaces, produced as they slide past each other (Lynn and Williams, 1992), These surfaces, called *slickensides*, are an excellent indication of active argilliturbation in the soil. The Soil Survey Staff (2003) recognizes Bss horizons as those that have evidence of slickensides.

In some soils, clays accumulate via illuviation, in the B horizon. Under certain climatic regimes, the clays may then weather to smectites, and eventually lead to internal shrink-swell activity, restricted to the Bt horizon. In this case, argilliturbation is ongoing within the soil, though its outward expression may be muted (Johnson et al., 1991; Blank et al., 1996).

Graviturbation (soil mixing by gravity)

Downslope transport of soil and sediments under the influence of gravity is termed *mass wasting*, *mass movement*, or *mass transfer*. Usually, interstitial water aids in this movement by reducing the shear strength of the materials. Turbation of these unconsolidated sediments (regolith) while in transport is typically a function of the category of mass movement, of which there are four: slides, flows, falls, or heaves.

In slides, cohesive blocks of material move downslope along a distinct plane of failure. Mixing within the sliding material may be minimal. Potential for mixing within falls and flows, however, is considerable, either while the soil material is in transit or due to settling and compaction/rearrangement immediately upon cessation of movement.

Turbation via heave is due primarily to ice crystal growth, and has been introduced above (see section on *cryoturbation*), although slight expansion docs occur due to wetting and drying. Heave contributes in large part to the slow but persistent process of seasonal creep or *soil creep*, which is generally confined to the upper 20–40 cm of soil and diminishes rapidly in intensity with depth (Young, 1960; Finlayson, 1981). Frost heaving is most efficient in silty materials.

Obviously, graviturbation processes are more active as slope angle increases, and have been significantly correlated to the sine of the slope angle (Schumm, 1967). Slope aspect, in that it affects the microclimate of the slope, may also affect slope movement processes. Finally, since graviturbation has been little studied from a pedological perspective, it is difficult to be specific about the type and amount of mixing caused by this vector of pedoturbation. Thus, graviturbation, long studied from a geomorphological perspective, represents a fruitful avenue for future soils research.

Aeroturbation (soil mixing by gases)

Mixing of soils by gases occurs on a macro-scale as soil particles are transported by wind, and on a micro-scale as gases, emitted as byproducts of organic or inorganic reactions, move soil particles fractions of a millimeter. Obviously the former has great importance, in light of soil erosion, transportation and deposition of aeolian (wind-blown) sediments. The latter is only minimally important and has been little studied, if at all.

Most soil particles are erodible by wind. Silt and very fine sand grains are perhaps the most erodible by winds of average velocity. It must be noted, however, that erosion and transportation of sediments by wind is not, strictly speaking, pedoturbation, although it clearly can and will affect pedogenesis (Johnson, 1985) and soil productivity (Morgan, 1979). Only when the particles are translocated within (more likely, from place to place on top of) the same pedon can wind transport be considered pedoturbation in a strict sense.

Other forms of pedoturbation

The remaining forms of pedoturbation have been little studied, but, based on our knowledge of surficial processes, we know that they must occur. We have inadequate knowledge, however, of their overall impact on soils. *Aquaturbation* (mixing by water or liquids), *crystalturbation* (mixing by crystal growth and decay), *seismiturbation* (mixing by seismic waves and motions), and *impacturbation* (mixing by impacts from celestial bodies such as comets or meteoroids) are the remaining forms of pedoturbation.

Aquaturbation is postulated to occur in all soils, usually on microscopic or otherwise very small scales. As water tables rise and fall, and as wetting fronts penetrate the soil, some soil particles are indisputably moved, if only a few micrometers. In most instances, water flow in soils is viewed as an organizing, rather than a mixing vector. Examples of the latter include the translocation of colloids and ions to form B horizons enriched in those constituents and eluvial zones from which these constituents have been lost (Simonson, 1959). Water can, however, be a mixing vector, or it can be a vector that inhibits organization. A spring seep would be an example of the latter, where water that is slowly flowing upward inhibits the formation of horizons.

Crystal growth (other than ice) has been shown to be an effective agent of weathering (Winkler and Wilhelm, 1970), but has been less studied as an agent of pedoturbation. Crystal growth commonly occurs, as the water in an ion-rich soil solution is lost to evaporation, root uptake, etc. The resultant evaporite crystals grow and expand into the surrounding matrix. Crystals that form authigenically in soils include sodium chloride (NaCl), gypsum ($CaSO_4 \cdot H_2O$), calcite ($CaCO_3$), dolomite ($MgCO_3$), silica (SiO_2), jarosite ($KFe_3(OH)_6(SO_4)_2$), and many others (Kittrick et al., 1982; Dixon and Weed, 1989; Nettleton, 1991). Most of these minerals are so small as to be insignificant as pedoturbation vectors. However, when the volume of minerals is great relative to the soil matrix, or when their formation/dissolution frequencies are high relative to horizonation processes, they can be disruptive on small scales. Salt playas in desert regions seldom have any appreciable horizon development, surely due to lack of infiltrating water but also due to salt crystal growth during the repeated periods of hydration and drying.

Seismic activity is capable of moving and crushing solid rock; the soil that exists above that rock also is exposed to mixing processes as the seismic waves traverse through the crust. Seismiturbation, as this type of mixing is called, is usually associated with small-scale forms of graviturbation and mass wasting, as the disrupted soil moves, slumps, slides and flows into more stable positions.

The last form of pedoturbation, impacturbation, was only recently coined by Johnson et al. (1987), and has been little studied. At least 140 terrestrial astroblemes are now known, and about five new ones are discovered annually (D.L. Johnson, pers. comm.). Nonetheless, impacts of various sorts continually affect the Earth, and many occur on land, which retains a cover of soil. Their effect on soils is spatially minuscule in comparison to other forms of pedoturbation.

Conclusions: pedologic implications of pedoturbation

Soil mixing is found wherever soil occurs, at all temporal and spatial scales. It is an ongoing process that has, until recently, received little attention and study, in comparison to those pedogenic processes that act to sort and/or horizonate surficial sediments. Although pedoturbation is generally thought of as a process that retards soil development (Schaetzl et al., 1990), if confined to certain particle size fractions, horizons or depths, it may actually promote layering or soil horizon formation. This is especially true when one considers the actions of mammals in forming stone zones below the depth of burrowing, as large clasts are slowly lowered through time (Johnson, 1990; Johnson and Balek, 1991).

Mixing of surficial sediments destroys some or all of any stratification that may have been present, and thus may lead to inverted age sequences (older over younger deposits) or sediments that are so thoroughly mixed as to preclude age assessment. Thus, the extent of pedoturbation is important information to those who study archeological sites, recent surficial deposits, and other layered strata that lie within the upper few meters of the surface of the Earth.

Randall J. Schaetzl

Bibliography

Ahmad, N., 1983. Vertisols. In Wilding, L.P., Smeck, N.E., and Hall, G.F., eds., *Pedogenesis and Soil Taxonomy.* New York: Elsevier, pp. 91–123.

Alban, D.H., 1974. Soil variation and sampling intensity under red pine and aspen in Minnesota. *U.S. For. Serv. Res. Paper. NC-106*.

Baxter, P.P., and Hole, F.D., 1967. Ant (*Formica cinerea*) pedoturbation in a prairie soil. *Soil Sci. Soc. Am. Proc.*, **31**: 425–428.

Bocek, B., 1986. Rodent ecology and burrowing behavior: predicted effects on archaeological site formation. *Am. Antiq.*, **51**: 589–603.

Bronswijk, J.J.B., 1991. Relations between vertical soil movements and water-content changes in cracking clays. *Soil Sci. Soc. Am. J.*, **55**: 1220–1226.

Brown, J.L., 1979. Etude systematique de la variabilite d'un sol Podzolique, le long d'une tranchee dans une erabliere a bouleau jaune. *Can. J. Soil Sci.*, **59**: 131–46.

Buol, S.W., Southard, R.J., Graham, R.C., and McDaniel, P.A., 2003. *Soil Genesis and Classification.* 5th edn. Ames, IA: Iowa University Press, 494 pp.

Carpenter, C.C., 1953. A study of hibernacula and hibernating associations of snakes and amphibians in Michigan. *Ecology*, **34**: 445–453.

Cox, G.W., Gakahu, C.G., and Alien, D.W., 1987. Small-stone content of Mima mounds of the Columbia Plateau and Rocky Mountain regions: implications for mound origin. *Great Basin Naturalist*, **47**: 609–619.

Dixon, J.B., and Weed, S.B., eds., 1989. *Minerals in Soil Environments*, 2nd edn. Soil Sci. Soc. Am. Book Series 1. Madison, WI: Soil Science Society of America, 1244 pp.

Erlandson, J.M., 1984. A case study in faunalturbation: delineating the effects of the burrowing pocket gopher on the distribution of archaeological materials. *Am. Antiq.*, **49**: 785–790.

Finlayson, B., 1981. Field measurements of soil creep. *Earth Surf. Proc. Landforms.*, **6**: 35–48.

Fitzpatrick, E.A., 1975. Particle size distribution and stone orientation patterns in some soils of north east Scotland. In Gemmell, A.M.D., ed., *Quaternary Studies in North East Scotland.* Annual field meeting of the Quaternary Research Association, Aberdeen, pp. 49–60.

Carver, C.L., and Raj, D.R.M., eds., 1989. *Management of Vertisols for Improved Agricultural Production.* Proceedings of IBSRAM Inaugural Workshop, International Board for Soil Res. and Mgmt. India. ICRISAT Center, 278 pp.

Goodyear, A.C., Foss, J.E., and Sassaman, K.E., 1997. *Proceedings of the Second International Conference on Pedo-Archaeology.* University of South Carolina. 157 pp.

Green, R.D. and Askew, G.P., 1965. Observations on the biological development of macropores in soils of Romney Marsh. *J. Soil Sci.*, **16**: 342–349.

Gregorich, E.G., Turchenek, L.W., Carter, M.R., and Angers, D.A., 2001. *Soil and Environmental Science Dictionary.* Boca Raton, FL: CRC Press, 577 pp.

Hallsworth, E.G., Robertson, G.K., and Gibbons, F.R., 1955. Studies in pedogenesis in New South Wales. VII. The "gilgai" soils. *J. Soil Sci.*, **6**: 1–31.

Heath, G.W., 1965. The part played by animals in soil formation. In Hallsworth E.G., and Crawford, D.V., eds., *Experimental Pedology.* London: Butterworths, pp. 236–243.

Hintikka, V., 1972. Wind-induced root movements in trees. *Commun. Inst. For. Fenn.*, **76**: 1–56.

Hole, F.D., 1961. A classification of pedoturbations and some other processes and factors of soil formation in relation to isotropism and anisotropism. *Soil Sci.*, **91**: 375–377.

Hole, F.D., 1981. Effects of animals on soil *Geoderma*, **25**: 75–112.

Hole, F.D., 1988. Terra vibrata: Some observations on the dynamics of soil landscapes. *Phys. Geog.*, **9**: 175–185.

Humphreys, G.S., 1994. Bioturbation, biofabrics and the biomantle: an example from the Sydney Basin. In Ringrose-Voase, A.J., and Humphreys, G.S., eds., *Soil Micromorphology: Studies in Management and Genesis.* London: Elscvier, pp. 421–436.

Isard, S.A., and Schaetzl, R.J., 1995. Estimating soil temperatures and frost in the lake effect snowbelt region, Michigan, USA. *Cold Regions Sci. Tech.*, **23**: 317–332.

Jayawardane, N.S., and Greacen, E.L., 1987. The nature of swelling in soils. *Aust. J. Soil Res.*, **25**: 107–113.

Johnson, D.L., 1985. Soil thickness processes. In Jungerius, P.O. ed., *Soils and Geomorphology Catena Suppl. 6*. Braunschweig, pp. 29–40.

Johnson, D.L., 1989. Subsurface stone lines, stone zones, artifact-manuport layers, and biomantles produced by bioturbation via pocket gophers (Thomomys bottae). *Am. Antiq.*, **54**: 370–389.

Johnson, D.L., 1990. Biomantle evolution and the redistribution of earth materials and artifacts. *Soil Sci.*, **149**: 84–102.

Johnson, D.L., and Balck, C.L., 1991. The genesis of quaternary landscapes with stone lines. *Phys. Geog.*, **12**: 385–395.

Johnson, D.L., Watson-Stegner, D., Johnson, D.N., and Schaetzl, R.J., 1987. Proisotropic and proanisotropic processes of pedoturbation. *Soil Sci.*, **143**: 278–292.

Johnson, D.L., Glassow, M.A., and Graettinger, K.B., 1991. A field guide to the geoarchaeology of the Vandenberg-Lompoc-Point Conception Area, Santa Barbara County, California. In Walawender, M.J., and Hanan, B.B., eds., *Geological Excursions in Southern California and Mexico.* San Diego, CA: San Diego State University, 255–280.

King, T.J., 1977. The plant ecology of ant-hills in calcareous grasslands. *J. Ecol.*, **65**: 235–316.

Kittrick, J.A., Fanning, D.S., and Hossner L.R., eds., 1982. Acid sulphate weathering. *Soil Sci. Soc. Am. Spec. Publ. 10*, Madison, WI: Soil Science Society of America, 234 pp.

Kladivko, E.J., and Timmenga, H.J., 1990. Earthworms and agricultural management. In Box, J.E. and Hammond, L.C., eds., *Rhizosphcrc Dynamics*. AAAS Selected Symposium, pp. 192–216.

Langmaid, K.K., 1964. Some effects of earthworm invasion in virgin podzols. *Can. J. Soil Sci.*, **44**: 34–37.

Levan, M.A., and Stone, E.L., 1983. Soil modification by colonies of black meadow ants in a New York old field. *Soil Sci. Soc. Am. J.*, **47**: 1192–1195.

Litaor, M.I., Manicelli, R., and Halfpenny. J.C., 1996. The influence of pocket gophers on the status of nutrients in alpine soils. *Geoderma.* **70**: 37–48.

Lynn, W., and Williams, D., 1992. The making of a Vertisol. *Soil Survey Hor.* **33**: 45–50.

Mackay, A.D., Syers, J.K., Springett, J.A., and Greg, P.E.M., 1982. Plant availability of phosphorous in superphosphate and a phosphate rock as influenced by earthworms. *Soil Biol. Biochem.*, **14**: 281–287.

Mandel, R.D., and Sorenson, C.J, 1982. The role of the Western Harvester ant (Pogonomyrmex occidentalis in soil formation. *Soil Sci. Soc. Am. J.*, **46**: 785–788.

Morgan, R.P.C., 1979. Soil Erosion. In *Topics in Applied Geography.* London: Longman Group.

Nettleton, W.D. ed., 1991. Occurrence, characteristics, and genesis of carbonate, gypsum$_r$ and silica accumulations in soils. *Soil Sci. Soc. Am. Spec. Publ. no. 26*, Madison, WI: Soil Science Society of America. 149 pp.

Paton, T.R., Humphreys, G.S., and Mitchell, P.B., 1995. *Soils A New Global View.* New Haven: Yale University Press, 213 pp.

Pawluk, S., and Dudas, M.J., 1982. Floralpedoturbattons in black chernozemic soils of the Lake Edmonton Plain. *Can. J. Soil Sci.*, **62**: 617–629.

Percez, F.L., 1987. Soil surface roughness and needle ice-induced particle movement in a Venezuelan Paramo. *Carib. J. Sci.*, **23**: 454–460.

Price, A.G., and Bauer, B.O., 1984. Small-scale heterogeneity and soil-moisture variability in the unsaturated zone. *J. Hydrol.*, **70**: 277–293.

Roberts, E.G., 1961. Soil settlement caused by tree roots. *J. For.*, **59**: 25–26.

Salem, M.Z., and Hole, F.D., 1968. Ant (Formica exsectoides) pedoturbation in a forest soil. *Soil Sci. Soc. Am. Proc.*, **32**: 563–567.

Schaetzl, R.J., 1986. Complete soil profile inversion by tree uprooting. *Phys. Geog.*, **7**: 181–189.

Schaetzl, R.J., 1990. Effects of tree throw microtopography on the characteristics and genesis of Spodosols, Michigan, USA. *Catena*, **17**: 111–126.

Schaetzl, R.J., Burns, S.F., Small, T.W., and Johnson, D.L., 1990. Tree uprooting: review of types and patterns of soil disturbance. *Phys. Geog.*, **11**: 277–291.

Schenck, C.A., 1924. Der Waldbau des Urwalds. *Allgemeine Forst und Jadg Zeitung*, **100**: 377–388.

Schumm, S.A., 1967. Rates of surficial rock creep on hillslopes in western Colorado. *Science.* **155**: 560–562.

Simonson, R.W., 1959. Outline of a generalized theory of soil genesis. *Soil Sci. Soc. Am. Proc.*, **23**: 152–156.

Small, T.W., Schaetzl, R.J., and Brixic, J.M., 1990. Redistribution and mixing of soil gravels by tree uprooting. *Prof. Geog.*, **42**: 445–457.

Soil Survey Staff, 2003. *Keys to Soil Taxonomy.* 9th edn. Washington D.C: U.S. Department of Agriculture, Natural Resources Conservation Service, 332 pp.

Southard, R.J., and Graham, R.C., 1992. Cesium-137 distribution in a California Pelloxerert: Evidence of pedoturbation. *Soil Sci. Soc. Am. J.*, **56**: 202–207.

Stein, J.K., 1983. Earthworm activity: a source of potential disturbance of archaeological sediments. *Am. Antiq.*, **48**: 277–289.

Stockdill, S.M.J., 1982. Effects of introduced earthworms on the productivity of New Zealand pastures. *Pedobiology*, **24**: 29–35.

Stone, E.L., 1977. Abrasion of tree roots by rock during wind stress. *For. Sci.*, **23**: 333–336.

Stone, E.L., 1993. Soil burrowing and mixing by a crayfish. *Soil Sci. Soc. Am. J.*, **57**: 1096–1099.

Thorn, C.E., 1976. A model of stony earth circle development, Schefferville, Quebec. *Proc. Assoc. Am. Geog.*, **8**: 19–23.

Thorp, J., 1949. Effects of certain animals that live in soils. *Sci. Mon.*, **68**: 180–191.

Veneman, P.L.M., Jacke, P.V., and Bodine, S.M., 1984. Soil formation as affected by pit and mound microrelief in Massachusetts, USA. *Geoderma*, **33**: 89–99.

Washburn, A.L., 1980. Geocryology. *A Survey of Periglacial Processes and Environments.* New York: Wiley, 406 pp.

Winkler, E.M., and Wilhelm, E.J., 1970. Salt bursts by hydration pressures in architectural stone in urban atmosphere. *Gcol. Soc. Am. Bull.*, **81**: 567–572.

Wood, W.R., and Johnson, D.L., 1978. A survey of disturbance processes in archaeological site formation. In Schiffer, M.B., ed., *Advances in Archaeological Method and Theory,* Vol. 1. New York: Academic Press, 315–381.

Young, A., 1960. Soil movement by denudational processes on slopes. *Nature*, **188**: 120–122.

PENEPLAIN, PEDIPLAIN, ETCHPLAIN

All three are examples of erosion or planation surfaces that closely approximate a gently undulating plain with no dramatic features of relief. The proposed differences between the three are genetic. A peneplain is considered to have formed by the lowering of an entire region containing more than one watershed to a common base level. Later uplift may lead to a rejuvenation of erosional processes so that the area is cut by new valleys and interfluves to produce a dissected peneplain. Rather than a top-down origin, a pediplain is assumed to have formed by the lateral cutting back of a cliff or scarp so that a steep slope becomes progressively gentler. The origin proposed for an etchplain is by deep weathering (common in the humid tropics to depths of a hundred meters or more), followed by a gradual flushing away of the weathered material.

The original authors of these hypotheses are Davis (peneplanation), Penck (pediplanation), and Wayland (etchplanation). See Gerrard (1992, p. 92).

Lester C. King developed schemes of chronological sequences of planation surfaces, first for Africa then for the world (King, 1983). His oldest surface (the Gondwanaland surface, predating the break-up of the southern continents) originated in the Mesozoic, possibly 140 million years ago. Considering changes in climate and vegetation over such a period, any soils on surfaces as old as this, will have been subjected to a succession of different soil-forming regimes (i.e., they will be polygenetic). Also, millions of years of weathering seems to be conducive to the formation of duricrusts, especially laterites and silcretes.

Bibliography

Gerrard, J., 1992. *Soil Geomorphology: An Integration of Pedology and Geomorphology.* London: Chapman & Hall, 269 pp.

King, L.C., 1983. *Wandering Continents and Spreading Sea Floors on an Expanding Earth*. Chichester UK: Wiley, 232 pp.

Cross-references

Duricrusts and Induration
Landscape and Soils

PENETRABILITY

The ability of a soil or other substance to be penetrated. It is measured by means of a penetrometer, an instrument which determines the consistency or hardness of the soil by measuring the depth or the rate of penetration of a rod or needle driven by a known force.

Cross-references

Plant Roots and Soil Physical Factors
Soil Engineering

PEPTIZATION

The process by which a colloid is converted from gel to sol. In pedological terms colloidal particles of clay in soil, are dispersed from an aggregated to a dispersed state. As a dispersion in soil water, clay is capable of being transported within a profile.

PERCOLATION

Percolation is the downward movement of soil moisture through the vadose zone that is located between the root zone and the capillary fringe of the permanent groundwater table (Hill, 1979). Percolation is also called internal drainage (Hillel, 2004). The rate of percolation is highest shortly after rain has infiltrated the soil surface (see *Infiltration*). This rate generally decreases with time until the next infiltration event. Given any particular rainstorm event, the percolation rate is higher for an initially wet soil than for a dry soil. As capillary forces act to maintain moisture between pores (see *Capillary pressure*), any percolating moisture is primarily controlled by gravitational forces and under steady-state conditions the rate of percolation P is the vertical hydraulic conductivity $k(\theta)$ given by

$$P = k(\theta) \tag{1}$$

Equation (1) is derived from Darcy's Law assuming that the suction gradient is negligible (see *Water movement*).

The speed and the residence time of percolating moisture in the vadose zone is of concern in many branches of soil science and hydrology e.g., groundwater hydrology, contaminant transport and irrigation scheduling. In these disciplines, a precise estimate of the percolation rate is required. However, the percolation rate is difficult to measure as it is highly dependent on the medium through which the moisture moves and to a lesser extent the characteristics of the water itself (Hill, 1979). Density, viscosity and surface tension of water affect the percolation rate. Viscosity effects are related to soil temperature and the concentration of solutes. However, pore size distribution is the predominant mechanism affecting percolation rates (see *Soil pores*). The soil is not uniform but comprises a mixture of organic material, entrapped gases and grains and particles of varying sizes. Preferential percolation is the rapid and nonuniform transport of soil moisture through the vadose zone. This form of percolation often occurs through macropores and subsurface channels, which result from either biological activity (biopores, e.g., roots, worm holes, etc), geological forces (e.g., subsurface erosion, cracks and fractures) or agrotechnical practices (e.g., plowing, bores and wells). Soils are also often layered and each layer possesses characteristically differing hydraulic conductivities and consequently different percolation rates.

Preferential percolation was recognized as early as last century. Lawes, Gilbert and Warington (1882), theorized that moisture could be separated into two parts: “direct” and “general” drainage. Direct drainage or preferential percolation may be initiated when moisture is transported through near surface cracks and deeper, down channels following a precipitation or irrigation event. On the other hand, general drainage or matrix flow occurs whenever the percolating moisture in the soil matrix is transported by a hydraulic gradient resulting from pore-scale diffusion and gravity-maintained convection. General or matrix percolation obeys Darcy’s Law. Preferential percolation exceeds transport velocities predicted by Darcy’s Law. The relative importance of the two forms of percolation (preferential and matrix) is dependent on the soil type and rainfall intensity. For example, well-structured soils consisting of clay and loam mixes, typically experience low permeability rates. In such soils, typically less than 1% of the pore volume consists of cracks and subsurface channels. However, often during precipitation, water infiltrating from the soil surface, flows through these channels in preference to the surrounding soil matrix, whose small pores are penetrated comparatively slowly. Even though these channels consist of a relatively small percentage of the total pore volume, they may be responsible for the bulk of moisture and solute transport after an infiltration event. Further, preferential flow in these soils can be initiated well below soil-water saturation.

Even in homogeneous, sandy soils, percolation rates may be highly spatially variable. Hill and Parlange (1972) were first to document, preferential flow in homogeneous sand at low infiltration rates. This phenomenon has also been widely observed and documented by many others (see Steenhuis et al., 1996, for excellent reviews). This research has shown that moisture may be transported through a soil in a number of paths called soil-water fingers. A poorly conducting layer of top soil at the surface, for example, produces a wetting front instability that leads to finger formation. The number of fingers, their size and rate can be predicted. Gravity is the main driving force. Figure P8a–d, reproduced from Glass et al. (1989) illustrate the development of fingers in a homogeneous sandy soil.

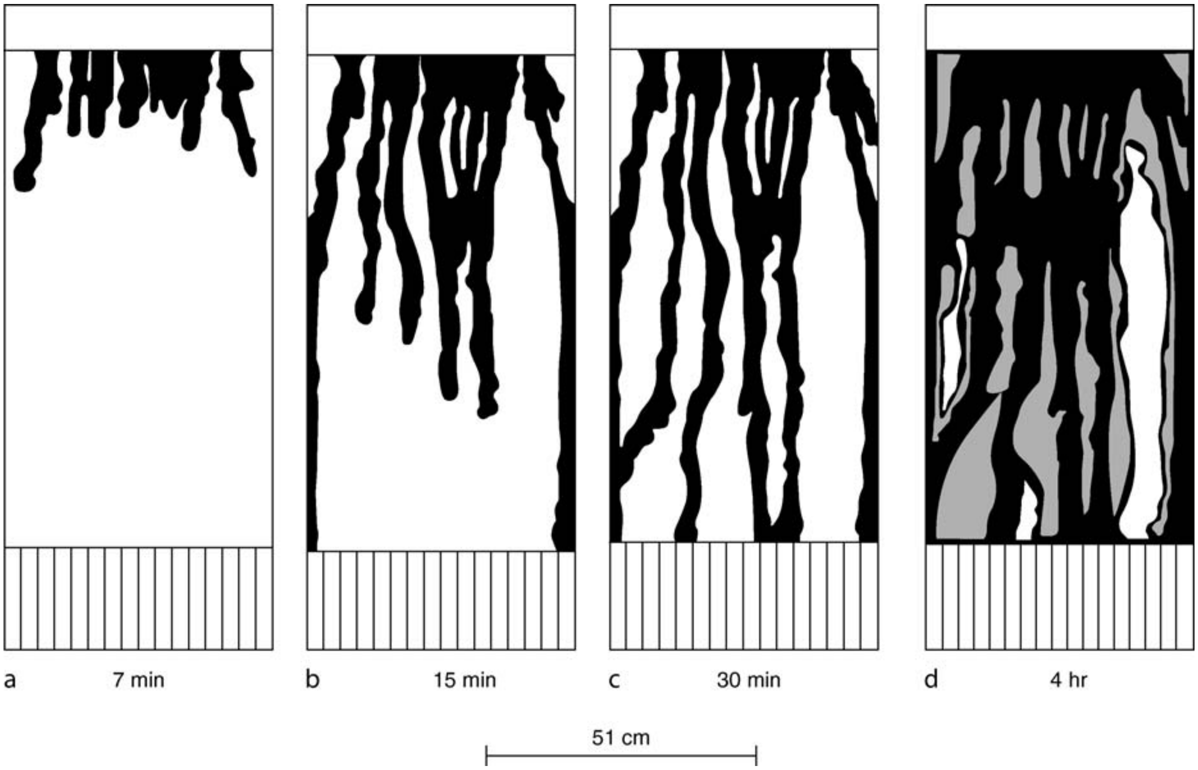


Figure P8 Development of the finger core area-fringe area in time. Core areas grow from the textural interface downward to the bottom of the chamber within the first 30 min (**a, b, c**). Finger fringe areas are formed as wetting fronts leave the fingers and move laterally into the dry sand on either side of the finger core areas (**d**) (reproduced from Glass et al., 1989).

The existence of preferential flow paths in soils have important implications for agricultural land management, storage of industrial chemicals and waste disposal (see *Fertilizers; Leaching*), For example, the chemical composition of percolating moisture in direct drainage paths often reflects the concentration of surface water rather than the concentration of moisture in the surrounding matrix. If the concentration of chemicals in the surface water is high, for instance, as a result of applying fertilizers or pesticides in irrigation water or prior to a precipitation event, then the concentration of chemicals in the direct drainage paths is likely to be higher than the equilibrium concentration in the soil matrix. Figures P9a and P9b, from Andreini and Steenhuis (1990), illustrate moisture transport through an undisturbed soil core from an experimental farm in northern New York state. These figures illustrate that structured soils, regardless of farm management practices engender preferential percolation.

Experimental determination of percolation rates is difficult due to the inability to properly characterize the soil's pore structure (Germann and DiPetro, 1996). Recently, computer-based imaging techniques have been useful in describing the macroporous nature of soils and providing estimates of percolation rates in undisturbed soil cores (e.g., see Posadas, et al., 1996), however, these techniques cannot be used on a field scale. Agricultural tile lines seem to offer the best strategy for sampling preferential percolation on a field scale (Steenhuis, et al., 1990). On a smaller scale, multi-segment percolation systems like the one described in Boll, Steenhuis and Selker (1992) may be used to provide an estimate of the average percolation rate and its variability. These systems usually consist of a grid of individual fiberglass wick sampling units and are installed in the field at a certain depth below the soil surface. Moisture and solutes flow through the wicks into bottles, which are periodically collected for analysis. The fiberglass wicks provide a suction (see *Capillary pressure*) close to that of the unsaturated soil. They act as hanging water columns and sample unsaturated flow without the need to apply external suction.

In sanitary engineering the determination of a single, average percolation rate is used in designing wastewater treatment facilities, such as septic systems, rapid and slow infiltration basins and field applications of wastes. Procedures known as the standard percolation test determine the required size of a soil adsorption system for in situ sewage disposal. This method involves auguring holes with diameters ranging from 150 to 300 mm and at depths from 0.6 m to 1.0 m. After the test hole and surrounding soil has been pre-soaked for a certain time (usually 24 hours), the percolator rate is determined by measuring the drop in elevation of the head of water in the hole. The units are either expressed as the time the head drops a certain distance or the distance the head drops in a certain time. The flow of water from the percolation test is not strictly confined to downward drainage; even though this is the usual situation. The test also includes lateral flow and possible upward movement by capillary forces. Exact details for performing the percolation test vary according to local and state municipalities. For further details see, for example, (Tchobanoglous et al., 2003).

Mathematical and computer prediction of percolation rates is complicated not only because of the non-uniformity of the soil layer but also because of the difficulty in prescribing boundary conditions at both the near surface or root zone end and at the capillary end of the vadose zone (see *Transport Processes*). One approach to modeling is to partition the soil conceptually into groups consisting of flow paths, which experience approximately the same average percolation rate. This may be accomplished, for example, by approximating the hydraulic conductivity of Equation (1) by piece-wise linear segments given by

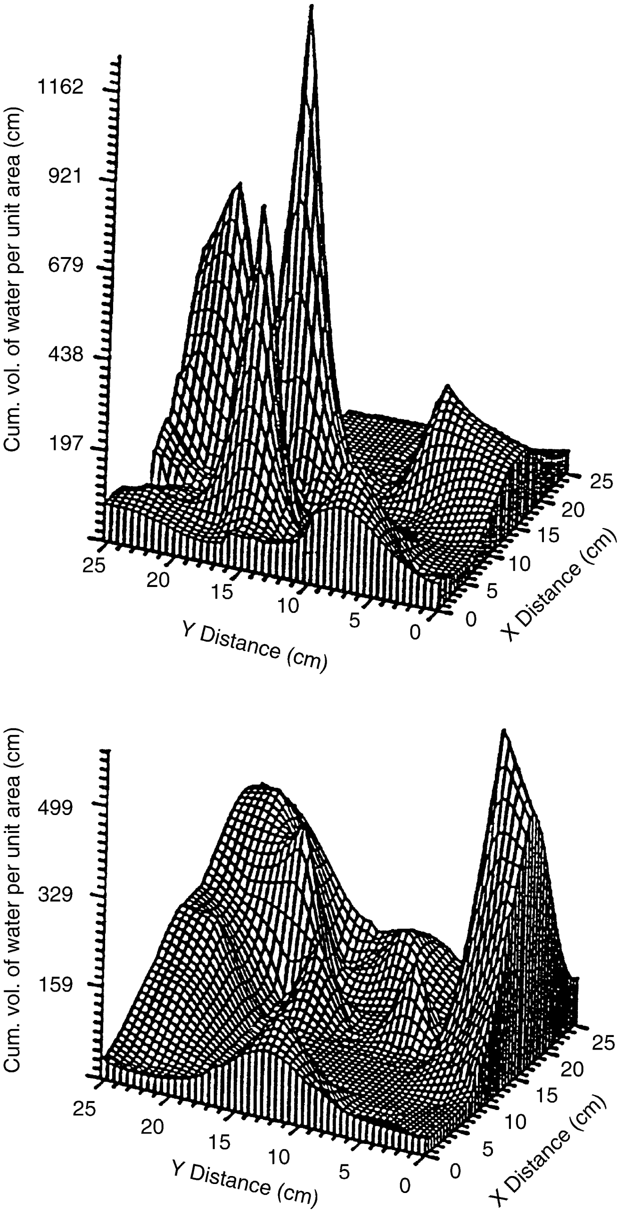


Figure P9 (**a**) The cumulative volume of water per unit area that flowed through the tilled soil column after 30 days as a function of location (reproduced from Andreini and Steenhuis, 1990). (**b**) The cumulative volume of water per unit area that flowed through the no-till soil column after 30 days as a function of location (reproduced from Andreini and Steenhuis, 1990).

$$P_i = k_i(\theta) = K_i - 1 + [K_i - K_{i-1}]\left[\frac{\Theta - M_{i-1}}{M_i - M_{i-1}}\right] \qquad (2)$$

$$i = 1, 2, \ldots, n$$

where n is the number of capillary bundles with mobile water, M_i is the upper limiting moisture content of the ith capillary bundle, K_i is the upper limiting value of the conductivity and P_i is a constant, average percolation rate in the ith capillary bundle. Equation (2) applies to percolation rates within the range of fluxes described by Darcy's Law. Macroporous flow may be modeled by including additional pore groups, say $n + 1$ to N with higher percolation rates. Assuming that gravity is the major force acting on percolating water, then the transport equation for each capillary bundle may be expressed as (Stagnitti et al., 1995).

$$\frac{\Delta\theta_i}{\delta t} + v_i\frac{\delta\theta_i}{\delta z} = A_i(z,t) \quad i = 1,2,\ldots,n,..,N \tag{3}$$

where t is time, z is distance downward with $z = 0$ being the soil surface, θ_i is the moisture content in the ith capillary bundle, v_i is a constant related to the average percolation rate in the ith capillary bundle, $A_i(z, t)$ is a source-sink term which models the effect of precipitation and evapotranspiration on the ith bundle and mixing with other capillary bundles. Notice that the same convective transport equation is applied to n micropore and N-n macropore capillary bundles. This approach was successfully used to predict moisture and solute transport on a number of different soil types.

The term percolation has both qualitative and quantitative connotations and the use of the term by different disciplines may have different meanings (Hill, 1979). However, the amount of water that percolates through the soil is very important in understanding drainage design, irrigation scheduling, sewerage and waste disposal. The percolation rate is highly dependent on soil structure and weakly dependent on characteristics of the water. Calculation of a single average percolation rate for many soils may be misleading for predicting the movement of toxic chemicals resulting from land application given the complex network of preferential flow paths.

F. Stagnitti, J.-Y. Parlange, and T. S. Steenhuis

Bibliography

Andreini, M.S., and Steenhuis, T.S., 1990. Preferential paths of flow under conservation and conventional tillage. *Geoderma*, **46**: 85–102.

Boll, J., Steenhuis, T.S., Selker, J.S., 1992. Fiberglass wicks for sampling of water and solutes in the vadose zone. *Soil Sci. Soc. Am. J.*, **56**: 701–707.

Germann, P.P., DiPietro, L., 1996. When is porous-media flow preferential? A hydromechanical perspective, *Geoderma*, **72**(1): 1–15.

Glass, R.J., Steenhuis, T.S., and Parlange, J.-Y., 1989. Wetting front instability, 2. Experimental determination of relationships between system parameters and two-dimensional unstable flow field behavior in initially dry porous media, *Water Resour. Res.*, **25**: 1195–1207.

Hill, D.E., 1979. Percolation. In *The Encyclopedia of Soil Science, Part 1: Physics, Chemistry, Biology, Fertility and Technology,* Fairbridge, R.W., Finkl Jr., C.W., eds., Dowden: Hutchinson and Ross, Inc., 358–359.

Hill, D.E., and Parlange, J.-Y., 1972. Wetting front instability in layered soils, *Soil Sci. Soc. Am. J.*, **36**: 697–702.

Hillel, D., 2004. *Introduction to Environmental Soil Physics*. Amsterdam: Elsevier, 494 pp.

Lawes, J.B., Gilbert, J.H., and Warington, R., 1882. On the amount and composition of the rain and drainage water collected at Rothamstead, London: Williams Clowes and Sons, Ltd. Originally published in *J. R. Agric. Soc. England* XVII, 1881, 241: XV3H, 1882, 167 pp.

Posadas, D.A.N., Tannus, A., Panepucci, H., and Crestana, S., 1996. Magnetic resonance imaging as a non-invasive technique for investigating 3-D preferential flow occurring within stratified soil samples. *Comput. and Electron. Agric.*, **14**(4): 255–256.

Stagnitti, F., Parlange, J.-Y., Steenhuis, T.S., Boll, J., Pivertz, B., and Barry, D.A., 1995. Transport of moisture and solutes in the unsaturated zone by preferential flow, Chapter 7. In Singh, V.P., ed., *Environmental Hydrology.* Water Science and Technology Library, Volume 15. Dordrecht: Kluwer Academic Publishers, 193–224.

Steenhuis, T.S., Staubitz, W., Andreini, M.S., Surface, L., Richard, T.L., Paulsen, R., Pickering, N.B., Hagerman, J.R., Geohring, L.D., 1990. Preferential movement of pesticides and tracers in agricultural soils. *J. Irrig. Drain. Eng.*, **116**: 50–66.

Steenhuis, T.S., Ritesema, C.J., and Dekker, L.W., eds., 1996. Fingered Flow in unsaturated soil: from nature to model, special issue. *Geoderma*, 70(2–4), 1–326.

Tchobanoglous, G., Burton, F.L., and Stensel, H.D., 2003. *Wastewater Engineering: Treatment and Reuse*, 4th edn. Boston: McGraw-Hill, 1819 pp.

Cross-references

Capillary Pressure
Carbon Sequestration in Soil
Conductivity, Hydraulic
Conservation
Dispersion
Drainage
Fertilizers, Inorganic
Fertilizers, Organic
Humic Substances
Infiltration
Leaching
Permeability
Soil Drainage
Soil Pores
Soil Variation
Soil Water and Its Management
Tillage
Transport Processes
Water Budget in Soil
Water Movement
Wetting Front

PERIGLACIAL

Used to designate an area, or features or processes within an area, which is, or was, adjacent to an ice sheet or glacier, so that the action of freezing and thawing, is or has been dominant in forming or modifying the landscape.

PERIODIC TABLE IN SOIL SCIENCE

The Periodic Table is a creation of the nineteenth century and according to Rouvray and King (2004) there were six independent discoverers: de Chancourtois 1862, Newlands 1864, Odling 1864, Hinrichs 1867, Meyer 1868, and Mendeleev 1869. Mendeleev's version became the most famous and it marks the starting point for later developments.

Figure P10 is a modern, long form of the Periodic Table with the elements arranged in order of increasing atomic number (alternative arrangements are considered by Katz, 2001). The vertical columns are called Groups and the horizontal lines,

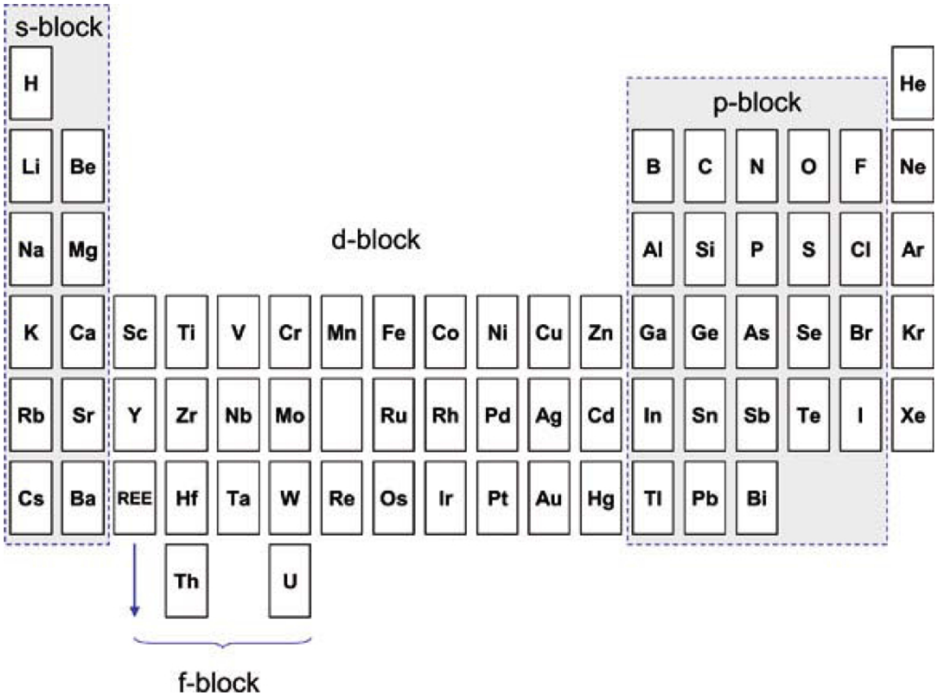


Figure P10 Periodic table of the elements. Note that hydrogen is anomalous in that it does not fit well into any one group. Only naturally occurring elements are shown. IUPAC sanctioned atomic weights are shown in Table P5.

Periods. The members of a Group have the same outer electron configuration but different quantum numbers at that outermost level. Within the table a number of blocks are labeled in terms of the nature of the orbital occupied by the highest energy electron in the atomic ground state of any element in the block. The following blocks are recognized.

1. s-block: highest energy electron (outermost) is s^1 or s^2.
2. p-block: outermost electrons are p^1 to p^6.
3. d-block: outermost electrons are d^1 to d^{10}, also called "transition elements"
4. f-block: outermost electrons f^1 to f^{14}.
5. g-block: predicted by quantum theory, not found in nature.

Periodicity in chemical and physical properties occurs as a reflection of the fact that the outermost electronic structure may repeat in going from a lower to a higher quantum number e.g., Na resembles K because their respective electronic structures are $1s^2 2s^2 2p^6 3s^1$ and $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. The periodic repetitions within the table are superimposed upon a systematic variation as the atoms increase in size. Figure P11 shows this feature of the table in terms of a number of properties important to the geochemist and soil chemist.

Two notable attempts have been made to adapt the periodic layout to the needs of Earth scientists.

Goldschmidt's version

Goldschmidt classified the elements into four groups according to their geological behavior: atmophile, lithophile, siderophile, chalcophile (Figure P12, and Krauskopf and Bird, 1995). Reasonable in explaining the primary geochemical layering of the Earth but somewhat misleading in that the groupings are not mutually exclusive. The lithophile elements are predominantly on the left of the table, though separated from Al and Si, two of the most important, and O the quintessential lithophile element.

In terms of soils and soil-forming processes, the geochemical classification is not particularly helpful. What might be called the solophile ('soil-loving') elements, cut right across Goldschmidt's categories (Figure P13). This is not particularly surprising since his ideas were based on the essentially high temperature processes of planetary formation, as hypothesized particularly from a study of meteorites and metallurgical smelting.

However, Goldschmidt was the first to use ionic potential, the ratio of ionic charge (Z) to ionic radius (r), both of which depend on chemical periodicity. Figure P14 demonstrates the usefulness of this function, in describing the behavior of elements in the pedosphere. In addition, both factors are instrumental in determining the strength of bonding between a cation and a cation exchange surface. The order of diminishing strength is the lyotropic series, commonly shown as $Al > Ca > Mg > (K = NH_4) > Na$.

Generalizations concerning the pedological behavior of the five groups of elements in Figure P14 are as follows.

- *Group A*. Long range mobility as simple cations. Readily mobilized in soils from humid regions, especially in warmer climates. Particularly impoverished in ferralitic soils. Accumulate in the solum in soils of arid and semi-arid climates (for example Calcisols, Gypsisols, and sodic soils), where they precipitate as salts with oxyanions (and Cl) of group

Table P5 Atomic weights for the chemical elements arranged in terms of atomic number (derived from Coplen, 2001; supplemented for the elements with no stable nuclides by information from http://www.webelements.com/)

Atomic number	Name	Symbol	Atomic weight
1	Hydrogen	H	1.007
2	Helium	He	4.002
3	Lithium	Li	6.941
4	Beryllium	Be	9.012
5	Boron	B	10.811
6	Carbon	C	12.011
7	Nitrogen	N	14.007
8	Oxygen	O	15.999
9	Fluorine	F	18.998
10	Neon	Ne	20.1800
11	Sodium	Na	22.990
12	Magnesium	Mg	24.305
13	Aluminum	Al	26.982
14	Silicon	Si	28.086
15	Phosphorus	P	30.974
16	Sulfur	S	32.065
17	Chlorine	Cl	35.453
18	Argon	Ar	39.948
19	Potassium	K	39.098
20	Calcium	Ca	40.078
21	Scandium	Sc	44.956
22	Titanium	Ti	47.867
23	Vanadium	V	50.942
24	Chromium	Cr	51.996
25	Manganese	Mn	54.938
26	Iron	Fe	55.845
27	Cobalt	Co	58.933
28	Nickel	Ni	58.693
29	Copper	Cu	63.546
30	Zinc	Zn	65.39
31	Gallium	Ga	69.723
32	Germanium	Ge	72.64
33	Arsenic	As	74.921
34	Selenium	Se	78.96
35	Bromine	Br	79.904
36	Krypton	Kr	83.80
37	Rubidium	Rb	85.468
38	Strontium	Sr	87.62
39	Yttrium	Y	88.905
40	Zirconium	Zr	91.224
41	Niobium	Nb	92.906
42	Molybdenum	Mo	95.94
43	Technetium[a]	Tc	(99)
44	Ruthenium	Ru	101.07
45	Rhodium	Rh	102.905
46	Palladium	Pd	106.42
47	Silver	Ag	107.868
48	Cadmium	Cd	112.411
49	Indium	In	114.818
50	Tin	Sn	118.710
51	Antimony	Sb	121.760
52	Tellurium	Te	127.60
53	Iodine	I	126.904
54	Xenon	Xe	131.293
55	Cesium	Cs	132.905
56	Barium	Ba	137.327
57	Lanthanum	La	138.906
58	Cerium	Ce	140.116
59	Praseodymium	Pr	140.907
60	Neodymium	Nd	144.24
61	Promethium[a]	Pm	(145)
62	Samarium	Sm	150.36
63	Europium	Eu	151.964
64	Gadolinium	Gd	157.25
65	Terbium	Tb	158.925
66	Dysprosium	Dy	162.50
67	Holmium	Ho	164.930
68	Erbium	Er	167.259
69	Thulium	Tm	168.934
70	Ytterbium	Yb	173.04
71	Lutetium	Lu	174.967
72	Hafnium	Hf	178.49
73	Tantalum	Ta	180.948
74	Tungsten	W	183.84
75	Rhenium	Re	186.207
76	Osmium	Os	190.23
77	Iridium	Ir	192.217
78	Platinum	Pt	195.078
79	Gold	Au	196.967
80	Mercury	Hg	200.59
81	Thallium	Tl	204.383
82	Lead	Pb	207.2
83	Bismuth	Bi	208.980
84	Polonium[a]	Po	(209)
85	Astatine[a]	At	(210)
86	Radon[a]	Rn	(222)
87	Francium[a]	Fr	(223)
88	Radium[a]	Ra	(226)
89	Actinium[a]	Ac	(227)
90	Thorium[a]	Th	232.038
91	Protactinium[a]	Pa	231.036
92	Uranium[a]	U	238.029
93	Neptunium[a]	Np	(237)
94	Plutonium[a]	Pu	(244)
95	Americium[a]	Am	(243)
96	Curium[a]	Cm	(247)
97	Berkelium[a]	Bk	(247)
98	Californium[a]	Cf	(251)
99	Einsteinium[a]	Es	(252)
100	Fermium[a]	Fm	(257)
101	Mendelevium[a]	Md	(258)
102	Nobelium[a]	No	(259)
103	Lawrencium[a]	Lr	(262)
104	Rutherfordium[a]	Rf	(261)
105	Dubnium[a]	Db	(262)
106	Seaborgium[a]	Sg	(266)
107	Bohrium[a]	Bh	(264)
108	Hassium[a]	Hs	(269)
109	Meitnerium[a]	Mt	(268)
110	Darmstadtium[a]	Ds	(281)
111	Roentgenium[a]	Rg	(272)

[a] Elements with no stable nuclides. Atomic weights are estimates to three significant figures, except for Th, Pa, and U, which each have a characteristic isotopic composition in terrestrial minerals.

E. Constitute an important proportion of the exchange complex in near neutral soils.

- *Group B*. Mobilized as hydroxy or bicarbonate complexes in acid pedological environments. Precipitate as carbonates in lower horizons of Luvisols or Chernozems for example (Ca, Mg), or are scavenged by Fe and Mn oxides and hydroxides. Fe and Mn mobilized under reduced conditions and reprecipitated as hydroxides on re-oxidation (gleysolization, alternating episodes of water saturation and drainage).
- *Group C*. Immobile under normal conditions by virtue of the low solubility of their hydroxides in most soil-forming environments (Al, Fe), or because of the unreactivity of the primary minerals in which they occur (Ti, Zr). Short range mobilization (profile scale) in oxic environments, at

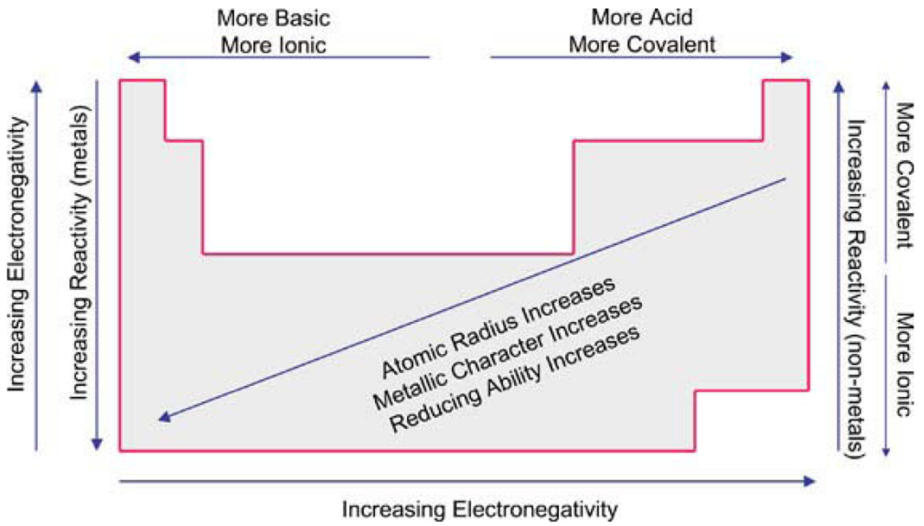


Figure P11 General trends in elemental properties within the periodic table (adapted from Chesworth, 1991).

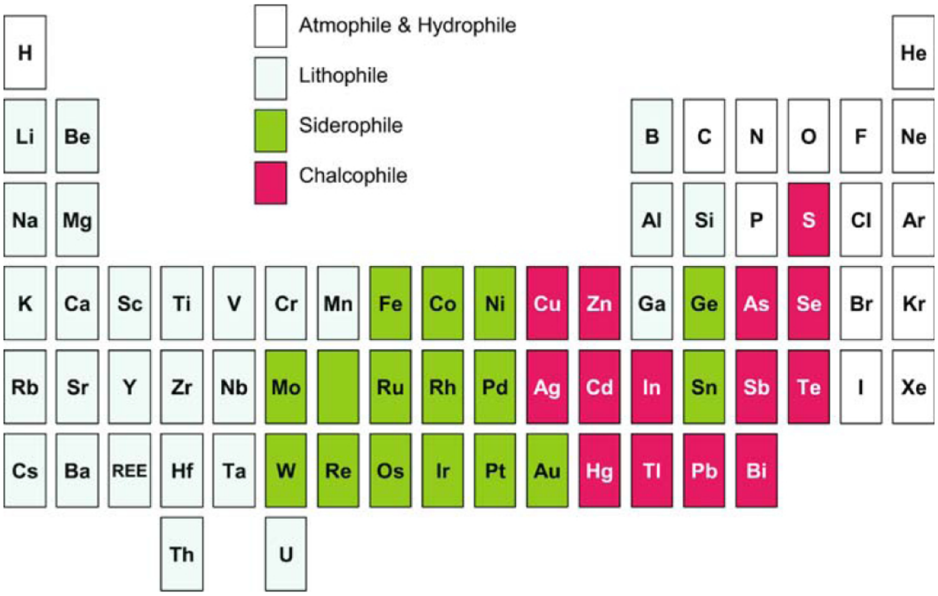


Figure P12 A geochemical grouping of the elements based principally on Goldschmidt (1954). Atmophile and Hydrophile: elements characteristic of the atmosphere and hydrosphere. Lithophile: elements enriched in silicate phases of the lithosphere. Siderophile: elements with a weak affinity for oxygen or sulfur, and assumed to be associated with metallic iron in the Earth's core. Chalcophile: elements with an affinity for sulfur and enriched in sulfides.

the low and high pH extremes of normal pedogenesis, especially under the influence of organic complexants (Al, and Fe in Podzols), and under hyperacid conditions (Fe in thionic Luvisols for example). Fe and Mn reduced under waterlogging and mobilized as in group B.

- *Group D*. Mobilized as hydroxy-acids (e.g., H_4SiO_4) of low solubility. Immobilized as neoformed clays (Si) with Al, in red-beds environments (V with U in carnotite for example), or co-precipitating with Fe hydroxides (Mo).
- *Group E*. Long range mobility as oxyanions. Immobilized with elements of groups A and B in high pH soils (generally greater than 8) of arid and semi-arid environments (Calcisols, Gypsisols, alkaline soils).

Railsback's version

Railsback argues that forms of the Periodic Table that have proven to be of great utility in explaining and predicting relationships in chemistry, have been of less use in the Earth sciences. Neither elements concentrated in soil, nor those that are critical in biological processes, are grouped as naturally occurring sets. He points out that most species of interest to the soil scientist carry charge, consequently a table orientated to the pedologist needs to be organized according to charge if it is going to be conducive to the needs of the geochemist. For soils, and biochemical processes generally, we need to concentrate on the behavior of ions in aqueous solution. Furthermore, oxygen, or (oxy-)anions are generally the largest species volumetrically in the systems of interest here. Bonding and coordination with oxygen is therefore of great importance in the geochemistry of the land surface, where trends in mineralogy, aqueous geochemistry, soil and sediment chemistry, and nutrient chemistry are all largely controlled by coordination of cations with O^{2-}. Of fundamental importance is the difference in bonding exhibited by hard and soft cations, which favor O^{2-} and S^{2-}, respectively. In Goldschmit's terms, the former accounts for lithiophile behavior, the later for siderophile. A second important feature is the extent to which the cationic charge is sufficiently focused (i.e., ionic potential is sufficiently high) to provide strong bonds to O^{2-} without causing repulsion between those cations.

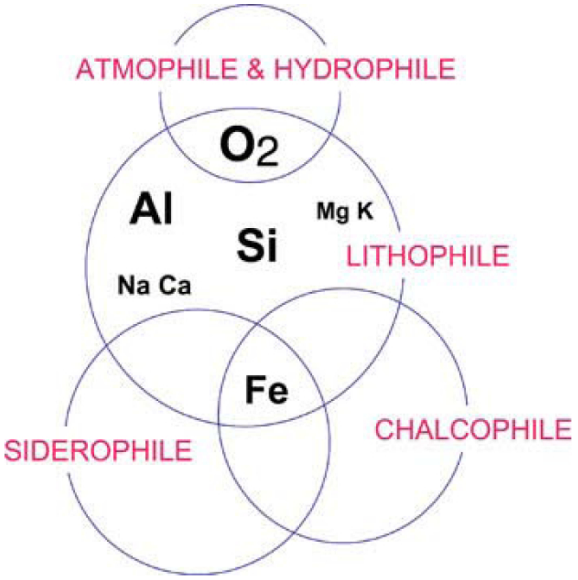


Figure P13 Ven diagram showing the major solophile elements, in relationship to the Goldschmidt classification.

To appreciate Railsback's recasting of the periodic table as a masterpiece of condensed scientific synthesis, the original should be consulted. Figure P15 is a poor substitute, tailored to the present purpose. Notice that when an element has more than one ion, it will occur more than once. Note also that there is a direct link to Goldschmidt's ideas in that the diagram is contoured in terms of ionic potential. Those elements that tend to accumulate in soils, generally fall between Z/r 4 to 8. Elements that tend to be mobilized and to be leached from the solum under humid conditions, lie outside this bracket.

This is particularly clear when elements that concentrate in the soils of the terrestrial land surface are contrasted with the elements that eventually make their way to the ocean (Figure P16).

Ward Chesworth

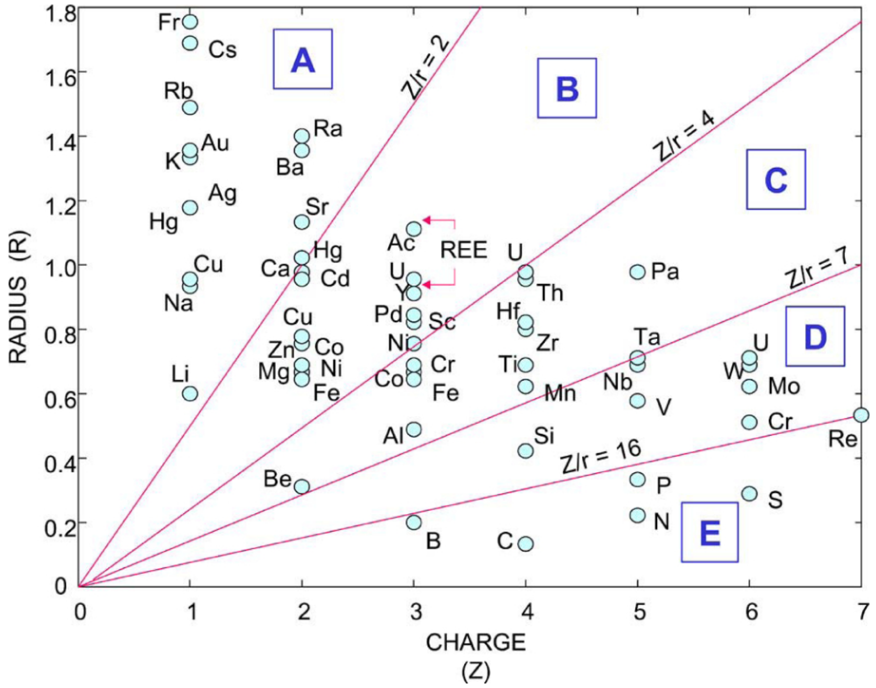
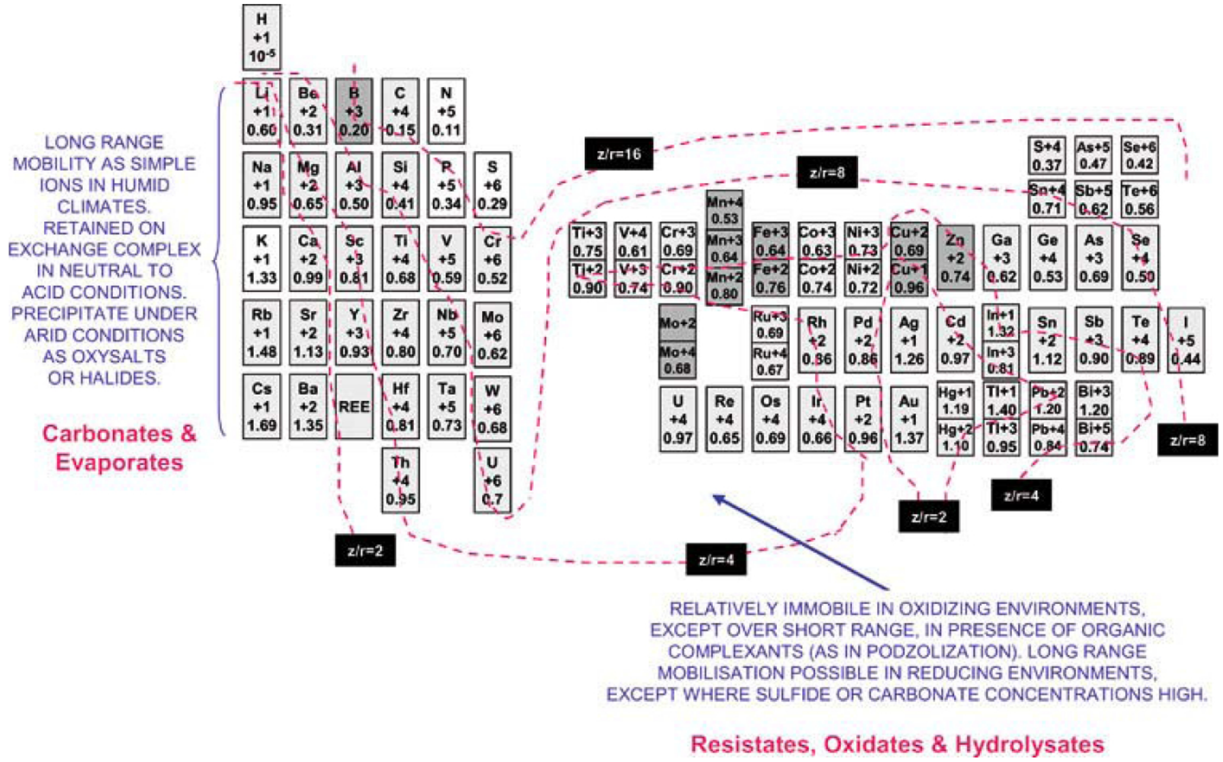


Figure P14 Ionic potential, Z/r, and the general behavior of the chemical elements in the zone of soil formation.



LONG RANGE MOBILITY AS SIMPLE IONS IN HUMID CLIMATES. RETAINED ON EXCHANGE COMPLEX IN NEUTRAL TO ACID CONDITIONS. PRECIPITATE UNDER ARID CONDITIONS AS OXYSALTS OR HALIDES.

Carbonates & Evaporates

RELATIVELY IMMOBILE IN OXIDIZING ENVIRONMENTS, EXCEPT OVER SHORT RANGE, IN PRESENCE OF ORGANIC COMPLEXANTS (AS IN PODZOLIZATION). LONG RANGE MOBILISATION POSSIBLE IN REDUCING ENVIRONMENTS, EXCEPT WHERE SULFIDE OR CARBONATE CONCENTRATIONS HIGH.

Resistates, Oxidates & Hydrolysates

Figure P15 Part of Railsback's version of the periodic table (Railsback, 2004).

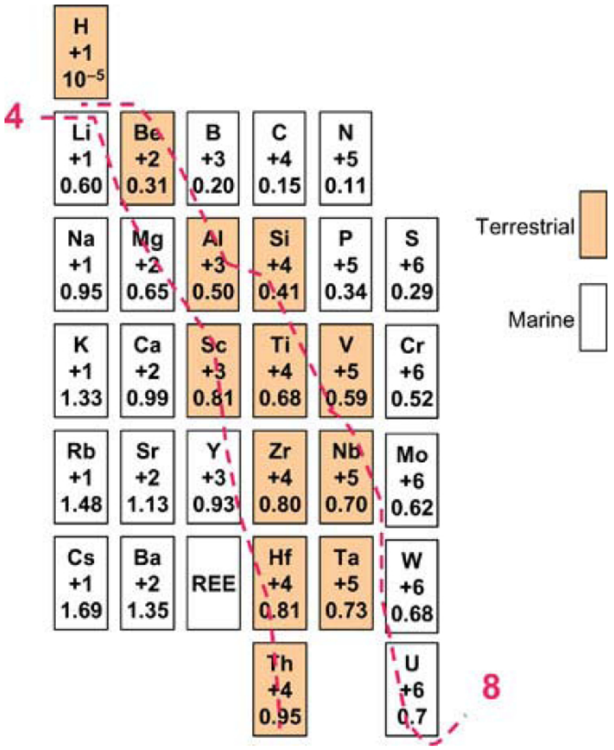


Figure P16 The contrast between elements that concentrate on the land surface and those that tend to become impoverished there by continued weathering and leaching (Railsback, 2004).

Bibliography

Chesworth, W., 1991. Geochemistry of micronutrients. (Chap. 1). In Mortvedt, J.J., Cox, F.R., Shuman, L.M., and Welch, R.M., eds., *Micronutrients in Agriculture*, 2nd edn. Madison, WI: Soil Science Society of America, pp. 1–30.

Coplen, T.B., 2001. Atomic weights of the elements 1999. IUPAC Technical Report. *Pure Appl. Chem.*, **73**: 667–683.

Goldschmidt, V.M., 1954. In Muir, A., *Geochemistry.* Oxford: Clarendon 730 pp.

Katz, G., 2001. The periodic table: an eight period table for the 21st century. *Chem. Educator*, **6**: 324–332.

Krauskopf, K.B., and Bird, D.K., 1995. *Introduction to Geochemistry.* New York: McGraw-Hill. 647 pp.

Railsback, L.B., 2003. An earth scientist' periodic table of the elements and their ions. *Geology*, **31**: 737–740.

Railsback, L.B., 2004. An earth scientist' periodic table of the elements and their ions (version 4.7). *Gelogical Society of America Map and Chart Series*, MCH 092.

Rouvray, D.H., and King, R.B., 2004. *The Periodic Table: Into the 21st century.* England/Philadelphia: Baldock/Research Studies Press, 396 pp.

Cross-references

Geochemistry in Soil Science
Micronutrients

PERMAFROST

Near-surface materials such as the sub-soil and any underlying deposits, that are frozen year round (i.e., their temperature remains below 0 °C. Permanently frozen ground exists in the

Arctic and Antarctic regions as continuous permafrost, with discontinuous permafrost on the lower latitude margins of the continuous zones. The siting of transportation routes, foundations and pipelines in permafrost, presents particularly challenging problems for the engineer (Zufelt, 1999).

Bibliography

Zufelt, J.E. (ed.), 1999. *Cold Regions Engineering: Putting Research into Practice*. Proceedings of the Tenth International Conference, August 16–19, 1999, Lincoln, New Hampshire. Reston, VA: American Society of Civil Engineers, 901 pp.

Cross-references

Cryosols
Ice Erosion
Pedoturbation
Soils of the Coastal Zone

PERMEABILITY

Permeability is a property of a soil (or any porous medium) that permits the transmission of fluids. This property, denoted by k, is also called *intrinsic permeability* to stress that k is only a property of the soil and is independent of fluid properties such as viscosity or density. The *permeability* is related to the *hydraulic conductivity* (K) by the relation

$$K = \frac{k\rho g}{\mu} = \frac{kg}{v} \tag{1}$$

where ρ is fluid specific mass, g is the acceleration of gravity, μ is the (dynamic) viscosity, and v is the kinematic viscosity. Because K depends on both soil and fluid properties, it measures the mobility of a given fluid in a given porous medium. Both k and K are macroscopical properties distinctly defined by the two versions of Darcy's Law:

$$q = -K\nabla\phi; \quad q = -\frac{k}{\mu}\nabla(p + \gamma z) \tag{2}$$

where q is the specific flux vector, $\nabla\phi$ the gradient of the total hydraulic head, z is the vertical coordinate oriented positive upward, and γ is the specific weight. The permeability k is a univalued scalar for an isotropic incompressible porous medium with stable structure. For anisotropic porous medium, Equation (2) is valid if K and k are understood as second-order tensors.

In unsaturated soils, Equation (2) is still generally used with φ defined for water by the relation:

$$\phi = \psi + z + \frac{P_a}{\gamma} \tag{3}$$

where ψ is the *capillary head*, and P_a is the air pressure (defined equal to zero when atmospheric pressure prevails). In this case K can be considered a function of the *moisture content* (θ), or ψ, for a given soil. The generalized version of Equation (2) for the unsaturated case is

$$q = -K(\theta)\nabla\left[\psi(\theta) + z + \frac{p_a}{\gamma}\right]$$

$$q = -\frac{k(\theta)}{\mu}\nabla[\gamma\psi(\theta) + \gamma z + P_a] \tag{4}$$

Frequently the *degree of saturation* ($S = \theta/\theta_s$ where θ_s is the saturated values of θ) is used as the independent variable instead of the moisture content. It is commonly assumed that $k(S)$ relates to the saturated value k_s by a unique function, the so called *relative permeability* k_r

$$k_r = \frac{k(S)}{k_s} \tag{5}$$

It is generally assumed that k_r is a scalar function even for anisotropic soils whereas k is a tensor. Note also that from the relation of equivalence, Equation (1), the *relative permeability* is equal to the *relative hydraulic conductivity*, namely, $k_r = K/K_s$.

Empirical formulas

The $K(S)$ relationship constitutes a hydraulic property, which together with the corresponding $\psi(S)$ function completely characterizes the flow system (see Equation (4)). Therefore, simple mathematical formulas adjustable to experimental data are sometimes very useful because they simplify computation. They may permit solution of unsaturated flow problems in analytical closed form and minimize the truncation error in numerical solutions. Several such empirical formulas are given in Table P6.

It is worthwhile to note that the $K(\psi)$ relationship is known to display a considerable hysteresis (see hysteresis of the hydraulic conductivity). All the empirical formulas for $K(\psi)$ can represent a continuous drainage or wetting process at best. For each process a different formula or different coefficient may be required. Also no single $K(\psi)$ relationship is valid for all types of soils. Moreover, even if a certain formula is suitable for a class of soils, the coefficients may vary considerably from soil to soil. Hence the empirical formulas do not permit in fact accurate predictions of K, and they can be used with confidence only after coefficients have been determined by a curve fitting of experimental measurements. It is generally preferable to use $K(S)$ rather than $K(\psi)$ because the relationship between K and S is less sensitive to hysteresis and in principle better adapted to unsaturated soils.

Quantitative models

The experimental determination of the relative permeability relationship down to low water contents is laborious, time-consuming, and costly especially when field measurements are concerned. Often only a few data are available for computation thereby reducing considerably, the significance of the rigorous numerical procedures customarily used in solving unsaturated flow problems. Consequently, theoretical models that predict relative permeability are extremely important.

One may distinguish between two main groups of models used for relative permeability prediction. The first one is based on a generalization of Kozeny's approach for saturated porous media. The porous system is viewed as a conduit of irregular shape. The wetting fluid is thought to creep, more or less uniformly, along the entire solid surface while the nonwetting fluid occupies the internal portion. By introducing a "hydraulic radius" parameter, equal to θ/A_s, where A_s is the solid surface area, the relative permeability can be derived as a power function of the effective saturation (S_e),

Table P6 Empirical formulas for the unsaturated hydraulic conductivity

Reference	Wind (1955)	Gardner (1958)	Gardner's Type
Function	$K = a\lvert\psi\rvert^{-n}$	$K_r = e^{\alpha\psi}$ $\quad K = \frac{a}{\lvert\psi\rvert^{n} + b}$	$K_r = \left[\left(\frac{\psi}{b}\right)n + 1\right]^{-1}$
Reference	Brooks & Corey (1964) $\psi \geq \psi_{cr} \quad \psi \leq \psi_{cr}$		Averjanov (1950)
Function	$K = K_s \quad K_r = \left(\frac{\psi}{\psi_{cr}}\right)^{-n}$		$K_r = S_e^n; \quad S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}$
Reference	Rijtema (1965) $\psi \geq \psi_{cr} \quad \psi_1 \leq \psi \leq \psi_{cr} \quad \psi < \psi_1$		King (1964)
Function	$K = K_s \quad K_r = e^{\alpha(\psi - \psi_{cr})} \quad K = K_1\left(\frac{\psi}{\psi_1}\right)^{-n}$		$K_r = a\frac{\cosh[(\psi/\psi_1)^n] - 1}{\cosh[(\psi/\psi_1)^n] + 1}$

For detailed reference, see Mualem and Dagan (1976).

$$k_r = S_e^n; \quad S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{6}$$

where θ_r is the residual saturation (see *Capillary pressure*). Averjanov (1950) and Yuster (1951) derived Equation (6) with n equal to 3.5, 2.0, and 3.0, respectively. This power law formulation is very convenient for obtaining analytical solutions of partially saturated flows. It appears, however, that n is not a universal constant. While values of n in the range of 2.5 to 3.5 may fit well sandy soils, higher values (up to 8) need to be used to accurately represent heavy soils (loamy and clay soils). Consequently, though Equation (6) was derived on a relatively rigorous theoretical basis, the residual moisture content (θ_r) and the power n have to be determined by adjustment of the formula to measured data.

The second group, the "statistical models," includes those of Purcell (1949), Childs and Collis George (1950), Burdine (1953) and Wyllie and Gardner (1958), Farrel and Larson (1972), and Mualem (1976a). These models make use of the measured capillary head-moisture content $\psi(\theta)$ curve to derive the relative permeability in the unsaturated state. The basic assumption common to these models is that a porous medium can be characterized by a one-variable density distribution function $f(r)$, where r is length scale, geometrically interpreted as the radius of the pore. Using the mechanical modeling of a porous medium (see *Capillary pressure*), r is uniquely related to ψ by the capillary law:

$$r = \frac{c}{\psi} \tag{7}$$

where c is a constant coefficient. On this basis the measured $S(\psi)$ curve is viewed as the pore water distribution function with

$$\mathrm{d}S(\mathrm{r}) = f(r)\mathrm{d}r; \quad S(R) = \int_0^R f(r)\mathrm{d}r \tag{8}$$

Naturally, different assumptions regarding the geometrical configuration of the capillary model and the contribution of the elementary pore domain to the total permeability of the pore domain will yield different final formulas of k_r.

The first and the most simple model (Purcel, 1949) considered a porous medium to be analogous to a bundle of uniform, parallel capillaries whose radii distribution are given by $f(r)$. The unsaturated state is represented by assuming that for a given ψ, only tubes with a radius less than $R = \alpha/\psi$ are filled. Capillaries having a radius greater than R remain empty.

According to the Hagen-Poiseuille Equation, the specific discharge through the bundle of capillaries is

$$q(R) = \frac{g}{8v}\frac{\mathrm{d}\phi}{\mathrm{d}x}\int_{R_{\min}}^{R} r^2 f(r)\mathrm{d}r \tag{9}$$

The analogy of (9) and (2) indicate that the contribution of the filled tube to the hydraulic conductivity of the bundle is proportional to the integral in Equation (9) leading to:

$$k_r = \frac{\int_{R\,\min}^{R} r^2 f(r)\mathrm{d}r}{\int_{R_{\min}}^{R_{\max}} r^2 f(r)\mathrm{d}r} \tag{10}$$

or as a direct function of ψ and S

$$k_r(S) = \frac{\int_{S_{\min}}^{S}(\mathrm{d}S/\psi^2)}{\int_{S_{\min}}^{1}(\mathrm{d}S/\psi^2)} \tag{11}$$

where the subscripts min and max hold for the minimum and the maximum values. This approach has been modified by Fatt and Dykstra (1951) to account for the *tortuosity* of the flow path. They assumed that the tortuosity is inversely proportional to r^b and obtained the formula

$$k_r(S) = \frac{\int_{S_{\min}}^{S}(dS/\psi^{2+b})}{\int_{S_{\min}}^{1}(dS/\psi^{2+b})} \tag{12a}$$

From comparing their formula with measured results, they found that b is close to 1. They indicated, however, that b may vary with the type of soil. Burdine (1953) accounted for tortuosity by applying a correction factor to Equation (11) equal to S_e^2 leading to

$$k_r(S) = S_e^2\frac{\int_{S_{\min}}^{S}(\mathrm{d}S/\psi^2)}{\int_{S_{\min}}^{1}(\mathrm{d}S/\psi^2)} \tag{12b}$$

Considering two-phase flow, (e.g., water and air), a similar equation can be written for the nonwetting fluid:

$$k_m(S) = (1 - S_e)^2\frac{\int_{S}^{1}(\mathrm{d}S/\psi^2)}{\int_{S_{\min}}^{1}(\mathrm{d}S/\psi^2)} \tag{13}$$

Using relative permeability data for both gas and oil, Burdine found that the suggested correction factors considerably improve the prediction of k_r for both the wetting and the nonwetting fluids (Figure P17).

To take into account the random variation of the pore size, Childs and Collis George (1950) considered a porous column fractured at a plane normal to the direction of flow. The resulting identical faces are then randomly jointed together. The probability that a pore of radius r in one section should be connected to a pore of radius ρ in the other is

$$a(r,\rho) = f(r)f(\rho)\mathrm{d}r\mathrm{d}\rho \tag{14}$$

To simplify the matter, they assumed that the resistance to flow was dominated by the pore of smaller radius. Mualem (1974, 1976a) showed that this model leads to the final formula

$$k_{\mathrm{r}}(S) = \frac{\int_{S_{\min}}^{S}\left[(S-s)/\psi^2\right]\mathrm{d}s}{\int_{S_{\min}}^{1}\left[(S-s)/\psi^2\right]\mathrm{d}s} \tag{15}$$

where s is a dummy variable of integration representing saturation as a function of ψ. This model has been discussed and experimentally tested by Marshall; Millington and Quirk; Jackson et al; Brutsaert; Kunze, Uehara, and Graham; Green and Corey; Bruce; Reisenauer; and Mualem and Dagan (see review and references in Mualem and Dagan, 1976). The attempt to use the model for a direct computation of the saturated hydraulic conductivity very often yields an error as large as several orders of magnitude. One would have to measure one value (probably K_s) to derive $K(S)$ with the aid of Equation (15). Comparison between predicted and measured k_r values shows that better agreement is achieved by multiplying Equation (15) with a correction factor S_e^n. Again no universal value of n has been found compatible to all types of soil. Millington and Quirk (1961) suggested $n = 4/3$ while Kunze, Uehara, and Graham found that using $n = 1$ improved the prediction of Equation (15). Using a model similar to that featured by Childs and Collis George, Wylie and Gardner (1958) argued that as a result of the random rejoining of the cut porous slab, the probability of a pore of radius r at one slab to encounter pores of the other slab is $a_e = f(r)\theta/\lambda$, where λ is a constant correction factor. Hence the porosity of the contact interface reduces to θ^2/λ, which is interpreted as if each pore had an effective radius of $r_e = \sqrt{\theta/\lambda}$. Substitution of a_e and r_e instead of $f(r)$ and r in Equation (10) yields Burdine's formula (Equation (12b)) analytically. Yet the idea of joining two cross-sections and considering a hydraulic conductivity of the intermediate interface is physically questionable because in flow there is no resistance at the cross-section.

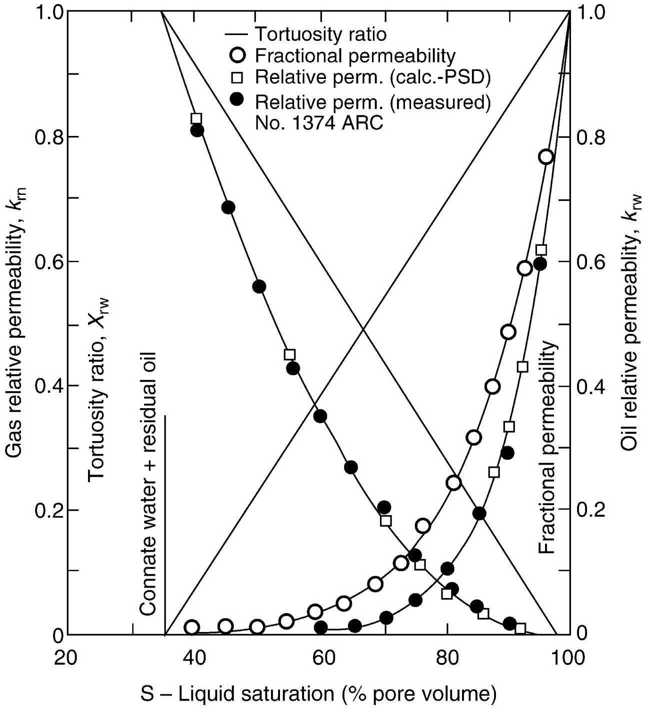


Figure P17 Measured and calculated relative permeabilities for liquid and gas as a function of liquid saturation (after Burdine, 1953).

Mualem (1976a) developed a conceptual modeling of porous media instead of the physical one of Wylie and Gardner. Consider a porous slab of thickness Δx ($x \to x + \Delta x$ along the axis). The pore area distribution at the two slab sides is identical. For $\Delta x \ggg R_{\max}$, complete randomness of the relative position of the two slab faces is assumed. The probability of having pores of radii $r \to r + \mathrm{d}r$ at x encountered with pores of radii $\rho \to \rho + \mathrm{d}\rho$ at $x + \Delta x$ is given by Equation (14). Here, no direct connection between the pores r and ρ exists along the x-axis. The other extreme case occurs when $\Delta x \to 0$. Then the correlation between the two faces of the slab is complete. Since we are concerned with the effect of pore changes on the hydraulic conductivity, it is more relevant to consider Δx to be of the same order of magnitude as the pore radii. Then the probability of a pore of radius between r and $r + \mathrm{d}r$ being connected to a pore of radius between ρ and $\rho + \mathrm{d}\rho$ is

$$a(r,\rho) = G(R,r,\rho)f(r)f(\rho)\mathrm{d}r\mathrm{d}\rho \tag{16}$$

$G(R, r, \rho)$ is a correction accounting for partial correlation between the pores r and ρ at a given water content $\theta(R)$.

The contribution of the actual flow configuration in the slab to the hydraulic conductivity cannot be accurately assessed. Therefore, two simplifying assumptions are used: (*i*) there is no bypass flow between the slab pores, and (*ii*) the pore configuration may be replaced by a pair of capillary elements whose lengths (l) are proportional to their radii $l_1/l_2 = r/\rho$. The hydraulic conductivity is then found to vary as $r_e^2 = r\rho$. A correction factor $T(R, r, \rho) < 1$ is used to account for eccentricity of the flow path (tortuosity factor). To simplify the computations, it is assumed that both correlation and tortuosity are power functions of the effective saturation, which leads to the final formula:

$$k_{\mathrm{r}}(S) = S_{\mathrm{e}}^{n}\left[\frac{\int_{S_{\min}}^{S}\mathrm{d}S/\psi}{\int_{\mathrm{S}_{\min}}^{1}\mathrm{d}S/\psi}\right]^2 \tag{17}$$

Obviously, n depends on the soil type. However, as a universal n is commonly desired, data of 45 various types of soils were used to determine n (by an analytical best-fitting procedure). The value $n = 0.5$ yields the minimum computed discrepancies between measured and predicted k_r.

All $K_r(S)$ formulas require the knowledge of the residual water content θ_r. However, $\theta(\psi)$ curves are very rarely measured up to this lower value of θ. Kunze, Uehara, and Graham

(1968) investigated the influence of using partial and complete $\psi(\theta)$ curves on the computed hydraulic conductivity. It seems that complete $\psi(\theta)$ information improves the quality of the prediction mainly as a result of better fulfillment of the requirement that $K = 0$ for $\theta = \theta_r$. Mualem (1976a,b) suggested a computational method for the determination of θ_r and extrapolation of the partially measured $\psi(\theta)$ curve up to this value.

The accuracy and the deficiencies of the models of Averjanov, Childs and Collis George, Burdine and Mualem (Equations (6) ($n = 3.5$), (12), (15) (with $S_e = 4/3$ as correction factor), and (17) ($n = 0.5$), respectively) were mutually tested against measured data of 45 soils (Mualem, 1976a). The deviations between the measured and predicted curves were quantitatively evaluated. It was found that different soils are best represented by different methods (Figure P18). However, it seems that on an overall basis, Mualem's formula yields the best results. Averjanov's formula yields good results for sands while often the agreement with experimental data of heavy soils is not satisfactory (see Figure P18a). Among the other three statistical models, Burdine's formula yields the poorest results. For soils in which $d\theta/d\psi \rightarrow 0$ as $\psi \rightarrow 0$, there is an abrupt fall of the computed hydraulic conductivity near saturation (Figure P18b), which only rarely is sustained by observations. Recently Mualem and Dagan (1976) showed that in spite of the apparent differences between the statistical models, they might be derived systematically from a few common principles following Mualem's approach as stated above. Moreover, several other formulas of $K_r(S)$ can be derived on this basis.

Farrel and Larson (1972) attempted to evaluate the hydraulic conductivity using existing theories of heat and electrical conductivity of heterogeneous media constructed of spherical or cylindrical elements. They used the capillary law to derive the pore water distribution function from the $\psi(\theta)$ relation. Assuming that $\psi(S_e)$ can be represented by the function $\psi = \psi_{cr}^{e\alpha(1-S_e)}$, they obtained two integral functions for K_r (see Table P7), one when it is assumed that the pore domains are of spherical shape, and the other for cylindrical pore domains. The computation of K_r is carried out by an iterative method. They found that the results differ considerably from those based on Equation (15), for porous media of wide pore water distribution function. There is no evidence that this method is more theoretically sound than the other models. However, it is more tedious for practical use, and its predictive ability has not been adequately determined.

All the models discussed previously are presented in terms of a simple integral. It permits us, therefore, to derive direct analytical formulas for $K_r(S)$ or $K_r(\psi)$ when an analytical $\psi(S)$ curve is fit to the measured data. Mualem (1974) summarized the K_r formulas, obtained using the various models, for two $\psi(S_e)$ functions (Table P7). An interesting result is that the power function $k_r = S_e^m$ is obtained by the statistical models for $S_e = (\psi/\psi_{cr}) - \lambda$. Moreover, in this case the models of Childs and Collis George and Mualem yield identical formulas. Yet, there is no definite recipe for choosing the value of m as a function of the soil type. The value of λ is determined by adjusting the power function to the measured $\psi(S)$ curve. It can be done either graphically (Brooks and Corey, 1964) or analytically (Mualem, 1976a).

Hysteresis of the relative permeability

The hysteretical behavior of unsaturated soils is manifested by the $\theta(\psi)$ relationship (see *Capillary pressure*) and by the $K(\psi)$

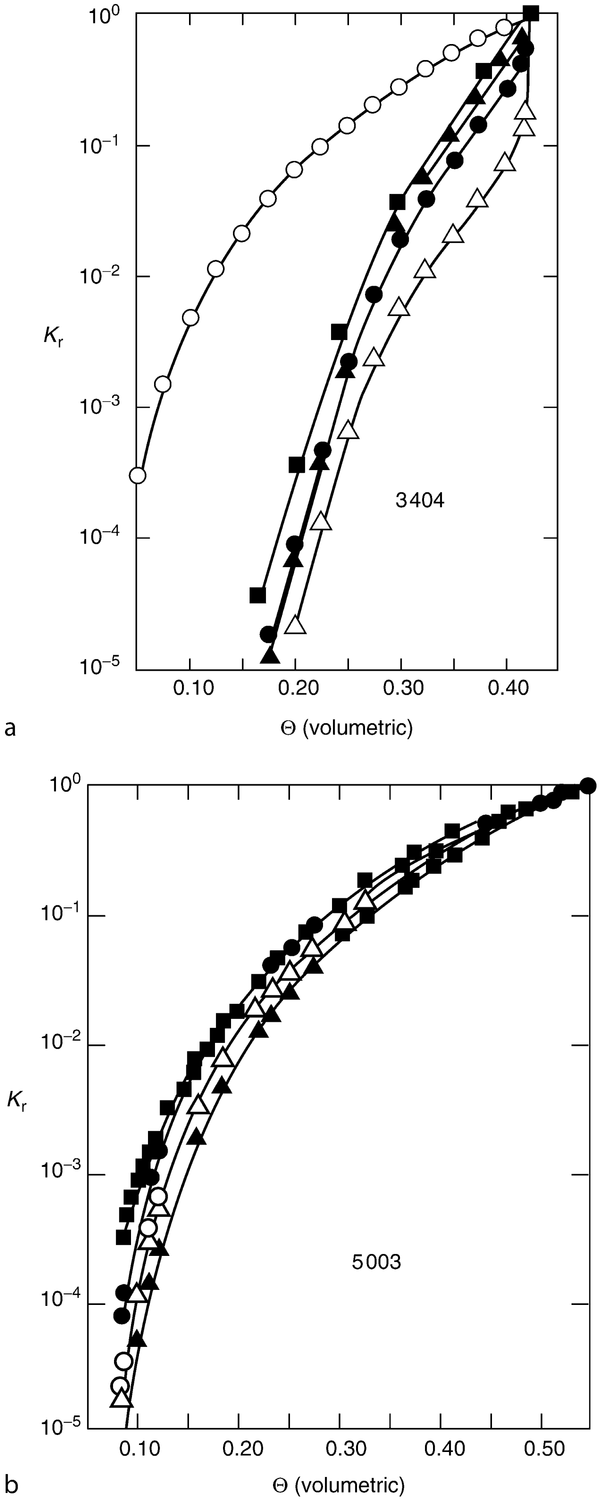


Figure P18 Computed relative hydraulic conductivities for two soils, using four models: Averjanov's (*hollow circles*); Wyllie and Gardner (*hollow triangles*); Childs and Collis George as modified by Millington and Quirk (*triangles*); and Mualem (*circles*). The measured curve is shown by *squares* (after Mualem, 1976a).

Table P7 Prediction methods of the relative hydraulic conductivities and the results for two analytic approximations of the $\psi - S$ relationship (after Mualem, 1974)

Reference	$f(\psi, S_e)$ $g(K, S_e, \psi)$	$S_e = (\psi/\psi_{cr})^{-\lambda}$	$\psi = \psi_{cr} e^{\alpha(1-S_e)}$
Mualem form of Childs and Collis George CCC, $n = 0$ MQ, $n = 4/3$ Kunze, $n = 1$	$K_r(S_e) - S_e^n \frac{\int_0^{S_e} [(S_e - s)/\psi^2(s)]ds}{\int_0^1 [(1-s)/\psi^2(s)]ds}$	$K_r(S_e) = S_e^{(2+2\lambda)/\lambda+n}$ $K_r(\psi) = \psi/\psi_{cr})^{-(2+2\lambda)-n\lambda}$	$K_r(S_e) = S_e^n \frac{[e^{2\alpha S_e} - 2\alpha S_e - 1]}{[e^{2\alpha} - 2\alpha - 1]}$
Burdine Wyllie and Gardner	$K_r(S_e) = S_e^2 \frac{\int_0^{S_e} ds/\psi^2(s)}{\int_0^1 ds/\psi^2(s)}$	$K_r(S_e) = S_e^{(2+3\lambda)/\lambda}$ $K_r(\psi) = (\psi/\psi_{cr})^{-(2+3\lambda)}$	$K_r(S_e) = S_e^2 \frac{[e^{2\alpha S_e} - 1]}{[e^{2\alpha} - 1]}$
Mualem $n = 0.5$	$K_r(S_e) = S_e^n \left[\frac{\int_0^{S_e} ds/\psi(s)}{\int_0^1 ds/\psi(s)}\right]^2$	$K_r(S_e) = S_e^{(2+2\lambda)/\lambda+n}$ $K_r(\psi) = (\psi/\psi_{cr})^{-(2+2\lambda)-n\lambda}$	$K_r(S_e) = \frac{[e^{2\alpha S_e} - 2e^{\alpha S_e} + 1]}{[e^{2\alpha - 2e^{\alpha}+1}]}$
Yuster $m = 2.0$ Irmay $m = 3.0$ Averjanov $m = 3.5$ Corey $m = 4.0$	$K_r(S_e) = S_e^m$	$K_r(\psi) = (\psi/\psi_{cr})^{-m\lambda}$	$K_r(\psi) = 1 - \frac{1}{\alpha}\ln(\psi/\psi_{cr})^m$
Farrel and Larson	$K_r(S_e) = \frac{\int_0^{S_e} [\nabla\phi(s)/\psi^2(s)]ds / \int_0^{S_e} \nabla\phi(s)ds}{\int_0^1 [\nabla\phi(s)/\psi^2(s)]ds / \int_0^1 \nabla\phi(s)ds}$ Spherical pores $\nabla\phi(s) = 3K/[2K + M/\psi^2(s)]$ Cylindrical pores $\nabla\phi(s) = 2K/[K + M/\psi^2(s)]$		$K_r = \left[\frac{\psi}{\psi_{cr}}\right]^{\overline{2}} \frac{[1 - e^{-4\alpha S_e/3}][e^{2\alpha/3} - 1]}{[1 - e^{-4\alpha/3}][e^{2\alpha S_e/3} - 1]}$ For spherical pores For cylindrical pores $K_r = \left[\frac{\psi}{\psi_{cr}}\right]^2 \frac{[1 - e^{-\alpha S_e}][e^{\alpha} - 1]}{[1 - e^{-\alpha}][e^{\alpha S_e} - 1]}$
Wind, Wesseling	$K_r = (\psi/\psi_{cr})^{-n}; \quad \psi < \psi_{cr}$ $K_r = 1 \quad \psi < \psi_{cr}$	$K_r(S_e) = S_e^{n/\lambda}$	$K_r(\psi) = e^{-\alpha n(1-S_e)}$
Gardner	$K = \frac{a}{\lvert\psi\rvert^n + b}; \quad K_r = \frac{1}{(\psi/\psi_{cr})^n + 1}$	$K_r(S_e) = \frac{1}{1 + S_e^{-n/\lambda}}$	$K_r(\psi) = \frac{1}{e^{\alpha n(1-S_e)}}$
Gardner	$K_r = e^{a(\psi - \psi_{cr})}; \quad \psi < \psi_{cr}$ $K_r = 1 \quad ; \quad \psi > \psi_{cr}$	$K_r = e^{a\psi} cr^{(S_e^{-1/\lambda} - 1)}$	$K_r(S_e) = e^{a\psi} cr^{[e^{\alpha(1-S_e)} - 1]}$

and the $K(\theta)$ relationships. Figure P19 shows the typical three hysteretical loops measured by Poulovassilis (1970) in experiments carried out on a sand sample. Obviously the $K(\psi)$ hysteresis is magnified relative to the $\theta(\psi)$ hysteresis, while the magnitude of the $K(\theta)$ hysteresis is very limited. Moreover, for a soil sample that is rewetted after it has been drained to a low water content, hysteresis should be even more significant. For a given ψ, the relative permeability in a drying process may take a value a hundred times greater than the corresponding k_r in the wetting process. Yet the $k_r(\theta)$ may be almost a unique function. Consequently, for practical use in solution of problems of *infiltration* (*q.v.*) under intermittent irrigation or rainfall, where drying and wetting processes are involved, it is better to use the unique function $k_r(\theta)$ rather than a $k_r(\psi)$ function as suggested in Tables P7 and P8. Even though this typical phenomenon has been reported by several investigators such as Nielsen and Biggar, Topp and Miller, Topp, Talsma, Vachaud and Thony (see references in Topp, 1969) who found no significant $k_r(\theta)$ hysteresis, it is suspected that in certain cases it is not negligible. Staple (1965) and Dan and Wierenga (1975) found considerable $K(\theta)$ hysteresis, with an order of magnitude deviation between corresponding values of k_r on the main wetting and the main drying curve. Also for some soils the higher conductivity is measured on the drying branch while for other soils it is observed on the wetting branch.

Quantitative models of the relative permeability hysteresis

All the models of the relative permeability discussed in the preceding section do not take into account the capillary hysteresis. The statistical models that use an observed $\theta(\psi)$ curve for predicting $K(\theta)$ or $K(\psi)$ are based on the assumption that the pore distribution function *f*(*r*) is characterized by only one variable, i.e., the pore is defined by only one geometrical length scale (r). Since r is related to ψ in a unique way, the relationships $\theta(\psi)$ and $K(\psi)$ are univalued. These models can be used for computation of $K(\psi)$ for a given $\theta(\psi)$ curve representing either drainage or imbibition (Kunze et al., 1968). Such an approach implies, however, that *f*(*r*) is not determined by the soil structure only, but also depends on the process by which the porous medium is brought to a certain θ. One has, therefore, to introduce a new variable related to the process described by the $\theta(\psi)$ curve. One of the contradictory results of the existing methods is the derivation of different values of K_{sat} (or of the matching factor) depending on what branch of the $\theta(\psi)$ hysteresis is used in the computational procedure.

Recently Mualem (1974, 1976b) set forth a theory that permits the prediction of the $K(\psi)$ or the $K(\theta)$ hysteresis as well as the $\theta(\psi)$ hysteresis. In essence, the new models are an extension of the domain theory of hysteresis (see *Capillary pressure*). A porous medium is characterized in terms of elementary pore

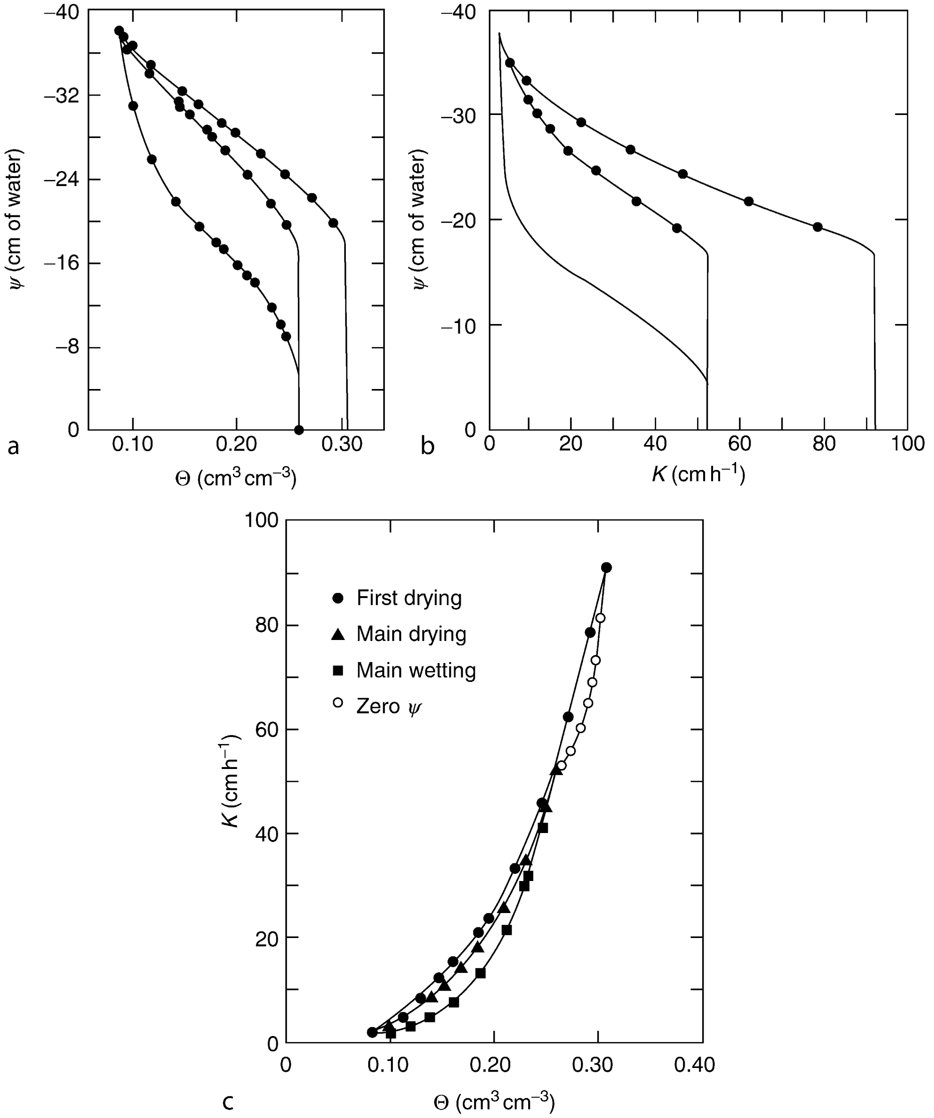


Figure P19 Experimentally observed (a) water content-capillary head hysteresis; (b) hydraulic conductivity-capillary head hysteresis; and (c) hydraulic conductivity-water content hysteresis (after Poulovassilis, 1970).

domains, each of which is defined by a two length scale r and ρ. The domains distribution function $f(r, \rho)$ for a medium can be quantitatively derived on the basis of some measured data. Moreover, the filled domains diagrams definitely determine the state of the system for a particular capillary head and a given process. Hence one can evaluate the corresponding contribution of an elementary pore domain to the hydraulic conductivity, and by integrating over the filled pore domains, obtain the actual hydraulic conductivity. Assuming that the hydraulic conductivity of such element is proportional to the product $r\rho$, the relative permeability can be expressed by the relation:

$$k_r(\theta) = \frac{\underset{\text{(filled pores)}}{\iint r\rho f(r,\rho)\mathrm{d}r\mathrm{d}\rho}}{\underset{\text{(all pores)}}{\iint r\rho f(r,\rho)\mathrm{d}r\mathrm{d}\rho}} \tag{18}$$

The domain of the integration in the r,ρ plane depends on the hysteretical process to which the porous medium is subjected, and therefore $k(\psi)$ or $k_r(\theta)$ are also hysteretic. In principle, then, if Equation (18) is applied to a model of hysteresis, it will derive the relative permeability and the water content as a function of ψ without additional data (to that required for the study of capillary hysteresis only).

Based on these principles, Mualem (1976b) applied the various models of hysteresis for prediction of the k_r hysteresis. The predicted $k_r(\psi)$ hysteresis displayed the same properties characterizing the $\theta(\psi)$ hysteresis, as sustained by experimental observations. Figures P20, P21, and P22 show a comparison between measured and predicted $K(\psi)$ and $K(\theta)$ hysteresis, using data of Topp and Miller (1966). The generalized dependent domain theory has been used. It should be noted that in this case not only the scanning curves but also the first drying and the

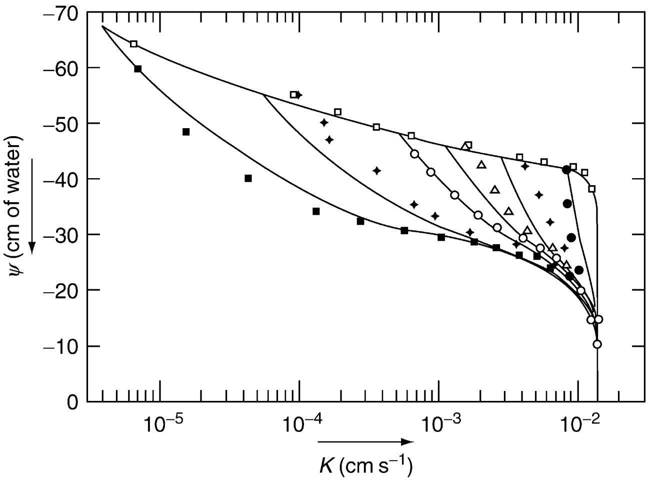


Figure P20 Predicted hydraulic conductivity-capillary head hysteresis (*solid lines*) compared with experimental results (after Mualem, 1976b).

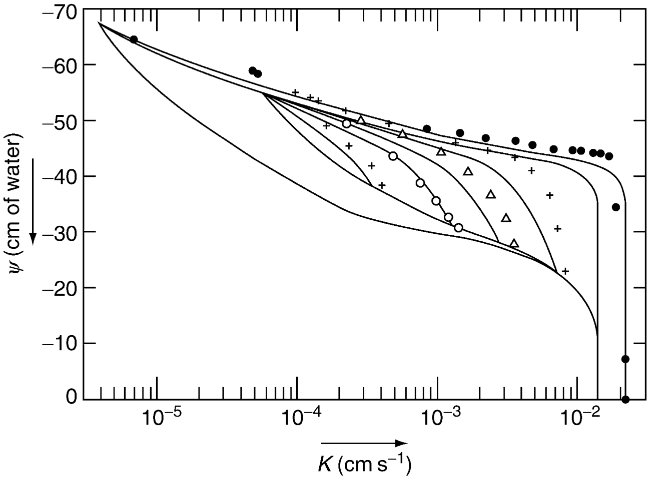


Figure P21 Predicted hydraulic conductivity-capillary head hysteresis including the first drying curve and the secondary scanning curves in drainage (*solid lines*) compared with the experimental results (after Mualem, 1976b).

boundary curves of the main loop are predicted. The agreement between theory and observation is surprisingly good.

This review shows that considerable progress has been made in studying the hydraulic properties of soil. The new models attain a high degree of generality and capability of representing observed phenomena more accurately. One may expect that a more sound and accurate solution of the unsaturated flow problems will be achieved when these new models are used.

The reader should be aware of the fact that chemical solutions that interact with the soil matrix, swelling soils, and agricultural treatment are parameters that considerably affect the hydraulic properties. There is no simple recipe for handling these cases in quantitative computations. The reader interested in these aspects should look for related subjects in this encyclopedia and other scientific papers.

Y. Mualem and H. J. Morel-Seytoux

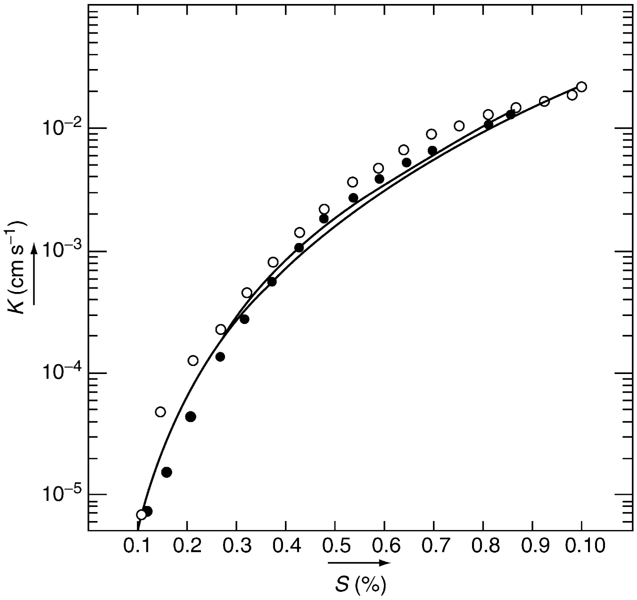


Figure P22 Predicted hysteresis of the hydraulic conductivity as a function of saturation (*solid lines*) compared with experimental results in drainage (*open circles*) and wetting process (*solid circles*) (after Mualem, 1976b).

Bibliography

Averjanov, S.F., 1950. About permeability of sursurface coils in case of incomplete saturation, Eng. Collection, Vol. VII, (1950) as quoted by P. Ya Palubarinova, 1962. *The Theory of Ground Water Movement* (translation by Roger DeWiest, I.M.). Princeton, NJ: Princeton University Press, pp. 19–21.

Brooks, R.H., and Corey, A.T., 1964. *Hydraulic properties of porous media, Hydrology Paper 3.* Fort Collins: Colorado State University, 27 pp.

Burdine, N.T., 1953. Relative permeability calculation size distribution data. *Petroleum Trans. AIME*, **198**: 71–78.

Childs, E.C., and George, N.C., 1950. The permeability of porous materials. *R. Soc. Proc.* (London), **A201**: 392–405.

Dane, J.H., and Wierenga, P.J., 1975. Effect of hysteresis on the prediction of infiltration redistribution and drainage of water in a layered soil. *J. Hydrol.*, **25**: 229–242.

Farrel, D.A., and Larson, W.E., 1972. Modeling the pore structure of porous media. *Water Resour. Res.*, **3**: 699–706.

Fatt, I., and Dykstra, H., 1951. Relative permeability studies, *AIME*, **192**: 249–255.Tran.

Gardner, W.R., 1958. Some steady state solutions of the unsaturated moisture flow equation with application to evaporation from a water table. *Soil Sci.*, **85**: 228–232.

King, L.G., 1964. Imbibition of fluids by porous solids. Ph.D. Thesis, Colorado State University, 231 pp.

Kunze, R.J., Uehara, G., and Graham, K., 1968. Factors important in the calculation of hydraulic conductivity, *Soil Sci. Soc. America Proc.*, **32**: 760–765.

Millington, R.J., and Quirk, J.P., 1961. Permeability of porous solids, *Faraday Soc. Trans.*, 57: 1200–1206.

Mualem, Y., 1974. Hydraulic properties of unsaturated porous media: a critical review and new models of hysteresis and prediction of the hydraulic conductivity, Technion, Project No. 38/74, Haifa:Israel Institute of Technology, 235 pp.

Mualem, Y., 1976a. A new model for predicting the hydraulic conductivity of unsaturated porous media, *Water Resour. Res.*, **12**(3): 593–622.

Mualem, Y., 1976b. Hysteretical models for prediction of the hydraulic conductivity of unsaturated porous media, *Water Resour. Res.*, **12**(6): 1248–1254.

Mualem, Y., and Dagan, G., 1976. Methods of predicting the hydraulic conductivity of unsaturated soils, project 442. Haifa:Israel Institute of Technology, 78 pp.

Poulovassilis, A., 1970. The effect of the entrapped air on the hysteresis curves of a porous body and its hydraulic conductivity. *Soil Sci.*, **109**: 154–162.

Purcell, W.R., 1949. Capillary pressures – their measurement using mercury and the calculation of permeability therefrom. *Petrol. Trans. AIME*, **186**: 39–48.

Rijtema, P.E., 1965. An analysis of actual evapotranspiration. *Agric. Res. Rep. 659.* Wageningen, The Netherlands, Center for Agricultural Publications and Documentation, 107 pp.

Staple, W.J., 1965. Moisture tension, diffusivity and conductivity of a loam soil during wetting and drying, *Can. J. Soil Sci.*, **45**: 78–86.

Topp, C.C., 1969. Soil water hysteresis measured in a sandy loam compared with the hysteretic domain model. *Soil Sci. Soc. Am. Proc.*, **33**: 645–651.

Topp, G.C., and Miller, E.E., 1966. Hysteretic moisture characteristics and hydraulic conductivities for glass-bead media. *Soil Sci. Soc. Am. Proc.*, **30**: 156–162.

Wind, G.P., 1955. Field experiment concerning capillary rise of moisture in heavy clay soil. *Neth. J. Agric. Sci.*, **3**: 60–69.

Wyllie, M.R.J., and Gardner, G.H.F., 1958. *The Generalized Kozeny–Carman Equation.* Houston, TX: World Oil, pp. 210–228.

Yuster, S.T., 1951. Theoretical considerations of multiphase flow in idealized capillary systems. *Proc. 3rd World Petrol. Congr.*, **2**: 437–445.

Cross-references

Capillary Pressure
Conductivity, Hydraulic
Flow Theory
Imbibition
Infiltration
Percolation
Soil Pores
Soil Water
Thermodynamics of Soil Water
Water Content and Retention
Water Movement
Wetting Front

PERMEAMETER

An instrument for measuring the hydraulic conductivity of a porous material such as a soil.

Cross-references

Plant Roots and Soil Physical factors
Soil Pores

PETROCALCIC

Descriptive of a horizon in soil, cemented by calcium carbonate.

PETROGYPSIC

Descriptive of a horizon in soil cemented by gypsum.

pH

See *Acids, Alkalis, Bases and pH*.

PHAEOZEMS

Phaeozems, like Chernozems and Kastanozems are soils of the major grasslands and their forested margins. They occur in the wetter regions, have dark, humus-rich surface horizons, and are more highly leached than the other two Reference Soil Groups mentioned. There are no accumulations of secondary calcite in the upper meter. The following account is taken from FAO (2001).

Connotation. Dark soils rich in organic matter; from Gr. *phaios*, dusky, and R. *zemlja*, earth, land.

Synonyms. In other classifications they appear as brunizems (Argentina, France), degraded Chernozems (former USSR), Parabraunerde-tsjernozems (Germany), ‘dusky red prairie soils’ (USA pre-Soil Taxonomy) or ‘udolls’ and ‘aquolls’ in the order of the mollisols (Soil Taxonomy).

Definition. Phaeozems are defined by FAO (2001) as soils having

1. a *mollic* horizon, and
2. a base saturation (in 1 M NH_4OAc at pH 7.0) of 50 percent or more and having no secondary carbonates to at least a depth of 100 cm from the soil surface, or to a contrasting layer (*lithic* or *paralithic* contact, *petrocalcic* horizon) between 25 and 100 cm, and
3. no diagnostic horizons other than an *albic, argic, cambic* or *vertic* horizon.

Parent material. Aeolian silt (loess), glacial till and other unconsolidated, predominantly base-rich materials, usually containing calcite.

Environment. Predominantly in warm to cool climates, on the flat to undulating land of the loessial plains of the northern hemisphere, but also in highland regions of the tropics. In the temperate regions tall grass prairie or steppe vegetation is normal, with forest on the borders of the grassland zones. Light forest occurs is the natural vegetation of the tropical occurrences. In North America, Phaeozems form in a belt extending from Canada with a rainfall of 400 mm yr^{-1} and an average temperature of 2 °C, to Missouri south, with 1 200 mm per annum and an average temperature of 18 °C. The surplus of precipitation over evapotranspiration is about the same in the whole belt, and is high enough to ensure a downward percolation of water most years. Periods of water deficit do occur however, when the soil dries out.

Distribution. The global extent of Phaezems is about 190 million ha, worldwide, with some 70 million in the USA, in the (sub-)humid Central Lowlands and easternmost parts of the Great Plains. In the South American pampas, there is a further 50 million ha of Phaeozems, and in northeastern China, 18 million more. Smaller, mostly discontinuous areas are found along the Danube in Europe, and in elevated parts of the tropics. Figure P23 shows the worldwide distribution.

Characteristics. AhBC profiles are commonest, and have a mollic surface horizon that is thinner than in Chernozems and

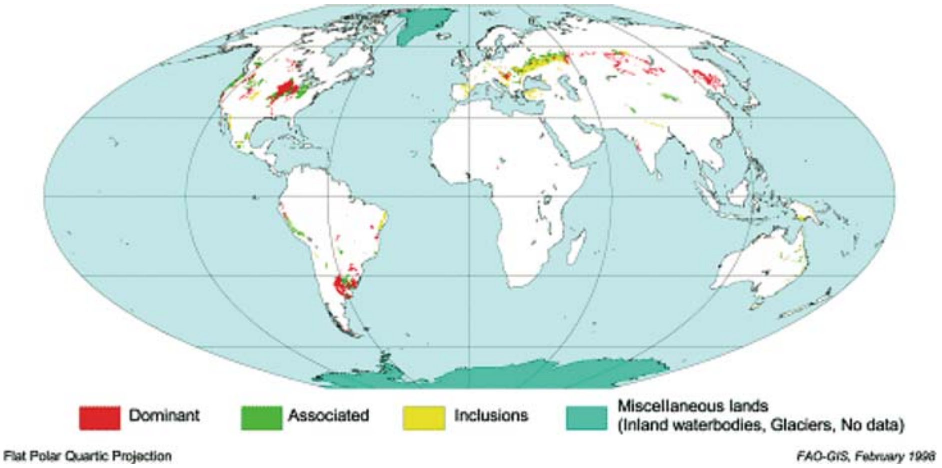


Figure P23 Global distribution of Phaeozems.

darker brown to gray in color. Below it in the B, a brown cambic or reddish-brown argic (with 10–20 percent more clay than in the A) horizon occurs. If the water table is shallow, or intermittently perched on an argic B, there may be some mottling in the A. Normally the soils are porous and well-aerated, with a crumb to blocky structure, have about 5 percent organic matter in the surface layer, and a pH from 5 to 7 that increases downwards. CEC is high and base saturation between 65 and 100 percent.

Origin. Phaeozems occur on similar parent materials to Chernozems and Kastanozems, that is sediments (particularly loess) rich in bases, calcite for example. Weathering and leaching under a more humid climate than the other two prairie soils mentioned are the principle genetic processes. Both are more advanced than in the other two cases, and carbonate is absent from the upper meter of soil. Faunal activity (worms, small mammals) homogenizes the soil, and where most intense leads to a thickening of the mollic horizon. In addition wormholes and krotovinas may extend into the parent material.

Argic B horizons do occur in Phaeozems but they are widely regarded as relics from an earlier development towards Luvisols (in areas with a more humid climate).

Use. Most Phaeozems are exploited. Having a high inherent fertility, and excellent hydrodynamic properties, they are used in arable agriculture or in ranching. Crops include soybean, wheat and other small grains (USA and Argentina), predominantly wheat (Canada and Russia), irrigated cotton (Texas), and, generally in the temperate climates, wheat, barley and vegetables alongside other crops.

The main problems are periodic drought, and wind and water erosion.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science*, 2nd edn. Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World*. Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Biomes and their Soils
Calcareous Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Near Neutral Soils

PHASE RULE AND PHASE DIAGRAMS

The Phase Rule dates from the classic work of J. Willard Gibbs that established the scientific basis of chemical thermodynamics between 1875 and 1878: see the reprint (Gibbs, 1961) and two useful commentaries (Donnan and Haas, 1936; and Seeger, 1974). The rule serves as a deductive check and balance to the science of pedology, which like all the Earth sciences is predominantly inductive in nature.

Being derived from classical thermodynamics the Phase Rule deals with systems at equilibrium. Since soils are clearly in a state of disequilibrium, application of the Phase Rule (or classical thermodynamics in general) to soil systems, needs some initial justification. The first justification is that a Phase Rule approach to soil mineralogy results in a model that represents the state a system strives towards, and in the humid tropics, comes close to achieving, provided that the requisite time and energy are available. Secondly, this equilibrium model represents a kind of end-bracket on all the disequilibrium paths of evolution of the natural system, even when not achieved. It thereby lays a fundamental constraint on any hypothesis of mineral genesis in soils. Thirdly, a megascopic disequilibrium system may be considered as a mosaic of microscopic systems, each of which approaches a local equilibrium (Korzhinskii, 1979; Chesworth and Dejou, 1980). Last, the equilibrium model is a rigorous one and although the natural disequilibrium state can be expected to differ from the model, the differences are themselves instructive.

A basic thermodynamic vocabulary

Connolly (1990) gives a thorough discussion of multivariable phase diagrams and includes a useful account of thermodynamic nomenclature. Regarding phase equilibria in aqueous systems under Earth-surface conditions (Pankow, 1999) is a helpful reference. The following terms constitute the basic vocabulary, and Morel (1983) provides a thorough examination of each.

System. Any arbitrary part of the universe considered as an entity, with a boundary between it and its surroundings, chosen for the sake of convenience. The three types of system are defined in terms of the nature of the boundary. In an isolated system the boundary allows neither mass nor energy to pass through. A closed system allows the passage of energy but not mass. An open system has a boundary that is permeable to both energy and mass. The word is also used in a purely chemical sense as in the phrase 'the system SiO_2–Al_2O_3–H_2O' where it means all possible thermodynamic systems made up of these specific components.

Surroundings. That part of the universe lying outside the boundaries of the arbitrary system – equivalent to the environment of the system.

Phase. A physically homogeneous part of a system, that is separable from all other phases, by physical means.

Components. The smallest number of chemical entities that are independently variable, and that are needed to express the composition of a system, all phases within it, and all reactions that take place there.

State function. Properties or parameters that are independent of the path by which the system reached its current state. These properties and parameters are necessary and sufficient to define that state. The two types are: intensive properties, which are independent of mass (e.g., pressure, temperature, chemical potential); and extensive ones, which are proportional to mass (e.g., volume, entropy, internal energy).

Path function. Properties or parameters that depend upon the path by which a system reached its current state (e.g., work, heat used in a process).

Variance. The number of intensive parameters that must be fixed in defining the system. Variance is also called the number of degrees of freedom of a system.

Derivation of the phase rule

For a phase at equilibrium in a system, disregarding the presence of external fields (gravitational, electrical, magnetic), considering work of only PV type, and ignoring all surface and boundary effects, the Gibbs-Duhem Equation holds:

$$VdP - SdT - \sum n_i d\mu_i = 0$$

Here, i is an individual component, and if c is the number of components in the system, the total number of variables is $c + 2$ that is: the chemical potentials of each individual component (μ_i), plus temperature (T) and pressure (P). An equation of this type is valid for each phase in the system. If the total number of phases is ϕ, then the system is defined by a total of ϕ Gibbs-Duhem Equations.

The variance (F) of a system is given by the total number of variables minus the number of simultaneous (Gibbs-Duhem) relationships between them. This operation produces Gibb's Phase Rule, which gives the number of variables that are undefined in the system, or the number of degrees of freedom that the system has:

$$F = c + 2 - c$$

Systems may be classified in terms of F (invariant, univariant, divariant, and so on); in terms of c (unary, binary, ternary, and so on); or in terms of ϕ (homogeneous – that is made up of a single phase, or heterogeneous or multi-phase – made up of several co-existing phases).

A note on components

In the derivation of the Phase Rule, it is the number of components that is significant, not their nature. A second important point: a component need have no independent existence as a chemical species. Indeed it may be entirely fictive, for example, the component NaK^{-1} which can be used in reactions involving the exchange of K with Na in a mineral structure. The fact that oxide components are often used by Earth scientists is a reflection of convenience and of history – mineral and rock analyses have usually been given in weight percentages of oxide constituents, since the old days of gravimetric analysis. The major point to stress in the usage of Gibbs is that the components chosen must be independently variable of each other and must represent the smallest possible number. In Prigogine and Defay (1954) the usage is different. They define components as the chemical variables whose masses sum to the total mass of the system. When the number of reactions between the components in this sense, is subtracted from the number of components, the equivalent of Gibbs' independently variable components is obtained.

Finally, Korzhinskii (1959) uses the terms inert and perfectly mobile in describing components. An inert component has its chemical potential determined inside the system of interest, whereas a perfectly mobile component has its chemical potential applied from outside, in an analogous way to partial pressure. Zen (1963) provides a commentary on this distinction.

Phase diagrams

A phase diagram is a graphic representation of phase equilibria with a one to one geometrical correspondence with the phase rule as in Table P8.

The phase diagram for the one component system $CaCO_3$ illustrates the relationship in terms of the Cartesian coordinates P and T, and is therefore referred to as a PT diagram (Figure P24). This system illustrates the fact that there may be more than one invariant point in a given phase diagram, each with $c + 2$ univariant curves emanating from it, and delimiting $c + 2$ divariant areas between each pair of curves. Also note that each univariant curve represents a reaction between the phases on either side of the curve. Figure P25 is an example of a PT diagram in a three component system (Al_2O_3–SiO_2–H_2O) important in soil science.

Of particular usefulness in the study of soil mineralogy are chemical potential diagrams or their equivalents: diagrams such as Figure P26, using activity or fugacity as variables (Garrels and Christ, 1965; Lindsay, 2001; Bowers et al., 1984).

Since the activity of Al^{3+} and pH are related by equations of the type

Table P8 Classification of thermodynamic systems in terms of the number of degrees of freedom

Degrees of freedom	Number of phases	Geometrical analogy
0 (invariant)	C + 2	Dimensionless point
1 (univariant)	C + 1	Line or curve
2 (divariant)	C	Area
3 (trivariant)	C − 1	Volume

gibbsite

$$Al(OH)_3 + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$$

kaolinite

$$Al_2Si_2O_5(OH)_4 + 6H^+ \rightleftharpoons 2Al^{3+} + 2H_4SiO_4 + H_2O$$

in which Al^{3+} and H^+ show a constant 1 : 3 stoichiometric correspondence, the solution-saturated equilibria in this system, under isobaric, isothermal conditions, can be plotted in terms of the variables shown in Figure P26.

Applications of the phase rule to soils

The basic problem in using the Phase Rule to set up an equilibrium model for weathering systems and soils in particular is that such systems are of great compositional complexity. Consequently, there is a need to simplify as much as possible, while still retaining sufficient complexity to enable reasonable statements to be made about real systems. In particular, we need to know what components and what phases we should consider, and what range of environmental conditions are appropriate.

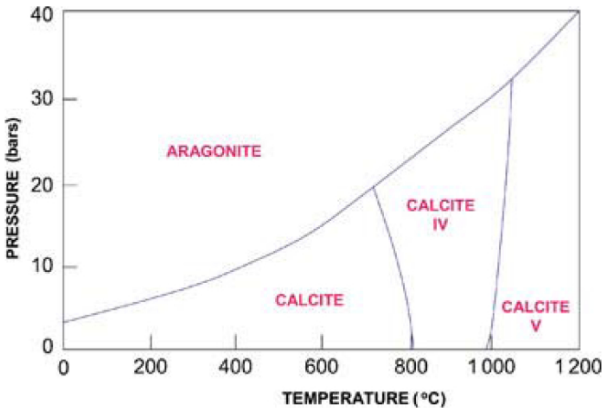


Figure P24 The system $CaCO_3$, which illustrates the phenomenon of polymorphism. Polymorphs are solid phases all having the same composition, in this case $CaCO_3$, but each with its own distinctive crystalline structure.

What are the important components? Over wide areas, the average composition of the Earth's continental surface is andesitic. Since the crust is also essentially a close packed framework of oxygens it can be considered initially as being made up of oxide components such as SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O and K_2O as majors, and TiO_2, MnO_2 and P_2O_5 as minors. In addition important components from the atmosphere and hydrosphere are H_2O, CO_2 and O_2. The biosphere provides further complications in terms of organic components.

What are the important phases? The important phases that need to be modeled in a soil system are the ones that form there. These include the following: oxides and hydroxides (e.g., quartz, goethite, hematite, gibbsite and boehmite), 1 : 1 sheet silicates (e.g., kaolinite and halloysite), 2 : 1 sheet silicates (e.g., illite, smectite and vermiculite), 2 : 1 : 1 sheet silicates (e.g., hydroxy-interlayered vermiculite), framework silicates (e.g., zeolites and possibly low temperature polymorphs of alkali feldspars), carbonates (e.g., calcite, siderite) and other minerals such as gypsum and halite, and in the special case of sulfidic soils, pyrite. No single system contains all of these phases. Generally no more than two to four need be considered together, the specific soil environment under consideration dictating the choice. Two important references concerning the mineral phases that form in soils are (Dixon and Schulze, 2002); and Meunier, (2005).

What are the appropriate environmental conditions? The most generally useful master variables of the weathering environment are pe (or Eh) and pH. The spread of pe-pH conditions in the stability field of water, and found in nature is

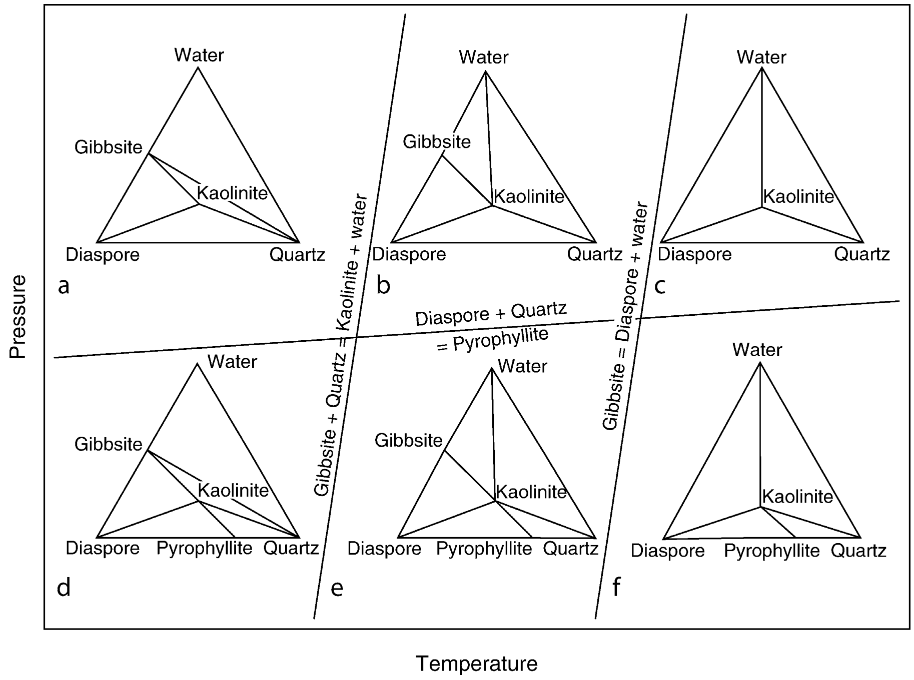


Figure P25 Schematic *PT* diagram of the system Al_2O_3–SiO_2–H_2O (from Chesworth, 1999).

approximately as shown (Figure P27) ignoring a number of rather rare environments at the surface of the Earth (e.g., acid sulfate soils, weathering sulfide-bearing ore deposits and gossans), the normally expected conditions cover a pe-pH field which shows three salients, each of which corresponds to one of the three lines of chemical evolution shown by soils in weathering.

The behavior of water dictates which trend is followed. The acid and alkaline trends are in the oxidizing (water-unsaturated) zone of weathering. The acid trend requires an excess of water with a net leaching or downward movement. The alkaline trend is found in dryer environments with a movement of soil water towards the soil surface and a net loss of water by evapotranspiration. A reduced trend is found in water-saturated conditions in a weathering profile.

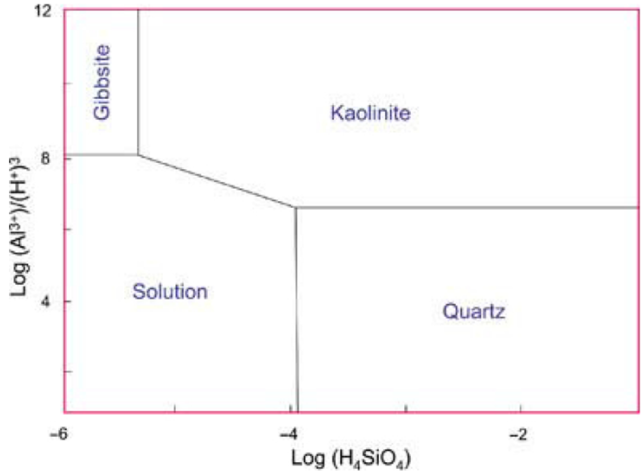


Figure P26 Equilibria in the system Al_2O_3–SiO_2–H_2O (from Chesworth, 1999).

Selected phase diagrams

The acid trend, the common one in weathering, is found in regions of humid climate on materials with a generally unimpeded drainage. Hydrolysis is the principal reaction, wherein acids from atmospheric and biospheric sources react within the solid earth as base. H^+ progressively displaces other cations, which are leached out of the system in solution. This acidification of the weathering materials pushes the soil towards the acid salient of Figure P27 and soils such as Podzols, Alisols, Acrisols and Ferralsols are produced. The result is an evolution of soils towards compositions made up chiefly of the four components SiO_2–Al_2O_3–Fe_2O_3–H_2O. This can be considered the fundamental system in soil science since all four components dominate virtually all soils.

Figure P28a is a compatibility diagram of this fundamental system showing phase assemblages stable at 25 °C and 100 kPa total pressure. It is constructed stepwise from the constituent 1, 2 and 3 component systems. Projection from the H_2O apex (Figure P28b) displays those minerals that can coexist with water at equilibrium at the surface of the Earth (assuming that H_2O, the thermodynamic activity of water, is equal to 1). Since goethite is a virtually ubiquitous phase in soils of humid climates, a projection from the Fe_2O_3 apex yields a further simplification of the compatibility diagram (Figure P28c). Finally the aqueous phase in the acid trend has a high mobility, and the chemical potentials of Al and Si species in this phase may be considered as environmental variables, applied to the solid minerals in the same way that temperature and pressure are, from outside. In this case, the four component system under consideration can be depicted as in Figure P26, with the additional information that goethite is also present in all fields. In effect Figure P28 depicts the situation after long term weathering and leaching, and the

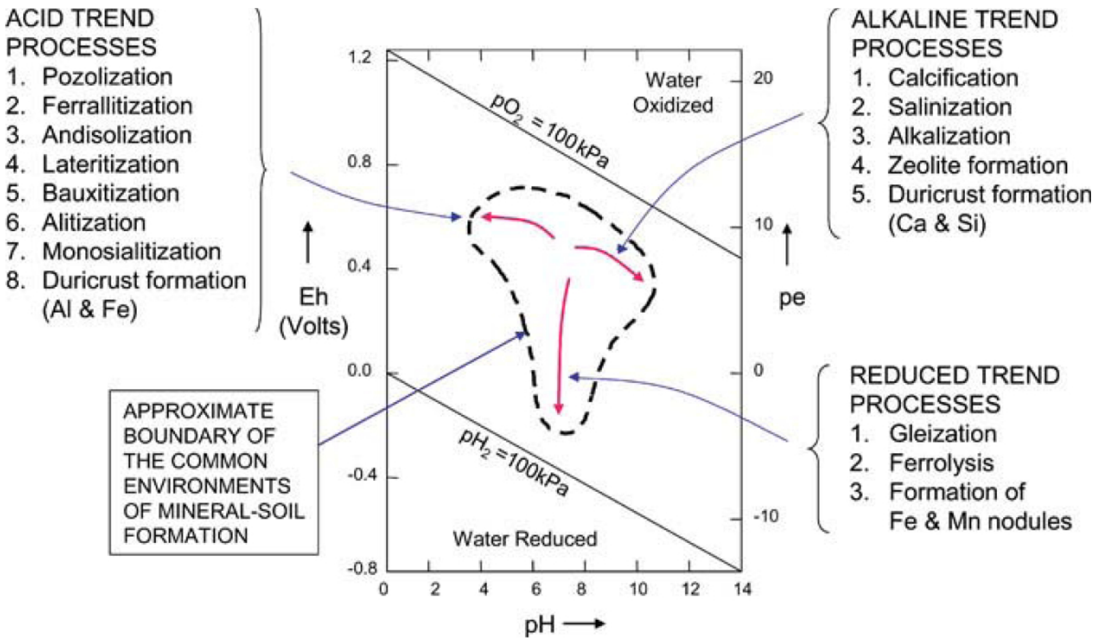


Figure P27 Mineral genesis in soils in terms of the master variables pe (or Eh) and pH. See also the article *Redox-pH Diagrams and Reactions*.

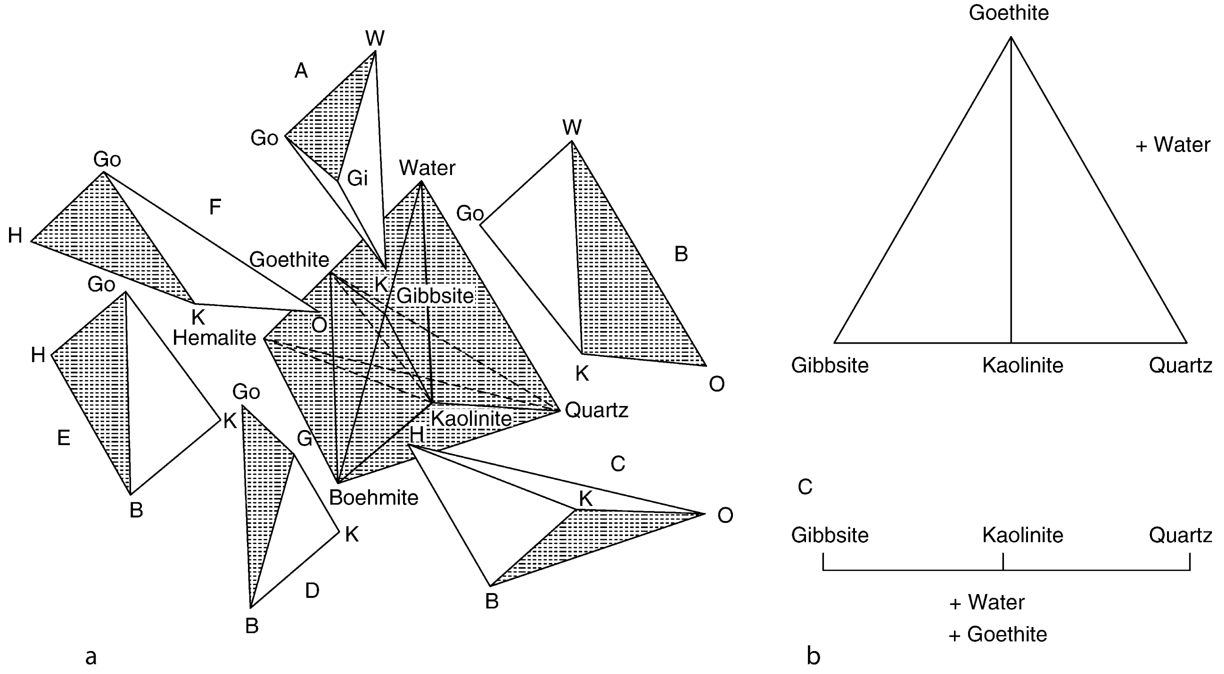


Figure P28 Part of the four component system Fe_2O_3–Al_2O_3–SiO_2–H_2O at 25 °C; and 100 kPa total pressure; (**a**) exploded view showing all assemblages of 4-phases that can co-exist together, as compatibility tetrahedral that are contained within the central tetrahedra; (**b**) projection from H_2O; (**c**) further projection from FeOOH. In (**a**) B, Gi, Go, H, K, Q, W represent Boemite, Gibbsite, Goethite, Hematite, Kaolinite, Quartz and Water, respectively. Modified from Chesworth (1975).

phase assemblages shown are characteristic of soils in tropical soils such as Alisols and Ferralsols.

Earlier stages of pedogenesis will contain notable amounts of the alkaline earth and alkali components, and equilibria involving smectites and illites will need to be considered. In the simplest depiction a minimum of two more components must be added, and if these are chosen as MgO and K_2O, Figure P29 can be derived.

The upper pH limit of the acid trend is found in Ca and Mg carbonate-bearing soils developed on limestones, dolomites, marbles and skarns. To some degree the carbonate-bearing system (e.g., Figure P30) can be considered as separate from the alumino-silicate one, though the presence of CaO as a component will certainly affect the stability field of smectite in Figure P29. One way of combining the aluminosilicate and carbonate subsystems is by means of the A-C-Fm diagram (Figure P31).

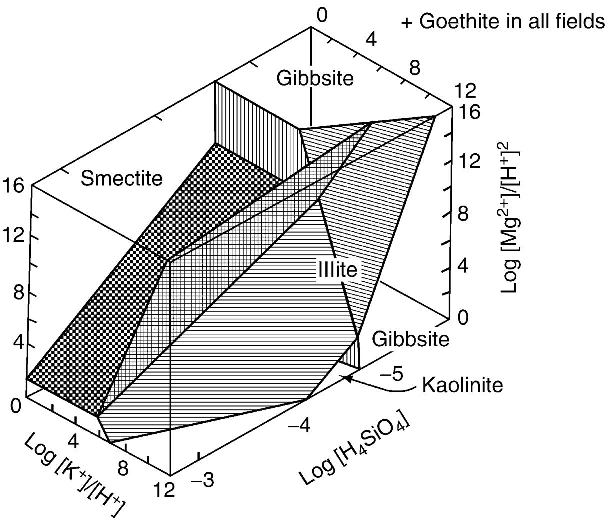


Figure P29 The haplosoil system – a minimal system that allows a consideration of allitization, monosiallitization and bisiallitisation during soil formation.

The alkaline trend occurs in relatively arid climatic zones, where the net annual movement of water is upwards in the weathering zone. For part of the year, the seasonal distribution of rainfall may determine that there is enough water to affect a solution and downward leaching of soil components. However, the distinctive features of this pedogenesis, is caused by capillary uprise and evaporation of soil water and precipitation of soluble salts. The geochemical result is that a number of electrolytes, (e.g., Na^+, Mg^{2+}, Ca^{2+}, HCO^{3-}, CO_3^{2-}, SO_4^{2-}, Cl^-) may reach high concentrations in the system, migrate in the profile, and produce precipitations of salts in certain horizons. An important feature of the solution phase will be that aH_2O is significantly less than 1. The order in which mineral phases precipitate in such systems is determined by their solubility products. See Hydrological Cycle. The early stages of this process can be followed in Figure P32. Later stages may involve the precipitation of alkali carbonates and zeolites (Figure P33).

The ultimate path of mineralization will depend upon the composition of the soil solution at the start, with each

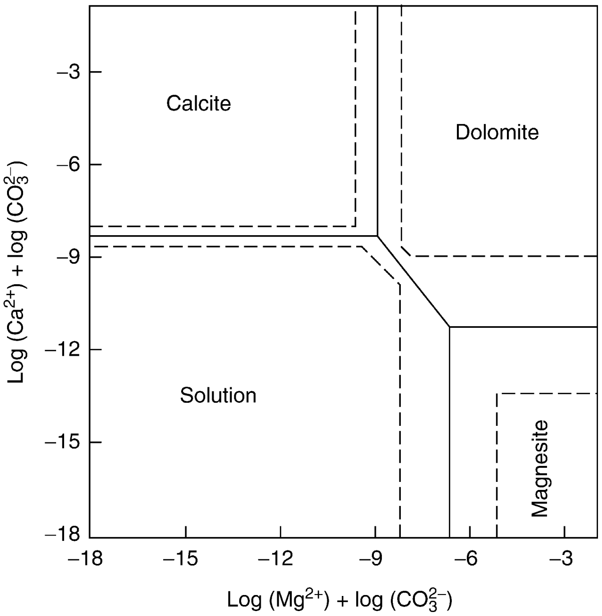


Figure P30 Calcite-dolomite relationships at 25 °C and 100 kPa total pressure (Schulman and Chesworth, 1985).

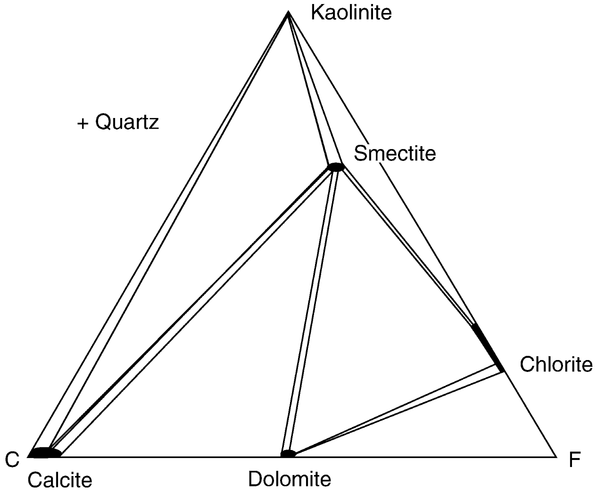


Figure P31 Calcite-aluminosilicate relationships under surface or near surface conditions (after Zen, 1959).

precipitating salt acting as a chemical barrier separating pairs of evolutionary trends (Hardie and Eugster, 1970, see Alkaline Soils). In pedology, the process is called alkalinization or solodization, and is qualitatively similar to the formation of evaporites in, for example, the East African Rift. Alkalinized soils may later be modified by a change to a wetter climate, to produce assemblages (including zeolites) in Figure P34.

The reduced trend in weathering is characterized by the presence of an excess of water. The weathering profile is completely or partially submerged, leading to a lowering of the partial pressure of oxygen in the system to the degree that anaerobic conditions develop. Elements with multiple oxidation states will be reduced. In the case of Fe and Mn, the reduced forms are readily mobilized, a contrast to the behavior of these elements in oxidizing environments. Close to the water table, fluctuations in water level produce alternating oxidations and reductions, commonly producing the mottling associated with Stagnosols.

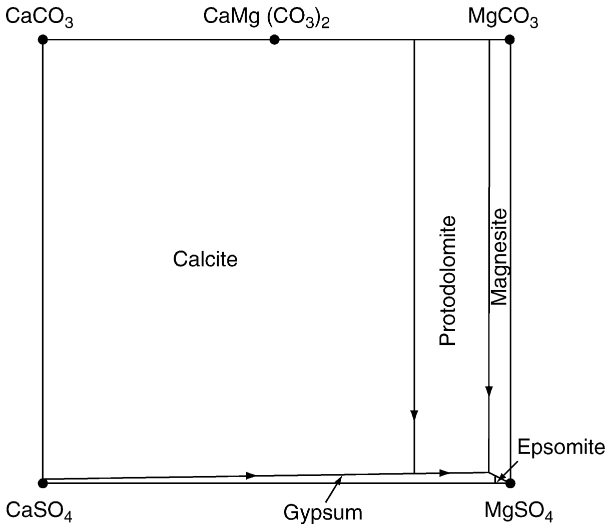


Figure P32 Carbonate and sulfate equilibria at 25 °C and 100 kPa (Eugster and Hardie, 1970).

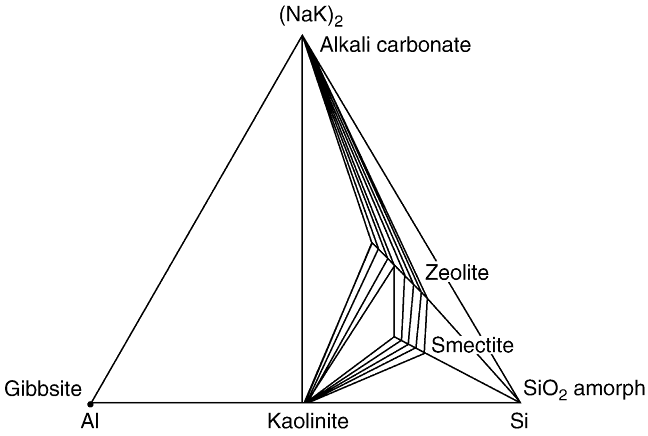


Figure P33 Alkali carbonate systems showing compatibility triangles involving zeolite (after Velde, 1985).

The major visible changes are those associated with Fe. As the solvated ferrous ion, Fe may leave the system so that the soil loses the dark colors associated with the presence of iron-bearing solids, and acquires lighter colors tending towards gray, (a process known as gleying). Other features of the chemical environment may affect the behavior of Fe. If the environment contains sulfate ion and sulfate-reducing bacteria are present, pyrite may form as in sulfidic Fluvisols. Where carbonate ions dominate, siderite may precipitate. Figure P35 shows the latter possibility in terms of the partial pressures of the two relevant components of the gas phase. Brookins

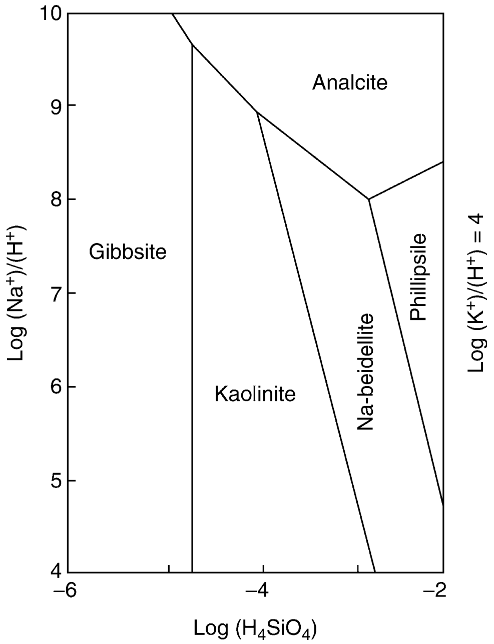


Figure P34 Aluminosilicate equilibria appropriate for a consideration of solodized soils in Alberta (Spiers et al., 1984).

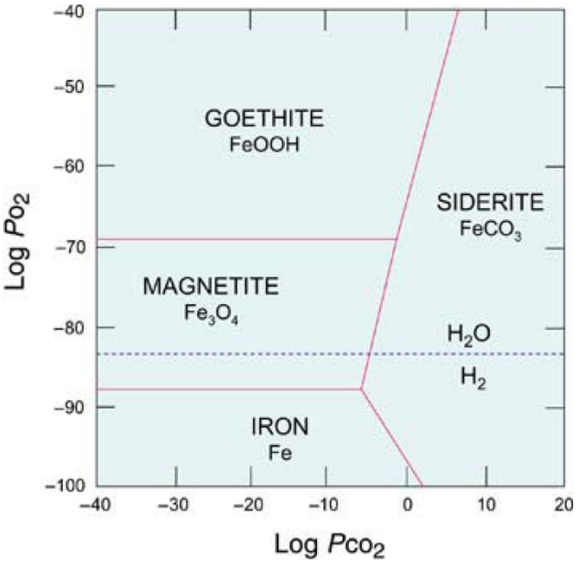


Figure P35 The system Fe–O–H–C at 100 kPa total pressure and 25 °C. Above the *dotted line* water accompanies the mineral phases, below it, water is reduced and the solids are in equilibrium with H_2 (modified from Garrels and Christ, 1965).

(1988) illustrates other possibilities using the parameters Eh and pH (see Redox Reactions and Diagrams in Soil).

Problems with the application of the phase rule to soils

Construction of a phase diagram to illuminate a problem will lead to difficulties if the choice of components and phases to be considered is not a judicious one. The diagram itself is only valid for the phases considered, and the most important difference between phases in theoretical diagrams and phases in nature is the fact that the latter exhibit various structural states, crystallinities, and isomorphous substitutions (solid solution). In addition, metastable equilibria need to be considered as well as stable ones. The phase diagrams used by soil scientists are generally based on calculation from the fundamental thermodynamic data, rather than an experiment as is the case in high PT geochemistry. The basic recipes for low PT calculations are clearly laid out by Lindsay (2001). The necessary data, tabulated for 25 °C and 100 kPa, is continually being revised and should always be critically examined for internal consistency (Helgeson et al., 1978; Berman, 1988). It should be noted that tabulated data is almost invariably for simple, stoichiometric compositions. Isomorphous replacements (of Fe for Al and vice versa, for example) may change stability fields significantly (Figure P36). Furthermore, 25 °C and 100 kPa may not always be the best choice of conditions for pedogenic models. Other temperatures may be more appropriate, especially where diagenetic effects need to be considered, for example in paleosols (see Figure P37).

The most important single component in the soil system is H_2O. Its activity is usually taken to be 1. However, there exists the possibility of aH_2O being less than 1, for example, in saline environments (see Chesworth 1972). The effect of lowering aH_2O will be to cause dehydration reactions to take place at lower temperatures than they would otherwise do (Figure P38). In other words the result is to diminish the field of stability of the hydrated phase in the presence of an aqueous solution.

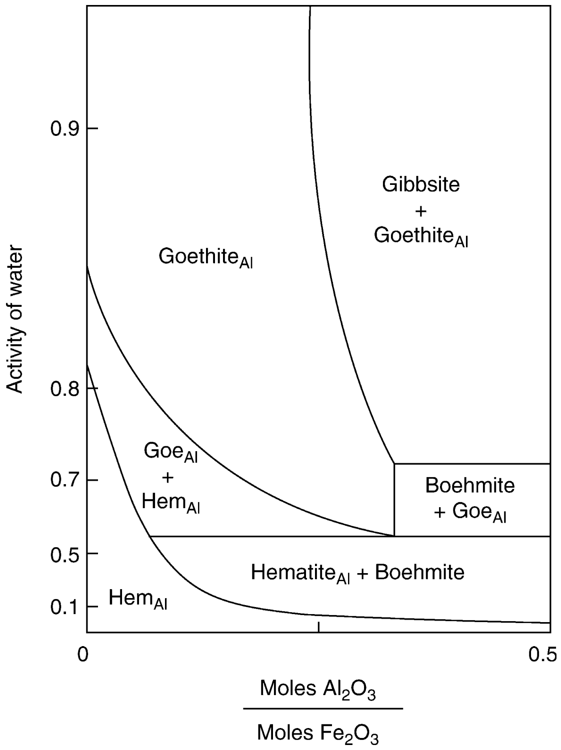


Figure P36 Effect of isomorphous replacement of Al for Fe on the stability field of goethite and hematite (Trollard and Tardy, 1989).

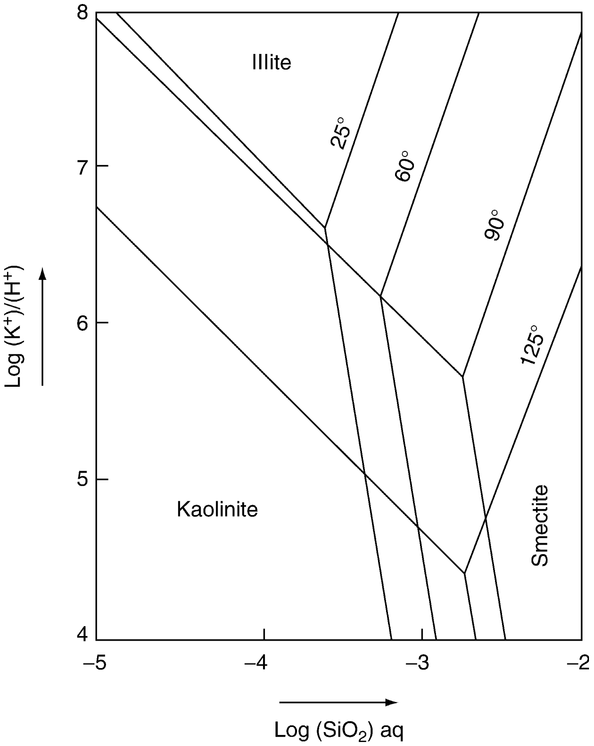


Figure P37 Temperature effect on stability fields of kaolinite, smectite and illite (Rosenberg et al., 1990).

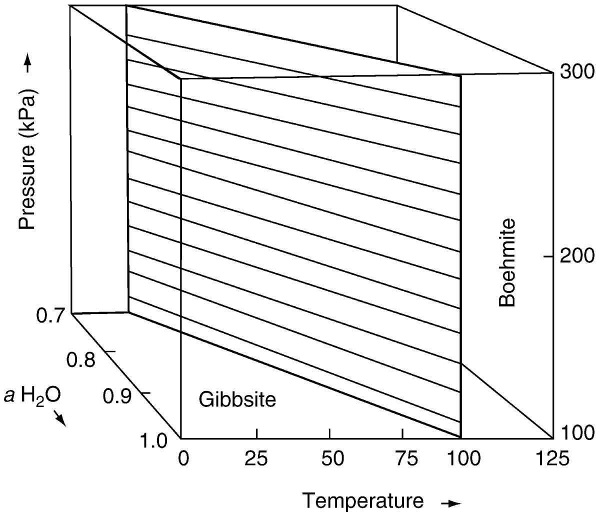


Figure P38 Gibbsite-boehmite relations as a function of *P*, *T* and the activity of H_2O.

Mixed layer clay minerals present a further problem. Should they be considered single or multiple phases? Both points of view have been defended, though the most recent work based on ^{39}Si NMR studies suggest that mixed layer illite/smectite structures act thermodynamically as two phases (Altaner et al., 1988).

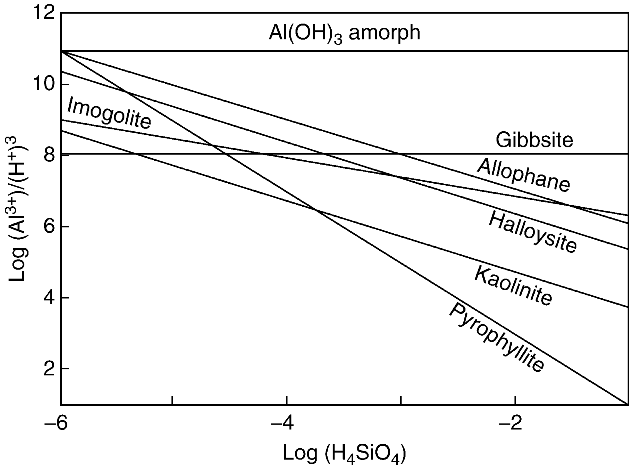


Figure P39 Mineral solubility curves in the system Al_2O_3–SiO_2–H_2O at 25 °C and 100 kPa.

In soils, surface reactions are the rule, so that it may seem unwise to use the unmodified Gibbs' Phase Rule, which specifically ignores surface phenomena. It is possible that surface energy contributions in soil mineralogical reactions are of such a magnitude as to change the product of reaction. Many important reactions involving common phases such as gibbsite, goethite or kaolinite, have ΔG_r values close to zero, so that the surface contribution could be decisive. In Figure P39, for example, kaolinite is the stable phase between $p(H_4SiO_4)$ 3 to 4, yet surface effects may result in metastable phases forming. Growth of such phases however, ultimately nullifies the surface effect (at, say, dimensions greater than 10^{-7} m), and the metastable phase or phases may be replaced sequentially by more stable ones (the Ostwald Step Rule, also known as ripening).

Ward Chesworth

Bibliography

Altaner, S.P., Weiss, C.A., and Kirkpatrick, R.J., 1988. Evidence from 29 Si NMR for the structure of mixed layer illite/smectite clay minerals. *Nature*, **331**: 699–702.

Berman, R.G., 1988. Internally consistent thermodynamic data for minerals in the system Na_2O–K_2O–CaO–MgO–FeO–Fe_2O_3–Al_2O_3–SiO_2–TiO_2–H_2O–CO_2. *J. Petrol.*, **29**: 445–522.

Bowers, T.S., Jackson, K.J., and Helgeson, H.C., 1984. *Equilibrium Activity Diagrams*. Berlin: Springer, 397 pp.

Brookins, D.G. 1988. *Eh–pH Diagrams for Geochemistry.* Berlin: Springer, 176 pp.

Chesworth, W., 1972. The relative stability of gibbsite and boehmite at the surface of the earth. *Clays and Clay Minerals*, **20**: 369–374.

Chesworth, W., 1975. The system SiO_2–AlOOH–Fe_2O_3–H_2O and the kaolinitic stage of the goethite facies. *Clays and Clay Miner.*, **23**: 389–392.

Chesworth, W., 1992. Weathering systems. In Martini, I.P., and Chesworth, W., eds., *Weathering, Soils and Paleosols.* NY: Elsevier, 19–40.

Chesworth, W., 1999. The phase rule in soil science. *Edafologia*, **7**: 107–119.

Chesworth, W., and Dejou, J., 1980. Are considerations of mineralogical equilibrium relevant to pedology? Evidence from a weathered granite in central France. *Soil Sci.*, **130**: 290–292.

Connolly, J.A.D., 1990. Multivariable phase diagram: an algorithm based on generalized thermodynamics. *Am. J. Sci.*, **290**: 666–718.

Defay, R., Prigogine, I., and Bellemans, A., 1966. *Surface Tension and Adsorption.* London: Longmans, 432 pp.

Dixon, J.B., and Schulze, D.G. (eds.), 2002. *Soil Mineralogy with Environmental Applications*. Madison, WI: Soil Science Society of America, 866 pp.

Donnon, F.G., and Haas, A., 1936. *A Commentary on the Scientific Writings of J. Willard Gibbs: v. I. Thermodynamics.* New Haven: Yale University Press, 742 pp.

Eberl, D.D., Srodon, J., Kralik, M., Taylor, B.E., and Peterman, Z.E., 1990. Ostwald ripening of clays and metamorphic minerals. *Science*, **248**: 474–477.

Eugster, H.P., and Hardie, L.A., 1970. Saline lakes. In Lerman, A., ed., *Lakes: Chemistry, Geology, Physics.* NY: Springer, 363 pp.

Garrels, R.M., and Christ, C.L., 1965. *Solutions, Minerals and Equilibria.* New York: Harper and Row, 450 pp.

Gibbs, J.W., 1961. *Collected Papers, v. I. Thermodynamics.* New York: Dover Books.

Korzhinskii, D.S., 1959. *Physicochemical Basis on the Paragenesis of Minerals.* New York: Consultant Bureau, 142 pp.

Lindsay, W.L., 2001. *Chemical Equilibria in Soils.* Caldwell, NJ: Blackburn Press, 449 pp.

Meunier, A., 2005. *Clays.* Berlin, New York: Springer, 472 pp.

Morel, F.M.M., 1983. *Principles of Aquatic Chemistry.* New York: Wiley, 446 pp.

Pankow, J.F., 1999. *Aquatic Chemical Concepts.* Chelsea, MI: Lewis Publishers, 673 pp.

Prigogine, I., and Defay, R., 1954. *Chemical Thermodynamics*. London: Longmans, 522 pp.

Ricci, J.E., 1951. *The Phase Rule and Heterogeneous Equilibrium.* New York: Van Nostrand, 505 pp.

Rosenberg, P.E., Kittrick, J.A., and Aja, S.U., 1990. Mixed layer illite/smectite: a multi-phase model. *Am. Miner.*, **75**: 1182–1185.

Schulman, D., and Chesworth, W., 1985. Calcium carbonate solubility in the c horizon of a southern Ontario, Canada, luvisol. *Chemical Geol.*, **51**: 173–181.

Seeger, R.J., 1974. In Gibbs, J.W., Oxford: Pergamon, 290 pp.

Spiers, G.A., Pawluk, S., and Dudas, M.J., 1984. Authigenic mineral formation by solonization. *Can. J. Soil Sci.*, **64**: 515–532.

Sposito, G., 1989. *The Chemistry of Soils.* New York: OUP, 277 pp.

Trolard, F., and Tardy, Y., 1989. A model of Fe^{3+}-kaolinite, Al^{3+}-goethite, Al^{3+}-hematite equilibria in laterites. *Clay Miner.*, **24**: 1–21.

Velde, B., 1985. *Clay Minerals: A Physico-Chemical Explanation of their Occurrence.* New York: Elsevier, 427 pp.

Zen, E-an., 1959. Clay mineral-carbonate relations in sedimentary rocks. *Am. J. Sci.*, **257**: 29–43.

Zen, E-an., 1963. Components, phases, and criteria of chemical equilibrium in rocks. *Am. J. Sci.*, **261**: 929–942.

PHI SCALE

See *Wentworth scale*.

PHOSPHORUS CYCLE

Introduction

Phosphorus comes 10th in order of elemental natural abundance in the Earth's crust, with an average concentration of about 1 g kg^{-1}. The various compartments and estimated annual fluxes of global P are shown in Figure P40. The largest pool of P resides in sediments and rocks: this also happens to be the pool whose quantity has the greatest uncertainty. The global P cycle can be resolved into three cycles (Emsley, 1980): in the primary inorganic cycle, mineral weathering, leaching and erosion transfer P from land to sediments, and volcanism and uplifting of sediments replenish terrestrial P, thereby completing the cycle. This cycle has a frequency measured in millions of years. The two biological cycles involve movements of P, measured in years or even weeks, through the land-based and water-based biospheres. According to Richey (1983) there is an annual flux between land and ocean on the one hand, and the atmosphere on the other, of 4.6 Tg P yr^{-1}, with the bulk of the transfer occurring between land and atmosphere. Those parts of the natural cycle are small and do not significantly alter the data in Figure P40. Richey's (1983) estimate of the other global P fluxes does not materially differ from Pierrou's (1976) that Figure P40 is based on. The highest flux occurs between the sea and marine biota, followed by the flux between the soil and its vegetation. It is the terrestrial P cycle that this article is about.

Phosphorus is present in all living cells mainly in the orthophosphate form, and to a minor extent as pyrophosphate, and plays an essential role in cell metabolism. The phosphate ion is believed to be uniquely suitable for its metabolic function because it resists polarization and nucleophilic attack, except in metal-enzyme complexes, thus providing water-stable anhydrides and esters. Organic phosphate compounds occur as: phosphate esters of sugars or alcohols which are intermediate compounds of carbohydrate metabolism; phospholipids (where phosphate forms a diester linking a hydrophobic moiety such as fatty acids with a hydrophilic moiety) which are essential components of biological membranes; phosphopyridine nucleotides (NAD and NADH) which mediate oxidation-reduction reactions; nucleic acids and inositol phosphates. The most important compound with a pyrophosphate bond is adenosine triphosphate or ATP, which acts as an energy carrier. There appears to be no suitable substitute for phosphate in its metabolic and linkage roles in cell biology. The phosphorus content in plants, normally between 0.1 and 0.4% of the dry weight (depending on the stage of plant development and plant part) is considerably less than that of nitrogen and potassium, the other two major macronutrients. The average total P content of the soil is about 430 mg kg^{-1}, the lowest among the major essential plant nutrients (Sposito, 1989). In contrast, soils contain on average 2 000 and 15 000 mg kg^{-1} of N and K, respectively. Therefore most agricultural soils require the addition of P fertilizers to achieve the crop productivity expected of modern agriculture. Worldwide P fertilizer use ranks just below potassium fertilizers, and usage of both is less than one-half of the amount of nitrogen fertilizer used.

Content and distribution of P in soils

The P concentration in the surface layer (nominally 0 to 15 cm depth) of soil varies considerably between regions of the world, with mean values of 380 to 1330 mg kg^{-1}, with tropical soils typically having concentrations less than half those of the temperate regions (Table P9). Total P is usually low in highly leached and weathered soils on old landmasses such as Australia (Wild, 1988). In unfertilized soils, the highest values are associated with parent materials formed from basic igneous rocks, and soils with high organic matter content. The low P content of soils and the tendency of the phosphate to react strongly with soil components to form relatively insoluble compounds, make it an element of major academic and economic interest in soil science and agriculture. Aluminum, iron and calcium compounds tend to react with and retain phosphate ions. Phosphorus is mostly concentrated near the topsoil partly because of P fertilizer

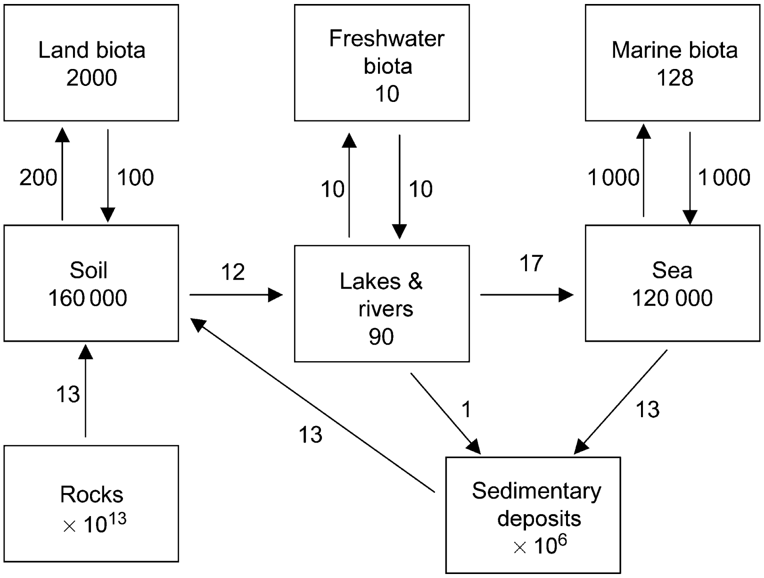


Figure P40 Major reservoirs and fluxes of P on Earth (values of P in Tg or 10^{12} g (modified from Emsley, 1980).

Table P9 Total and organic phosphorus in surface soils

Country	Total P (Pt)		Organic P (Po)			Source[a]
	Range (mg kg^{-1})	Mean (mg kg^{-1})	Range (mg kg^{-1})	Mean (mg kg^{-1})	% of Pt	
Australia	220–1 150	380	24–580	84	11–61	1
Brazil	40–1 590	490	13–206	94	12–54	2
Canada	507–1 510	980	21–802	226	27–67	3,4,5
New Zealand	210–2 560	1 090	45–1 360	530	4–79	6,7
Nigeria	38–1 170	385	11–454	148	19–73	8,9,10
Scotland	900–2 040	1 330	290–1 015	695	33–61	11
USA	152–1 200	543	31–744	236	13–88	12,13,14,15

[a] *1*. Williams and Steinberg (1958); *2*. Condron et al. (1990); *3*. Dormaar and Webster (1963); *4*. John et al. (1965); *5*. McLean (1965); *6*. Martin (1964); *7*. Williams et al. (1970); *8*. Enwezor and Moore (1966); *9*. Omotoso (1971); *10*. Ipinmidun (1973); *11*. Williams et al. (1960); *12*. Neptune et al. (1975); *13*. Bowman and Cole (1978); *14*. Bowman (1988); *15*. Bowman and Moir (1993).

use in cultivated soil, and biological cycling and deposition in leaf-fall and litter in uncultivated soil, and partly a consequence of its low mobility and high reactivity with soil colloids.

Forms of soil phosphorus

Phosphorus occurs in soils in a variety of inorganic (Pi) and organic (Po) forms, some of which are not well characterized because of difficulty of extraction and isolation. Among the mineral forms, apatite $[Ca_5(PO_4)_3(OH,F)]$ is by far the commonest, with variscite $[(Al,Fe)PO_4 \cdot 2H_2O]$, and cranadallite $[CaAl_3(PO_4)_2(OH)_5 \cdot H_2O]$, also known (Lindsay and Vlek, 1977). Other minerals such as vivianite $[(Fe^{2+}_{3-x},Fe^{3+}_x)(PO_4)_2\ (OH)_x(H_2O)_{8-x}]$, tarankanite $[K_3H_6Al_5(PO_4)_8(H_2O)_{18}]$ and minylite $[KAl_2(PO_4)_2(H_2O)_4]$ groups and octacalcium phosphate are also found, usually as reaction products of phosphate fertilizers in soil. These minerals, with the exception of octacalcium phosphate, are of little direct significance to the mineral nutrition of plants during a growing season because of their low solubility and dissolution rates in soils. In the long term the apatite minerals are the main source of soil phosphorus.

A considerable fraction of inorganic phosphate in most soils is sorbed onto hydrous oxides of aluminum and iron, organo-mineral complexes and alumino-silicate minerals, and also on calcium carbonate in calcareous soils. Whether the sorption occurs through adsorption, precipitation as microcrystals or surface complexation formed from nucleation is difficult to determine with certainty. The surface-associated forms of phosphate undergo anion exchange, constitute a major source of plant-available P, and are referred to as labile P. A certain amount of surface P becomes occluded as fresh precipitate forms over sorbed P over time, or sorbed phosphate migrates into the solid phase or micropores by diffusion. Thus P sorption is generally irreversible to some extent and this phenomenon is called P fixation. Phosphate held by bi-dentate complex formation is also believed to be non-labile (Mattingly, 1975).

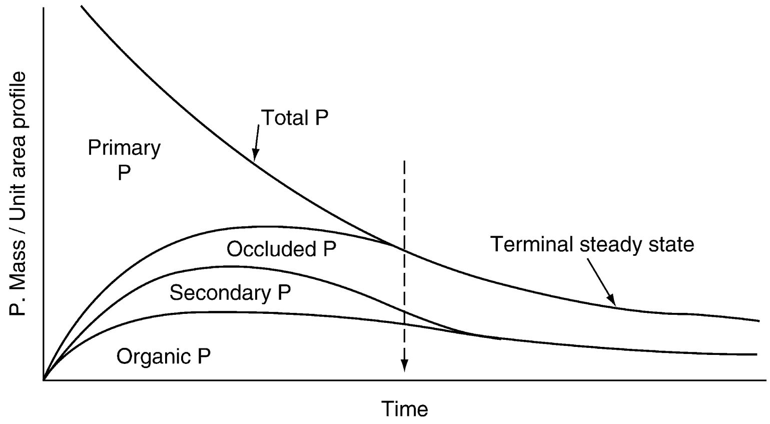


Figure P41 Changes in forms and amounts of soil P during pedogenesis. The *arrow* indicates an elapsed time of approximately 22 000 years under New Zealand conditions (modified after Walker and Syers, 1976).

Less is known about soil organic phosphorus the content of which cannot yet be determined directly. Presently Po is determined as the difference between total P and Pi. The Po content of soils constitutes a variable proportion, commonly between 15 and 70%, of total P (Table P9). For example, clay soils generally have higher Po than sandy soils, and soils derived from basaltic and basic igneous parent materials contain higher amounts of Po than granitic materials. The difficulty of extracting Po has hampered its characterization. To date only about 50 to 70% of soil Po has been identified, most of it (up to 60%) as inositol phosphates. Inositol phosphates are phosphate esters of hexahydroxy-cyclohexanes, a variety of which, from mono- through hexaphosphates, has been found. Typically, the hexaphosphate is the most abundant form (Stevenson, 1986). The accumulation of inositol phosphate is attributed to its low mobility (Cole et al., 1977), its stabilization by interaction with clays and sesquioxides (Stewart and Tiessen, 1987), and the inability of some phosphatase to dephosphorylate penta- and hexaphosphates (Tate and Newman, 1982). Up to about 9% of Po is in the form of nucleic acids, and less than 5% in form of phospholipids (Tate, 1985). About 2–5% of Po in cultivated soils, and as much as 20% in grasslands soils, are found in the microbial biomass (Stevenson, 1986). Although the rate of addition of nucleic acids to soils is probably much greater than that of inositol phosphates, in most soils nucleic acids are much more readily mineralized and bio-available. Both plants and soil microorganisms are important sources of phospholipids in soils. Recently, ^{31}P-nuclear magnetic resonance spectroscopy has been used to identify and quantify the forms of extractable P in soils. In tussock grasslands of New Zealand, inorganic orthophosphate comprised 26 to 59% of total extractable P, orthophosphate mono-esters 41 to 71%, and orthophosphate diesters up to 10% (Tate and Newman, 1982). Small amounts of phosphonates (compounds in which P is directly bonded to C) and polyphosphates were also found in some soils. Adams and Bryne (1989) found, in addition, significant amounts of pyrophosphate (3 to 13% of extractable P) as well as higher proportions (3 to 19%) of orthophosphate diesters in *Eucalyptus* forest soils of Western Australia.

Transformations of soil phosphorus

The ultimate source of all soil P is the primary apatite group of minerals. The transformation and fate of P in soil materials over a geological time scale is shown in Figure P41. According to the model developed by Walker and coworkers (Walker and Syers, 1976), P solubilized from apatite by weathering is transformed into secondary (i.e., pedogenic) P minerals, and occluded and organic P. In time, primary P is exhausted; secondary P increases initially then declines to very low levels. In the final steady state, only a fraction of the initial total P remains, and occluded and Po are the major forms present. During soil formation, significant quantities of P are lost by erosion and leaching. Letkeman et al. (1996) estimated that between 80 and 100 g P ha^{-1} was lost per year, mostly from the 20 to 50 cm depth, during 13 000 years of pedogenesis in Saskatchewan, Canada, with surface soil accumulation of mainly Po accounting for only approximately half that amount. Leaching losses of 7 g P ha^{-1} yr^{-1} from a northern hardwood forest in New Hampshire (Wood et al., 1984), 15 g P ha^{-1} yr^{-1} from an Illinois prairie landscape (Smeck and Runge, 1971), and up to 0.5 kg P ha^{-1} yr^{-1} from a glacial outwash in New Zealand (Walker and Syers, 1976) have been reported.

Over a shorter time scale of decades or even less, human activities have also transformed the P distributions in soils. Cultivation of grasslands in North America has led to substantial losses of soil organic matter and Po (Tiessen et al., 1982). Soils that have been in cultivation for between 60 and 90 years lost between 12 and 29% of the total P. The loss of P in clay and silt loam soils was almost entirely from the organic fraction until this fraction was depleted sufficiently to allow dissolution of apatite minerals to occur. On a lighter-textured sandy loam soil, soil P was lost from both organic and inorganic fractions. Replacement of native woodland in semi-arid northern Tanzania by low input agriculture has resulted in significant loss of Po and Pi from the soil: most of the depletion of soil Po occurred in the first three years. Three and fifteen years of cultivation resulted in a 53% depletion of orthophosphate diester-P (which includes phospholipids and nucleic acids), and a 30% and 39% reduction of orthophosphate monoester-P (which includes inositol phosphates) (Soloman and Lehmann, 2000). Those results concur with the suggestion that diester P is more readily mineralizable than monoester P. About 70% of inorganic orthophosphate P was depleted by cultivation. On the other hand, long-term fertilization of a pasture in New Zealand with superphosphate fertilizer resulted in almost all of the P accumulated in the monoester P fraction (Condron et al., 1985).

Reactions and processes affecting soil phosphorus

Although other processes occur, the main processes and reactions affecting soil P and the P cycle of the soil–plant system, are: inorganic P equilibrium and kinetics, P movement and mobility, mineralization-immobilization turnover, and uptake by plants.

Inorganic P equilibrium and kinetics

The behavior of inorganic P in soil and the reactions of immediate importance to plant life and soil microorganisms, in relation to their need to acquire sufficient P to maintain adequate growth rates, are summarized by the following equilibria:

$$\text{soil solution Pi} \overset{\text{fast}}{\rightleftharpoons} \text{labile Pi} \overset{\text{slow}}{\rightleftharpoons} \text{non-labile Pi}$$

The kinetics of P exchange between soil solution Pi and labile Pi has been studied by isotopic exchange with ^{32}P and can be explained on the basis of two or more reactions (Arambarri and Talibudeen, 1959): (*i*) a fast exchange with half-times of 0.3 to 1.6 h, which involves Pi in pore solution and Pi sorbed on readily accessible surfaces, (*ii*) an intermediate reaction of half-times of 1.8 to 3.6 h, and (*iii*) a slower reaction of half-times of 25.8 to 46.1 h. The slower reactions represent exchange of phosphate in micropores of 1 nm in diameter or less, and the penetration of the interior of crystals and crystal defects. Non-labile Pi includes occluded P and crystalline forms of P that are relatively insoluble. In soils at field moisture contents, the rate of equilibrium of soluble phosphate with non-labile forms is extremely slow. For example, the half-life for the reversion of soluble phosphate added to mineral soils into non-exchangeable forms is between one and six years (Larsen et al., 1965). This indicates that most fertilized soils have not generally reached this long-term equilibrium. Consequently, it is often more important to know which labile forms control the immediate Pi concentration in the soil solution.

Phosphorus movement and mobility in soil

Soil phosphorus may move in three ways: (*i*) by transport through plant roots and soil biota, (*ii*) by mass flow with water movement, and (*iii*) by diffusion down a concentration gradient. Of the three mechanisms, transport by live organisms, especially plant roots, has the most influence in the redistribution of P in the soil. Whereas soil biota activity will mostly initiate a random distribution, vegetation growth will bring about a unidirectional movement by depleting soil P, through root uptake, in a zone 20 to 60 cm below the surface and enriching the surface 20 cm upon root decay (Letkeman et al., 1996). Although movement of P by mass flow makes up only a small fraction of the P taken up by plant roots (Olsen et al., 1962), leaching can account for about half of the P lost from the depletion zone of soil (Letkeman et al., 1996). Both soluble Po and Pi are thought to be leached with the percolating water.

No net movement of phosphate ions occurs by diffusion unless a concentration gradient exists. Because roots absorb nutrients and equilibrium is established too slowly, phosphate ions in the soil are able to diffuse down a concentration gradient toward the root. The distance for diffusive movement through the soil toward the root is usually in the range of 0.1 to 15 mm, depending on the nutrient ion. The diffusion model of Olsen et al. (1962) showed that phosphate could diffuse fast enough to the root surface to account for the observed uptake rates for several days. Thus, the three types of P movement each dominate a specific process.

Mineralization-immobilization

Mineralization is the conversion of an organic form of an element to an inorganic form, and is mediated by microorganisms. In the process, the microorganisms incorporate a portion of the element into their cells for growth, and thereby immobilize a portion of the substrate being mineralized. Hence, it is convenient to refer to this pathway of the P cycle as mineralization-immobilization turnover (MIT). The processes involved in this conversion depend on the rate of growth and decay of the microbial population and on the decomposability of the substrates supplied in crop litter and residues. Net immobilization of Po occurs when the C:P ratio of the substrate is about 300 or greater, and net mineralization if the ratio is 200 or less (Stevenson, 1986). In addition, the critical P concentration above which mineralization proceeds is about 0.2% in the substrate (Dalal, 1977). The soil microbial biomass usually comprises about 2 to 3% of the total organic carbon in soil, however, it is a far more important repository of nutrients such as N and P than its small size would indicate because in a single year there may be several generations of growth of soil microorganisms, resulting in a high turnover rate.

McGill and Cole (1981) distinguished two forms of mineralization: biological and biochemical. Elements that are mineralized as a result of carbon oxidation to provide energy for microbial activity are said to undergo biological mineralization. (This is the classical use of the term mineralization.) According to McGill and Cole (1981) biochemical mineralization is controlled by the supply of and need for the element released rather than the need for energy, and is the primary mechanism for organic P release, so that P availability tends to be independent of organic matter decomposition. Phosphate associated with the organic moiety as esters, is mobilized by cleavage by the phosphatase group of enzymes of both plant root and microbial origin. Soil organic C and N, in contrast, are mineralized by substrate oxidation. Gressel and McColl (1997) advocate the alternative view in regard to P mineralization citing Dalal's (1979) and their evidence showing a close correlation between P and C mineralization, and data from ^{31}P and ^{13}C nuclear magnetic resonance spectroscopic analyses.

Estimates of P mineralization in temperate soil conditions range from 6 kg P ha^{-1} yr^{-1} for arable soils to 15 kg P ha^{-1} yr^{-1} for grassland soils (Tate, 1985). McLaughlin et al. (1988a,b) found during a cropping season with wheat in Australia that 22 to 28% of P in plant residues from a previous legume crop was recovered in the soil microbial biomass compared to about 5% in the wheat plant. However, most of the P taken up by the wheat plant and microorganisms was from the soil. Brookes et al. (1984) estimated the annual flux of P through the microbial biomass to be about 23 kg P ha^{-1} for eight grassland soils compared to 7 kg P ha^{-1} for six arable soils. Those numbers suggest that biomass P turnover could make a significant contribution to crop P nutrition.

Uptake of phosphorus by plants

Phosphorus is, generally, second to nitrogen as the most limiting nutrient for terrestrial plant growth. Transport of soluble Pi by diffusion to the root surface is normally the rate-limiting step in the supply of P for plant uptake. Inorganic phosphate concentration in the soil solution is in the range of $<1 \times 10^{-6}$ to 1×10^{-5} M while organically-bound phosphate can be in the range 5×10^{-6} to 3×10^{-3} M (Pierre and Parker, 1927). However, it is generally believed that the organic P is mineralized by extracellular phosphatase enzymes before absorption through plant roots occurs. In response to the low concentrations of Pi in the soil, plants have developed specialized physiological and biochemical mechanisms to acquire Pi from the soil. The methods include proliferation of the root system or root surface area resulting in lower shoot: root ratio, secretion of organic acids to enhance Pi solubility, and induction of phosphatase activity (Raghothama, 1999). The concentration of P in plant cytosol is generally 5 to 20 × 10^{-3} M. Roots, therefore, have to acquire P against a steep concentration gradient as well as the negative membrane potential that is characteristic of plant cells. An energy-mediated co-transport process, driven by protons generated by a plasma membrane H^+-ATPase (i.e., a proton pump), has been proposed for Pi uptake in plants (Marschner, 1986). Uptake of Pi is thought to mainly involve the $H_2PO_4^-$ ion: this is suggested by the good correspondence between the effects of pH on Pi uptake and the relative concentration of $H_2PO_4^-$ (Bieleski, 1973). pH has been shown also to control trans-membrane transport of Pi, either through the intrinsic kinetic properties of the transport system (low affinity or high affinity mechanisms) or through co-substrate concentration (H^+ for co-transport, OH^- or HCO_3^- for anti-transport) or both (Sentenac and Grignon, 1985). The internal P status of the plant is thought to regulate the rates of phosphate uptake by roots and its distribution within the plant.

Roots of more than 80% of land plants are able to form symbiotic associations with mycorrhizal fungi. In these plants, the fungal hyphae play a significant role in the acquisition of P and other nutrients such as zinc and copper. The network of hyphae extending several cm out into the bulk soil from the root substantially expands the effective volume of soil the plant can exploit. Influx of P into mycorrhizal roots can be three to five times higher than in nonmycorrhizal roots (Smith and Read, 1997). Mycorrhizal fungi appear also to be able to acquire P from organic sources that are not directly available to plants (e.g., phytic acid and nucleic acid) (Jayachandran et al., 1992).

The phosphorus cycle

An insight of the importance of the land cycle of phosphorus may be gained by a review of the major reservoirs and fluxes of global P. According to estimates of P fluxes by Richey (1983) the soil is a net receiver of P. Input as fertilizer P from rock phosphate sources was estimated to be 14 Tg yr^{-1} while net loss from land was estimated to be: to the ocean (through the atmosphere) about 1 Tg yr^{-1}, and to freshwater (through leaching and human activities) 4 to 7 Tg yr^{-1}. While it should be obvious that the P cycle of the biosphere is meaningful only when viewed across terrestrial and aquatic ecosystems, brevity would limit more detailed discussion of the P budget and cycle to the terrestrial component. Knowledge of the P budget of terrestrial ecosystems, especially agro-ecosystems, grasslands and forestry-based systems, are needed to assure sustainable management of those land-based resources and the environment. A generalized flow of P in the terrestrial environment is depicted in Figure P42, and fluxes and compartments of P shown for some ecosystems in Table P10. The P cycle does not have a measurable gaseous component, unlike the C, N and S cycles. It will become apparent from the examples below that the soil P cycle has the following key attributes: (*a*) soil microorganisms, aided by soil invertebrates which first break down plant litter and other organic debris into smaller particles and thus, by increasing the surface area available for enzyme

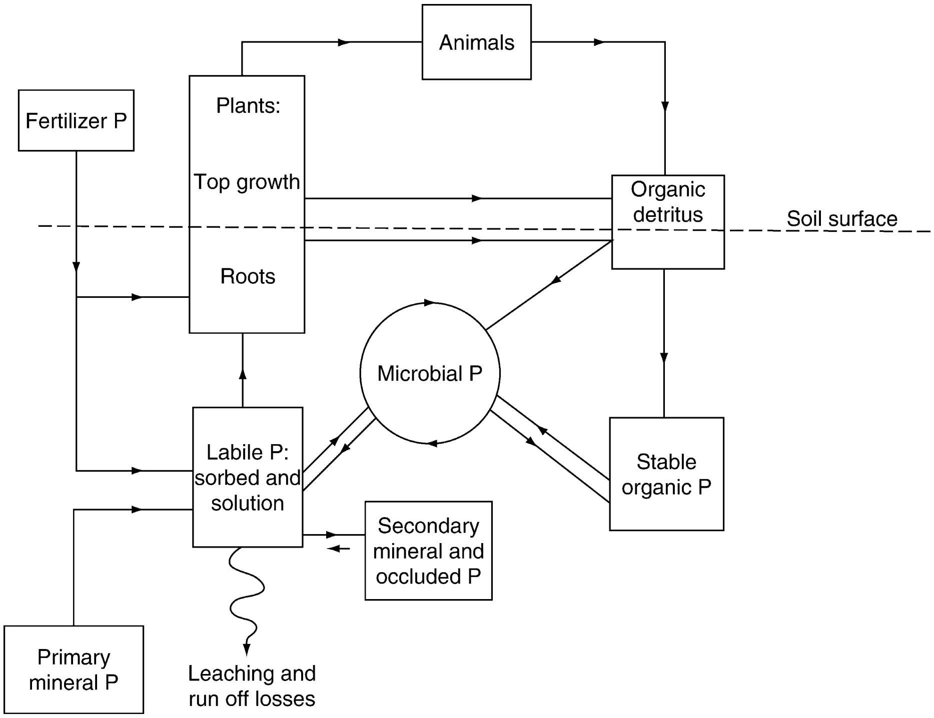


Figure P42 The phosphorus cycle in the terrestrial ecosystem (some components or inputs may not be present depending on the ecosystem).

Table P10 Major compartment and fluxes of P in four ecosystems[a]

Components	Mixed deciduous woodland[b]	Native prairie grassland[c]	Wheat crop	
			Monoculture[b]	Rotation wheat[d]
Compartments (kg P ha^{-1})				
Above-ground plant biomass	22.3	4.2	28.2	7.5
Below-ground plant biomass	23.4	10.7	1.0	na
Dead roots and litter	6.6	0.7	6.4	13.6[j]
Soil micro-organisms	1.1	}19.8	16.8	27.9
Soil fauna	3.3		na	na
Soil P fractions:				
a) Available	3.1	20	240	13
b) Inorganic	350	1 375	2 640	175
c) Organic	645	1 538	660	293
Annual flux (kg P ha^{-1})				
Soil to vegetation	11.4	12.0	33.4	5.6[k]
Litter to soil biota and organic P	9.5	6.0	6.4	8.9
Throughfall to soil	0.8	na[f]	0.2[h]	na
Mineralization	8.3[e]	43[g]	na[i]	4.0[l]
Fertilizer to soil	nil	nil	35	10
Fertilizer to plant	nil	nil	na	1.2
Exported in harvested crop	nil	nil	27	na
Drainage loss	0.2	na	<0.2	na

[a] The flux values have been simplified in some instances from more complex pathways. Readers should examine the underlying assumptions and sources of error for each term as given in the original sources.

[b] Harrison (1985). Soil data for forest ecosystem are for 50 cm depth, and for the wheat monoculture to 30 cm depth. The wheat monoculture is an example of intensive agricultural production.

[c] Halm et al. (1972) and Cole et al. (1977). Soil data are for 30 cm depth only.

[d] Mclaughlin et al. (1988c). Soil data are to 10 cm depth only. The rotational wheat is an example of extensive agriculture. The experiment was terminated after 95 days (because of the short half-life of ^{32}P) and the wheat was not yet mature.

[e] From decomposition of dead roots and litter, not including mineralization of soil Po.

[f] na: not applicable or data not available.

[g] Value shown is gross mineralization. Net mineralization is nil.

[h] Received in rainfall.

[i] No estimate of gross P mineralization. Net mineralization is nil.
Excludes 1.2 kg ha^{-1} of P derived from fertilizer.

[j] P added in residues of a legume (*Medicago truncculata*) pasture.

[k] Excludes 0.7 kg ha^{-1} P derived from pasture residues.

[l] Includes only P mineralized from pasture residues and incorporated into soil Pi fraction.

hydrolysis, recycle significant amounts of P returned to the soil in plant litter and animal excreta. Although the amount so recycled is relatively small (about 10 kg P ha^{-1} yr^{-1}) compared to the amount of extractable soil P, it is similar to annual plant P uptake rates. (*b*) Phosphorus loss through drainage is generally small (~0.2 kg P ha^{-1} yr^{-1}) although relatively greater amounts may be leached in coarse-textured soils in areas of high rainfall.

In natural ecosystems, such as forests, phosphorus undergoes a 'tight cycle'. This means that the amounts present within the ecosystem, in the biomass and soil, and the annual fluxes between the soil and vegetation are large in relation to the net gain or loss from it. Newman (1995) compiled data showing P release by rock weathering of 0.05 to 1.0 kg P ha^{-1} yr^{-1} and atmospheric deposition of 0.07 to 1.7 kg P ha^{-1} yr^{-1}. In a hardwood forest of the Adirondack Mountains, New York, Zhang and Mitchell (1995) reported a gain of 25 g P ha^{-1} yr^{-1} in precipitation and a leaching loss of 6.5 g P ha^{-1} yr^{-1} compared to fluxes between soil and vegetation in the range of several kg P ha^{-1} yr^{-1}. In agricultural systems, however, especially arable type agriculture, some of the P is removed in farm products, and losses of P occur through soil erosion, and to lesser extent, by leaching. To make up for crop removal and to sustain agricultural production, P fertilizers are added, usually annually. The bulk of P removed from agricultural production systems eventually ends up as waste products, which are discharged into the environment. The concentration of human population in urban centers, and of livestock production, aggravates the waste recycling problem. There are opportunities, not unlimited however, for recycling waste product P by land utilization and for its proper stewardship (Hucker and Catroux, 1981).

Forest ecosystems

The forest ecosystem data presented in Table P10 are those from a semi-natural non-fertilized, P-deficient oak-ash woodland situated on an acid, brown-earth soil (Harrison, 1985). A P budget for a pine forest situated on a Podzol in Ontario, Canada, is given by Foster and Morrison (1976). About 840 kg P ha^{-1} is estimated to be present in rocks and stones (not shown in Table P10). When this is included, the total P capital within the ecosystem is 1890 kg ha^{-1}, with 2.5% of the total being in the living biomass. Continued growth of the vegetation is almost entirely dependent on the recycling of nutrients through decomposition of organic matter returned each year. Some variations in fluxes and size of compartments of the P cycle can be expected for younger and older forest ecosystems. The amounts of P in compartments and fluxes in other forest ecosystems are somewhat similar (Heinrichs and Mayer, 1997; Miller et al., 1979; Yanai, 1992). Accumulated litter and forest floor may contain up to 68 kg P ha^{-1} (Zhang and Mitchell, 1995). Yanai (1992) estimated the turnover of P in the northern hardwood forest floor to be 7% yr^{-1} compared to 0.3% yr^{-1} for P in the mineral layers. Other key features of forest ecosystems are as follows (Harrison, 1985): (*a*) forests tend to gain more P from precipitation than they lose by drainage; (*b*) forest litters have wide C:P ratios and high lignin and tannin contents which retard their decomposition; (*c*) the acidifying effect of organic matter accumulation slows down P cycling. Soil disturbance on clear-cutting the forest can increase both soil bacterial and fungal populations and hasten the decomposition of accumulated organic matter. Up to 20 to 30% of the P in organic matter may be mobilized. However, because good forestry practice tends to promote pedogenesis the forest floor of second-rotation sites could have twice as much organic matter as first-rotation sites (Carey et al., 1982).

Grassland ecosystems

Nutrient cycling in a perennial plant-dominated system such as forests contrasts sharply with that of annual grasslands where the above-ground vegetation dies at the end of the growing season. As a result even though the standing biomass at its peak during the growing season is low compared to the forest biomass, the amounts of nutrients transferred between soil and vegetation can be relatively large, as shown by the data in Table P10 for a North American prairie grassland. In comparison to forest ecosystems, the amount of P accumulated in the vegetation is small, about 15 kg ha^{-1} and predominantly in the below-ground biomass. That contained in vegetation of a less productive montane *Agrostis-Festuca* grassland on an acid brown earth soil is even smaller, less than 8 kg ha^{-1} (Harrison, 1985). Phosphorus contained in accumulated litter and organic material is 5.7 kg ha^{-1} in montane grassland compared to <1 kg ha^{-1} in prairie grassland, presumably because of slower decomposition rates at higher elevations. Fluxes of P between vegetation and soil are more similar for the two grassland ecosystems. Estimates of P cycling for the montane ecosystem through grazing sheep were provided by Harrison (1985). About 2 kg P ha^{-1} was removed each year as "exported" feces and as sheep products.

The prairie grassland contains nearly five times as much P in soil fauna and microorganisms as the *Agrostis-Festuca* grassland, indicating a high level of cycling activity during the brief growing season. The ecosystem is in a state of equilibrium with respect to organic matter, and net mineralization of P during the growing season meets the demand required to maintain grass production (Cole et al., 1977). The quantities of P in compartments and fluxes of grasslands can vary quite considerably depending on site and management, particularly the level of fertilization (Harrison, 1985). This is quite apparent from the above comparison of two very different grasslands. Accumulation of organic matter in grasslands increases with time after establishment until an equilibrium level is reached, and this is reflected in the large amounts of P tied up in the soil organic fraction (Jackman, 1964). The P budget also has been studied for an annual grassland in a Mediterranean climate by Woodmansee and Duncan (1980), and for a sheep-grazed pasture by Nguyen and Goh (1992).

Arable agro-ecosystems

The P cycle in Table P10 is depicted for a continuous winter wheat ecosystem in Rothamsted, England, and the wheat phase of a legume pasture-wheat rotation in southern Australia. The former is a relatively high input system fertilized annually with nitrogen, phosphorus and potassium to meet the requirements of crop production while the latter crop derives nutrients from the legume crop residues and relatively low application rates of nitrogen and phosphate fertilizers. The soil organic matter at the Rothamsted site is at equilibrium after long-term continuous cropping. A relatively high rate of P fertilizer, 35 kg P ha^{-1}, is added annually. While root P in the standing crop at maturity is estimated at about 1 kg ha^{-1}, total P contribution from root decay through the growing season is estimated to be 5.2 kg ha^{-1}. The data from the legume-wheat rotation is estimated from an isotope-labeling study in which wheat was grown for only 95 days because of the short half-life of ^{32}P. Thus P uptake in the shoot is just 7.5 kg ha^{-1} while normally at maturity it would be about 10–11 kg ha^{-1} (Batten and Khan, 1987). Here, the rate of P fertilizer application (10 kg P ha^{-1}) is more representative of rates applied in agriculture managed extensively (as in Australia and the North American prairie) rather than intensively (as in western Europe). McLaughlin et al. (1988c) showed that most of the fertilizer P applied each year enters the soil inorganic P pool (70%) and only 12% is taken up by the wheat crop. Both plants and microorganisms obtain the bulk of their P from the soil pool, indicating the importance of residual P (both Po and Pi). A large proportion of plant residue P entering the soil P pool is found in the Po fraction including the microbial biomass. The P content of compartments and fluxes of P in other annual crop systems have been published elsewhere (Frissel, 1978; Stinner et al., 1984).

Superimposed on the natural cycle is human influence such as the mining and consumption of phosphates by society, and the release of P in domestic and industrial effluents. It has been estimated that globally about half of the 17 Tg P yr^{-1} carried to the oceans is derived from natural sources and the other half is dumped into rivers from human activities (Pierrou, 1976). The benefits of human influence on the P cycle to agriculture are obvious and the drawbacks to some aquatic ecosystems may be equally obvious. However, progress has been made in regard to the eutrophication problem although vigilance is necessary.

Y. K. Soon

Bibliography

Adams, M.A., and Bryne, L.T., 1989. ^{31}P-NMR analysis of phosphorus compounds in extracts of surface soils from selected karri (*Eucalyptus diversicolor* F. Muell) forests. *Soil Biol. Biochem.*, **21**: 523–528.

Arambarri, P., and Talibudeen, O., 1959. Factors affecting the isotopically exchangeable phosphate in soils. *Plant Soil*, **11**: 343–354.

Batten, G.D., and Khan, M.A., 1987. Uptake and utilisation of phosphorus and nitrogen by bread wheats grown under natural rainfall. *Aust. J. Exp. Agric.*, **27**: 405–410.

Bieleski, R.R., 1973. Phosphate pools, phosphate transport, and phosphate availability. *Ann. Rev. Plant Physiol.*, **24**: 225–252.

Bowman, R.A., 1988. A rapid method to determine total phosphorus in soils. *Soil Sci. Soc. Am. J.*, **52**: 1301–1304.

Bowman, R.A., and Cole, C.V., 1978. An exploratory method for fractionation of organic phosphorus from grassland soils. *Soil Sci.*, **125**: 95–101.

Bowman, R.A., and Moir, J.O., 1993. Basic EDTA as an extractant for soil organic phosphorus. *Soil Sci. Soc. Am. J.*, **57**: 1516–1518.

Brookes, P.C., Powlson, D.S., and Jenkinson, D.S., 1984. Phosphorus in the soil microbial biomass. *Soil Biol. Biochem.*, **16**: 169–175.

Carey, M.L., Hunter, I.R., and Andrew, I., 1982. *Pinus radiata* forest floors: factors affecting organic matter and nutrient dynamics. *N. Z. J. For. Sci.*, **12**: 36–48.

Cole, C.V., Innis, G.S., and Stewart, J.W.B., 1977. Simulation of phosphorus cycling in semi-arid grasslands. *Ecology*, **58**: 1–15.

Condron, L.M., Goh, K.M., and Newman, R.H., 1985. Nature and distribution of soil phosphorus as revealed by a sequential extraction method followed by ^{31}P nuclear magnetic resonance spectroscopy. *J. Soil Sci.*, **36**: 199–207.

Condron, L.M., Moir, J.O., Tiessen, H., and Stewart, J.W.B., 1990. Critical evaluation of methods of determining total organic phosphorus in tropical soils. *Soil Sci. Soc. Am. J.*, **54**: 1261–1266.

Dalal, R.C., 1977. Soil organic phosphorus. *Adv. Agron.*, **29**: 83–117.

Dormaar, J.F., and Webster, G.R., 1963. Status of organic phosphorus in some Alberta soils. *Can. J. Soil Sci.*, **43**: 27–34.

Emsley, J., 1980. The phosphorus cycle. In Hutzinger, O., ed., *The Handbook of Environmental Chemistry. Vol. 1. Part A: The Natural Environment and the Biogeochemical Cycles.* Berlin: Springer, 147–167.

Enwezor, W.O., and Moore, A.W., 1966. Comparison of two methods for determining organic phosphorus in some Nigerian soils. *Soil Sci.*, **102**: 284–285.

Foster, N.W., and Morrison, I.K., 1976. Distribution and cycling of nutrients in a natural *Pinus banksiana* ecosystem. *Ecology*, **57**: 110–120.

Frissel, M.J. ed., 1977. Cycling of nutrients in agricultural ecosystems. *Agro-Ecosystems*, 4: 1–354.

Gressel, N.R., and McColl, J.G., 1997. Phosphorus mineralization and organic matter decomposition: a critical review. In Cadisch, G., and Giller, K.E., eds., *Driven by Nature: Plant Litter Quality and Decomposition.* Wallingford, U.K.: CAB International, 297–309.

Halm, B.J., Stewart, J.W.B., and Halsted, R.L., 1972. The phosphorus cycle in a native grassland ecosystem. In *Isotopes and Radiation in Soil-plant Relationships including Forestry.* Vienna: International Atomic Energy Agency, 571–586.

Harrison, A.F., 1985. Effects of environment and management on phosphorus cycling in terrestrial ecosystems. *J. Environ. Manage.*, **20**: 163–179.

Heinrichs, H., and Mayer, R., 1977. Distribution and cycling of major and trace elements in two central European forest ecosystems. *J. Environ. Qual.*, **6**: 402–407.

Hucker, T.W.G., and Catroux, G. eds., 1981. *Phosphorus in Sewage Sludge and Animal Waste Slurries.* Dordrecht: D. Reidel Co.

Ipinmidun, W.B., 1973. Comparison of some methods for determining organic phosphorus in some Nigerian soil. *Soil Sci.*, **115**: 324–325.

Jackman, R.H., 1964. Accumulation of organic matter in some New Zealand soils under permanent pasture. I. Patterns of change of organic carbon, nitrogen, sulphur and phosphorus. *N.Z.J. Agric. Res.*, **7**: 445–471.

Jayachandran, K., Schwab, A.P., and Hetrick, B.A.D., 1992. Mineralization of organic phosphorus by vesicular-arbuscular mycorrhizal fungi. *Soil Biol. Biochem.*, **24**: 897–903.

John, M.K., Sproul, P.N., and Kelley, C.C., 1965. The distribution of organic phosphorus in British Columbia soils and its relationship to soil characteristics. *Can. J. Soil Sci.*, **45**: 97–95.

Larsen, S., Gunary, D., and Sutton, C.D., 1965. The rate of immobilization of applied phosphate in relation to soil properties. *J. Soil Sci.*, **16**: 141–148.

Letkeman, L.P., Tiessen, H., and Campbell, C.A., 1996. Phosphorus transformation and distribution during pedogenesis of western Canadian soils. *Geoderma*, **71**: 201–208.

Lindsay, W.L., and Vlek, P.L.G., 1977. Phosphate minerals. In Dixon, J.B., and Weeds, S.B., eds., *Minerals in Soil Environments.* Madison, WI: Soil Science Society of Amercia, pp. 639–672.

Marschner, H., 1986. *Mineral Nutrition of Higher Plants*. London: Academic Press.

Martin, J.K., 1964. Soil organic phosphorus. 3. Patterns of organic phosphorus in a series of New Zealand soils. *N. Z. J. Agric. Res.*, **7**: 750–760.

Mattingly, G.E.G., 1975. Labile phosphate in soils. *Soil Sci.*, **119**: 369–375.

McGill, W.B., and Cole, C.V., 1981. Comparative aspects of cycling of organic C, N, S and P through soil organic matter. *Geoderma*, **26**: 267–286.

McLaughlin, M.J., Alston, A.M., and Martin, J.K., 1988a. Phosphorus cycling in wheat-pasture rotation. 1. The source of phosphorus taken up by wheat. *Aust. J. Soil Res.*, **26**: 323–331.

McLaughlin, M.J., Alston, A.M., and Martin, J.K., 1988b. Phosphorus cycling in wheat-pasture rotation. 2. The role of microbial biomass in phosphorus cycling. *Aust. J. Soil Res.*, **26**: 333–342.

McLaughlin, M.J., Alston, A.M., and Martin, J.K., 1988c. Phosphorus cycling in wheat-pasture rotation. 3. Organic phosphorus turnover and phosphorus cycling. *Aust. J. Soil Res.*, **26**: 343–353.

McLean, A.A., 1965. Organic phosphorus in some New Brunswick soils. *Can. J. Soil Sci.*, **45**: 185–188.

Miller, H.G., Cooper, J.M., Miller, J.D., and Pauline, O.J.L., 1979. Nutrient cycles in pine and their adaptation to poor soils. *Can. J. For. Res.*, **9**: 19–26.

Neptune, A.M.L., Tabatabai, M.A., and Hanway, J.J., 1975 Sulfur fractions and carbon-nitrogen-phosphorus-sulfur relationships in some Brazilian and Iowa soils. *Soil Sci. Soc. Am. Proc.*, **39**: 51–55.

Newman,E.I., 1995. Phosphorus inputs to terrestrial ecosystems. *J. Ecol.*, **83**: 713–726.

Nguyen, M.L., and Goh, K.M., 1992. Nutrient cycling and losses based on a mass-balance model in grazed pastures receiving long-term superphosphate applications in New Zealand. 1. Phosphorus. *J. Agric. Sci. (Cambridge)*, **119**: 89–106.

Olsen, S.R., Kemper, W.D., and Jackson, R.D., 1962. Phosphate diffusion to plant roots. *Soil Sci. Soc. Am. Proc.*, **26**: 222–227.

Omotoso, T.I., 1971. Organic phosphorus contents in some cocoa growing soils of southern Nigeria. *Soil Sci.*, **112**: 195–199.

Pierre, W.H., and Parker, F.W., 1927. Soil phosphorus studies. 2. The concentrations of organic and inorganic phosphorus in the soil solution and soil extracts and the availability of the organic phosphorus to plants. *Soil Sci.*, **24**: 119–128.

Pierrou, U., 1976. The global phosphorus cycle. In Svensson, B.H., and Söderland, R., eds., *Nitrogen, Phosphorus and Sulphur – Global Cycles*. SCOPE Report 7. *Ecol. Bull. (Stockholm)*, 22: 75–88.

Raghothama, K.G., 1999. Phosphate acquisition. *Ann. Rev. Plant Physiol. Plant Mol. Biol.*, **50**: 665–693.

Richey, J.E., 1983. The phosphorus cycle. In Bolin, B., and Cook, R.B., eds., *The Major Biogeochemical Cycles and their Interactions.* New York: John Wiley & Sons, pp. 51–56.

Setenac, H., and Grignon, C., 1985. Effect of pH on orthophosphate uptake by corn roots. *Plant Physiol.*, **77**: 136–141.

Smeck, N.E., and Runge, E.C.A., 1971. Phosphorus availability and redistribution in relation to profile development in an Illinois landscape segment. *Soil Sci. Soc. Am. Proc.*, **35**: 952–959.

Smith, S.E., and Read, D.J., 1997. *Mycorrhizal Symbiosis.* San Diego, CA: Academic Press.

Soloman, D., and Lehman, J., 2000. Loss of phosphorus from soil in semi-arid northern Tanzania as a result of cropping: evidence from sequential extraction and ^{31}P-NMR spectroscopy. *Eur. J. Soil Sci.*, **51**: 699–708.

Sposito, G., 1989. *The Chemistry of Soils.* New York:Oxford University Press.

Stevenson, F.J., 1986. *Cycles of Soil.* New York: John Wiley & Sons.

Stewart, J.W.B., and Tiessen, H., 1987. Dynamics of soil organic phosphorus. *Biogeochem.*, **4**: 41–60.

Stinner, B.R., Crossley, D.A., Odum, E.P., and Todd, R.L., 1984. Nutrient budgets and internal cycling of N, P, K, Ca and Mg in conventional tillage, no-tillage and old-field ecosystems on the Georgia Piedmont. *Ecology*, **65**: 354–369.

Tate, K.R., 1985. Soil phosphorus. In Vaughan, D., and Malcolm, R.E., eds., *Soil Organic Matter and Biological Activity.* Dordrecht, The Netherlands: Martinus Nijhoff/Dr. Junk Publ., pp. 329–377.

Tate, K.R., and Newman, R.H., 1982. Phosphorus fractions of a climosequence of soils in New Zealand tussock grasslands. *Soil Biol. Biochem.*, **14**: 191–196.

Tiessen, H., Stewart, J.B.W., and Bettany, J.R., 1982. Cultivation effects on the amounts and concentration of carbon, nitrogen, and phosphorus in grassland soils. *Agron. J.*, **74**: 831–835.

Walker, T.W., and Syers, J.K., 1976. The fate of phosphorus during pedogenesis. *Geoderma*, **15**: 1–19.

Wild, A., 1988. Plant nutrients in soil: phosphate. In Wild, A., ed., *Russell's Soil Conditions and Plant Growth.* UK: Longman Group, pp. 695–742.

Williams, C.H., and Steinbergs, A., 1958. Sulphur and phosphorus in some eastern Australian soils. *Aust. J. Agric. Res.*, **9**: 483–491.

Williams, C.H., Williams, E.G., and Scott, N.M., 1960. Carbon, nitrogen, sulphur and phosphorus in some Scottish soils. *J. Soil Sci.*, **11**: 334–346.

Willaims, J.D.H., Syers, J.K., Walker, T.W., and Rex, R.W., 1970. A comparison of methods for determination of soil organic phosphorus. *Soil Sci.*, **110**: 13–18.

Wood, T., Bormann, F.H., and Voight, G.K., 1984. Phosphorus in a northern hardwood forest: biological and chemical control. *Science*, **223**: 391–393.
Woodmansee, R.G., and Duncan, D.A., 1980. Nitrogen and phosphorus dynamics and budgets in annual grasslands. *Ecology*, **61**: 893–904.
Yanai, R.D., 1992. Phosphorus budget of a 70-year old northern hardwood forest. *Biogeochemistry*, **17**: 1–22.
Zhang, Y., and Mitchell, M.J., 1995. Phosphorus cycling in a hardwood forest in the Adirondack Mountains, New York. *Can. J. For. Res.*, **25**: 81–87.

PHREATIC

See *Water table*.

PHYSICAL CHEMISTRY

Physical chemistry of soils concerns the relationships between physical and chemical phenomena in soils (Sparks, 1999) especially borderline phenomena such as the common processes of adsorption (see *Adsorption*) and ion exchange (see *Exchange Phenomena*). Like physical chemistry in general, physical chemistry of soils aims at predicting the pathways of chemical processes over time as well as the final results under various conditions, beginning with a knowledge of structure and properties of the molecules involved in the reactions.

Historically, development of the physical chemistry of soils stems from the studies of Thompson and Way who discovered the ion exchange capacity of soils and formulated its main concepts from 1845–1854 (Russell, 1973). These studies provided the basis for the investigation, development, and extensive application of various ion exchangers not only in soil science but also in modern chemistry and technology.

The physical chemistry of soils involves the study of soil thermodynamics, electrochemistry and photochemistry of soils, and kinetics of chemical soil processes as well as the investigation of *soil solutions* (*q.v.*), surface phenomena, and acid-base (see *Acidity*) and reduction-oxidation (see *Redox-pH diagrams and reactions*) equilibria. The scope of physical chemistry is broad because the resolution of problems in each subfield requires data from the entire body of knowledge pertaining to the chemical properties (see *Chemical analyses*) of soils (Tabatabai and Sparks, 2005).

Scope

Soil is one of the most complicated systems encountered in nature or technology, and it possesses a number of highly peculiar features. Such features include multiplicity of phases in soils (the number of phases always exceeds three), low natural humidity and large specific surface (which may be as high as 50–150 $m^2 g^{-1}$ for bulk soil samples and up to 250–280 $m^2 g^{-1}$ for the fraction 0.001 mm). In such a system chemical interactions either occur at an interface or are directly affected by an interface (see Huang et al., 1998; Sposito, 2004). The chemical interactions may simultaneously involve clay minerals (montmorillonite, kaolinite, hydrous micas, etc.), organic substances (humic acids, fulvic acids, lipids, polypeptides, polycarbohydrates), ordinary and complex salts, and the products of reactions among the preceding components (Yariv and Cross, 2002). Soil air is typically rich in carbon dioxide, which affects all reactions occurring in the system. Finally, the natural or native soil is a changeable, dynamic formation, the processes in which are characterized by daily, seasonal, yearly, and secular dynamics (Rode, 1962). It is indeed not easy to apply the classical chemical laws derived for much simpler systems to such a complex multiphase and heterogeneous system. However, the discrepancies often observed between the theoretical predictions and experimental results should be ascribed to inadequacy of theoretical frameworks, mathematical formulations, and methods of analyzing and processing results rather than to any essential impossibility of describing chemical processes in soils in terms of mathematical models and equations.

Thermodynamics

Focal points of soil physical chemistry are: the application of thermodynamics in studies of soil formation (see *Phase Rule and Phase Diagrams, Thermodynamics of Soil Water*) and the theory of plant nutrition (see *Nutrient potentials*). Thermodynamics provides a basis for solving the problem of possible spontaneous chemical soil reactions, and it allows us to select the most plausible genetic hypotheses and the most probably pathways of transformations of minerals and organic substances in soils. The thermodynamics of soil moisture (see Sposito, 1981) has so far been studied most, but it is traditionally classified as soil physics even though water is but one of the normal chemical components of soil.

Inasmuch as there is an exchange of matter and energy between a soil and its environment, soils are thermodynamically typical open systems. This factor limits applications of the equations derived for closed systems, but at the same time it provides new approaches to determining matter and energy balances in soil formation. Only in few model experiments can soil be treated as an equilibrium system; in many cases the soil state is close to being a stationary state so that the chemical reactions in the system have to be treated as irreversible ones. For such systems, the conventional thermodynamical potentials are characterized in terms of inequalities, for instance,

$$\mathrm{d}H < T\mathrm{d}S + V\mathrm{d}p$$

and

$$\mathrm{d}Z < -S\mathrm{d}T + V\mathrm{d}p$$

where H is enthalpy, S is entropy, Z is Gibbs free energy (isobaric potential), T is absolute temperature, V is volume, and p is pressure. The principal thermodynamic functions for the mineral component of soil have been estimated to have the following values: internal energy U about 4 000–6 000 kcal/100 g, enthalpy H 300–450 kcal/100 g, Gibbs free energy Z 300–400 kcal/100 g, and entropy S 15–30 cal/100 g. The combustion heats of soil humus fall in the 5 000–6 000 cal g^{-1} range and depend significantly on the humus type.

Soil scientists are interested in the processes that alter the composition of the system. The equilibrium state for such reactions may be characterized by the following equation, taking into account variations in chemical potentials:

$$\mathrm{d}Z = V\mathrm{d}p - S\mathrm{d}T + \sum \mu_j \mathrm{d}n_j$$

The chemical potentials are assumed to be equal in all phases in a multiphase system in a state of equilibrium.

However, in the heterogeneous soil system a potential drop is developed at each interface due to dissociation of the absorbed cations. Such a system has to be treated at equilibrium in terms of electrochemical rather than chemical potentials. For example, the distribution of sodium ions between the absorbing complex and the solution is therefore described by the following equation:

$$\mu'_{\mathrm{Na}} + z\mathrm{F}\psi' = \mu''_{\mathrm{Na}} + z\mathrm{F}\psi''$$

where prime and double prime denote different parts (or phases) of the system, ψ is the electrostatic potential, and F is the Faraday number.

Surface phenomena and the reactions at interfaces between soil phases are dealt with in the most general way by colloid chemistry of soils, which is traditionally classified as a part of physical chemistry. The study of soil colloids concerns the structure of the substances comprising them (primarily, the structure of clay minerals), the structure of the surface, development of the double electrical layer, and the theory of coagulation and peptization of colloidal particles (Marshall, 1964). Of essential importance are the turnovers of substances and the equilibria between the soil absorbing complex and the soil solution. Studies of the absorbing capacities of soils deal with these problems (Kelley, 1948).

Absorbing capacity

Gedroiz (1931) suggested the following subdivision of the absorbing capacity of soils: (1) the mechanical absorbing capacity, i.e., the capacity to retain particles suspended in solution; (2) the physical absorbing capacity, which consists of adsorption and coagulation due to surface energy; (3) the physicochemical absorbing capacity or ion exchange capacity; (4) the chemical absorbing capacity due to formation and accumulation of difficulty soluble salts; and (5) the biological absorbing capacity.

Soil properties and plant growth are greatly affected by the capacity of soils to absorb and exchange cations, which depends on the pH value and the mechanical and mineral composition of the soil. A fundamental physico-chemical characteristic of the soils is the absorption capacity for cations, which ranges from 5–10 meq/100 g in podzolic soils up to 50–80 meq/100 g Chernozems. The absorption capacity of the soil organic component may be as high as 500–700 meq/100 g, and it is highly dependent on pH value of the medium. The properties of soils depend not only on the total amounts of cations absorbed but also on their composition (Tucker, 1971). This introduces an important characteristic of acid soils, namely, the degree of saturation of soil with bases, the percent base saturation (PBS):

$$\mathrm{PBS} = \frac{\mathrm{TEB} \cdot 100}{\mathrm{CEC}} = \frac{S \cdot 100}{T}\%$$

where TEB $= S$, the total exchangeable bases, and CEC $= T$, the cation exchange capacity (the absorption capacity). The corresponding expression for alkali and saline soils is ESP, the exchangeable sodium percentage.

The energy of cation absorption by soils depends on the charge of the cations, their radii, and their degree of hydration (Bolt and Bruggenwert, 1976). The absorption increases with increasing cation charge, and for the same charges it increases with increasing atomic weight according to the lyotropic series:

$$\mathrm{Li}^+ < \mathrm{Na}^+ < \mathrm{K}^+ < \mathrm{Rb}^+ < \mathrm{Cs}^+$$

and

$$\mathrm{Mg}^{2+} < \mathrm{Ca}^{2+} < \mathrm{Sr}^{2+} < \mathrm{Ba}^{2+}$$

The order in this series may be changed somewhat according to the crystallochemical features of the sorbent.

The relationships between the ion composition of the solution and the composition of the exchange cations have been described by ion exchange isotherms. A number of equations were suggested as mathematical descriptions of exchange isotherms, as for instance, those derived by Freundlich, Jenny and Wiegner, Gans, Vanselow, Gapon, and Nikolskij (Marshall, 1964). The majority of these equations stem from the mass-action law and in the case of the exchange

$$\mathrm{SCa} + 2\mathrm{Na}^+ \rightleftharpoons \mathrm{SNa}_2 + \mathrm{Ca}^{2+1}$$

where S is the soil-absorbing complex, we may write down the following relationship:

$$K = \frac{[S\mathrm{Na}_2] \cdot a_{\mathrm{Ca}^{2+}}}{[S\mathrm{Ca}] \cdot a^2_{\mathrm{Na}^+}}$$

In this equation K is the exchange constant, $a_{\mathrm{Ca}^{2+}}$ and a_{Na^+} are the activities of the calcium and sodium ions in the equilibrium solution, and $[\mathrm{SNa}_2]$ and $[\mathrm{SCa}]$ are the concentrations of Na^+ and Ca^{2+} in the absorbed state; the activity coefficients of the absorbed cations are taken to be unity. None of the equations agree fully with the experimental data over wide ranges of concentrations and cation ratios. This lack of agreement is due to the multifunctional nature of the soil-absorbing complex and to differences in the strength of bonding of the exchange cations with the adsorption centers. The latter fact may be taken into consideration if, when deriving the equation for equilibrium, we assume the electrochemical, rather than chemical, potentials in two parts of the system to be equal. The exchange isotherm is then most satisfactorily expressed as a log function.

The absorbed cations are capable of dissociation, which affects the composition of the soil solution. The highest degree of dissociation of univalent cations for weak dilutions ranges from 2–40% and for divalent cations, from 2–3%, frequently much less. The degree of dissociation depends on the mineral composition, the humus content, and the strength of cation absorption by the absorbing complex. The dissociation and the Donnan equilibrium have been often related to the Wiegner effect (the suspension effect), but many modern results suggest that the potential difference observed between the suspension and the intermicellar solution is due to the diffusion potential. There are fewer data on absorption of anions even though that is also of great practical importance for evaluating the phosphate and nitrogen nutrition of plants.

Equilibria

Physicochemical analysis of equilibria in the heterogeneous system of solid phases and soil solution is another important aspect of soil physical chemistry (Loeppert et al., 1995). Typical practical results are the development of concepts such as lime potential and phosphate potential (see *Nutrient potentials*). According to Schofield (1955), the phosphate potential PhP is given by the following expression:

$$\mathrm{PhP} = 0.5p\mathrm{Ca}^{2+} + p\mathrm{H_2PO_4^-}$$

where p is the negative logarithm of the activity of the respective component. The higher the PhP, the lower the activity and concentration of phosphates in the solution. If we make use of thermodynamical potentials, the decrease per mole of Gibbs free energy with transfer of phosphate from the solid phase into solution may be expressed through use of the chemical affinity of the reaction A as follows:

$$A = \frac{-2.3\mathrm{R}T}{0.5\mathrm{pCa}^{2+} + \mathrm{pH_2PO_4^-}}$$

which differs from the phosphate potential only in sign and dimension. According to Schofield (1955), the lime potential LP is given by

$$\mathrm{LP} = \mathrm{pH} - 0.5\mathrm{pCa}^{2+}$$

The potential LP does not depend on the ratio Ca:Mg; it is little affected by dilution, and many authors believe it to be a better characterization of soil *acidity* (*q.v.*) than pH valve. A similar formula may be written for the potassium potential: $\mathrm{p}K^+ – 0.5\mathrm{p}(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})$ (Woodruff, 1955). The preceding potentials are assumed to be stable characteristics of a soil though they may be used within only fairly narrow ranges. A similar concept underlies evaluation of provision of a certain element to plants using the quantity-intensity ratio according to Beckett (1971). For instance, to determine this parameter for potassium, the soil is stirred with a $\mathrm{KCl} + \mathrm{CaCl_2}$ solution, and in 12 hours the content of cations is measured in the filtrate; the difference yields the amount of the exchangeable potassium Δk in mg-equiv/100 g. The plot of Δk as a function of the ratio of the activities of K^+ and Ca^{2+} (or $\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}$) yields the activity of K^+ in the isotonic solution to characterize the state of the soil solution system at a given moment and the ability of soil to control the K^+ activity in the solution with changes in ambient conditions.

Soil solution

Despite the importance of the heterogeneous nature of soils to equilibria, the soil solution (Sposito, 1981) is usually characterized independently of the solid phases, particularly in salinity studies. The best description of the soil solution may be obtained in terms of isotonic (isohydric for pH) solutions, that is, the solutions whose composition is not changed following interaction with the solid phases of soil. However, extraction and analysis of such solutions is a labor-consuming and complicated procedure, and simpler approximate methods are commonly used. The simplest, but at the same time the least satisfactory method, is to analyze water extracts of soil samples. The basic difficulty encountered in producing the native soil solution is that the diffuse ion layer of colloidal particles is in direct contact with the intermicellar medium, and therefore, separation of the phases inevitably results in an altered general state of the system. The primary thermodynamic function describing the soil solution is the activity a of the solution components, which is essentially different from the concentration c and may be formally calculated using the activity coefficient f from the formula $a = cf$. In the solutions from non-saline mineral soils, the value of f for divalent ions ranges from 0.8 to 1.0, and for trivalent ions from 0.6 to 0.9. In the hydrocarbonate sodium solutions with salt concentrations of 0.5–0.7 g l^{-1}, the activity coefficients for the respective ions are 0.6–0.7 and 0.3–0.4, whereas in chloride-sulfate solutions with salt concentrations of 2.5–5.0 g l^{-1} they are as low as 0.2–0.3 and 0.03–0.05. Thus the activity coefficients cannot be treated as small correction factors; they should be considered important characteristics because their values may have greater effects on the final results than the concentrations of components. Determinations of f from equations of the type

$$\ln f = \frac{k \cdot \sqrt{J}}{1 + A\sqrt{J}}$$

where J is the ionic strength of the solution, and k and A are constants, are not always reliable and are labor-consuming, inasmuch as prior quantitative determinations of all components in solution are needed. A more promising method is the direct measurement of the activities of cations and anions using reversible ion-selective electrodes as is usual in electrometric determination of pH. Reliable enough electrodes have been suggested for direct determination in soils of the activities of K^+, Na^+, Ca^{2+}, Cl^-, and some other ions. One advantage of these electrodes is that they make possible characterization of soil without disturbing its native state.

The effects of the solid phases on the composition of the soil solution are especially strong in saline soils and in measuring pH values in a range from 3–5 to 8–9.

Acidity

The acid reaction (the *acidity*) of soils depends primarily on heterogeneous equilibria, the exchange cations H^+ and $\mathrm{A1}^{3+}$, and the organic acids (see *Acidity*). An alkaline reaction is usually related to the presence of the alkaline and alkali earth carbonates. For such systems, equations have been suggested taking into account the concentrations of $\mathrm{CO_2}$ and carbonates. For instance,

$$\mathrm{pH} = 6.00 - \frac{2}{3}\lg P_{\mathrm{CO_2}} + \frac{1}{3}\lg f_{\mathrm{HCO_3^-}} - \frac{1}{3}\lg f_{\mathrm{Ca^{2+}}}$$

or

$$\mathrm{pH} = \frac{\mathrm{p}K_1 + \lg \mathrm{HCO_3^-}}{[\mathrm{CO_2}] + \lg f_{\mathrm{H^+}}}$$

where K_1 is the first-step dissociation constant for carbonic acid. As a rule, such equations yield results differing from the experimental pH values. Apparently, development of alkalinity also depends to some extent on substances such as various phosphates, sulfides, and silicates. As in other cases, evaluation of the soil reaction should take into consideration both the quantity factor and the intensity factor. The intensity factor is the measured pH value; the quantity factor comprises the potential (exchange and hydrolytic) acidity. The potential acidity is associated with the ability of soils to resist changes in the reaction. This *buffer capacity* of soil, (see *Buffers, buffering*), as it may be called, is related not only to the reaction of the medium but also to many other characteristics such as reduction-oxidation potential and the C:N ratio. In contrast to the buffer capacity of an isolated system, however, the buffer capacity of soils under natural conditions depends on the effects of soil forming factors and can be referred to as a *dynamic buffer capacity*. This is due to the fact that man-made effects such as liming (see *Carbonates*) do not eliminate the permanent climatic factors; the soil acidity reduced by liming can be restored by dissolution and leaching of carbonates.

Oxidation-reduction

The reduction-oxidation processes in *automorphic* (well-drained) soils are characterized by reduction-oxidation potentials from +0.4 to +0.6 V, whereas in hydromorphic (waterlogged and submerged) soils in the presence of organic substances, reduction processes can decrease the potential down to +0.2 V and below. The principal factors controlling the potential level are aeration and the operation of biological processes. A decrease in potential results in the increased mobility of certain elements through transformations such as $Fe^{III} \rightarrow Fe^{II}$ and $Mn^{IV} \rightarrow Mn^{II}$, thus affecting plant nutrition and intensifying migration of reduced substances (see *Micronutrients*). The oxidation regime, as a rule, contributes to accumulation of many difficultly soluble compounds in oxidized forms. According to the character of water regimes, soil areas may be classified as follows: zones of stable oxidation processes with potentials exceeding 0.40–0.45 V, zones of stable reduction processes with potentials below +0.40–0.45 V transitional zones, and zones of unstable reduction-oxidation regimes. (see *Redox-pH Diagrams and Reactions*).

Photochemistry

We know relatively little about the photochemistry of soil processes. The electromagnetic waves in the form of solar radiation (direct or scattered) are a constant source of energy, especially great in equatorial zones. This energy is not only transformed into heat and thus affects the heat balance but it also has direct photochemical effects. The effect of radiant energy on organic substances has been studied more than has the effects on mineral substances. Under the effects of light, solutions of humic acids are more or less rapidly discovered, being completely bleached by large doses of radiation. The molecules of humic acids break down in the process into smaller units. On the other hand, other substances, for instance, some amino acids, are condensed under the effect of light to give rise to dark products. These processes involve primarily photochemical oxidation with formation of free radicals. Under natural conditions the photochemical reactions involve only the uppermost soil layer, but due to the transfers of matter among various layers, the products of photochemical reactions penetrate into the subsoil.

Conclusion

Although the thermodynamics of soils indicate that certain processes are possible in principle, their realization depends on kinetic parameters. The soil formation process as a whole, consisting of partial macro- and microprocesses proceeds through individual and often numerous stages (Rode, 1962). By analogy with the processes in chemical technology, we can assume that the character and the final results of the soil formation process and its constituents depend on the slowest stage of the phenomenon as a whole. It should be stressed here that one specific feature of the soil chemical processes that affects their rate is the fact that they occur in the presence of solid phases exhibiting marked catalytic properties. It has been shown experimentally, for instance, that montmorillonite has a catalytic role in humification and that iron oxides, silicon oxides, and allophanes play a catalytic role in oxidation of phenols and autolyzates. It has been suggested that the principal active substances of soil are its organomineral complexes, which may be peculiar enzyme systems.

D. S. Orlov

Bibliography

Bates, R.G., 1973. *Determination of pH: Theory and Practice.* New York: Wiley, 479 pp.

Beckett, P.H.T., 1971. Potassium potentials in soils, potash review (April/May 1971), Subject 5, *Soil Testing and Plant Analysis*, Suite 30, 41 pp.

Bolt, G.H., and Bruggenwert, M.G.M., eds., 1976. *Soil Chemistry: A. Basic Elements.* Amsterdam: Elsevier, 281 pp.

Gedroiz, K.K., 1931. *Die Lehre vom Absorptionsvermögen der Böden.* (transl. from Russian by Kuron, H.). Dresden: Steinkopf, 448 pp.

di Gleria, J., Klimes-Szmix, A., and Dvoracsen, M., 1962. *Bodenphysik and Bodencolloidik.* Budapest: Akedémiai Kiadó, 795 pp.

Hesse, R.P., 1972. *A Textbook of Soil Chemical Analysis.* New York: Chemistry Publications, 520 pp.

Huang, P.M., Senesi, N., and Buffle, J., 1998. *Structure and Surface Reactions of Soil Particles.* Chichester; New York: Wiley, 492 pp.

Kelley, W.P., 1948. *Cation Exchange in Soils.* New York: Rheinhold, 144 pp.

Loeppert, R.H., Schwab, A.P., and Goldberg, S., (editors-in-chief), 1995. *Chemical equilibrium and Reaction Models.* Madison, WI: Soil Science Society of America, 422 pp.

Marshall, C.E., 1964. *The Physical Chemistry and Mineralogy of Soils, Vol. 1. Soil Minerals.* New York: Wiley, 388 pp.

Rode, A.A., 1962. *Soil Science.* (transl. from Russian by Gourevich, A.). Jerusalem: Israel Progressive Scientist Translations, 517 pp.

Russell, E.W., 1973. *Soil Conditions and Plant Growth*, 10th edn. London: Longmans, 849 pp.

Schofield, R.K., 1955. Can a precise meaning be given to "available" soil phosphorus? *Soils Fertil.*, **18**: 373–375.

Sparks, D.L., 1996. *Methods of Soil Analysis. Part 3, Chemical Methods.* Madison, WI: Soil Science Society of America. 1390 pp.

Sparks, D.L., 1999. *Soil Physical Chemistry*, 2nd edn. Boca Raton, FL: CRC Press, 409 pp.

Sposito, G., 1981. *The Thermodynamics of Soil Solutions.* New York: Oxford University Press, 223 pp.

Sposito, G., 1994. *Chemical Equilibria and Kinetics in Soils.* New York: Oxford University Press, 268 pp.

Sposito, G., 2004. *The Surface Chemistry of Natural Particles.* New York: Oxford University Press, 242 pp.

Tabatabai, M.A., and Sparks, D.L., 2005. *Chemical Processes in Soils.* Madison, WI: Soil Science of America. 723 pp.

Tucker, B.M., 1971. Basic exchangeable cations in soil. CSIRO, (Australia) Div. Soils Tech. Paper, No. 8, 22 pp.

Wiklander, L., 1964. Cation and anion exchange phenomena. In Bear, F.E., ed., *Chemistry of the Soil.* New York: Reinhold, pp. 162–205.

Woodruff, C.M., 1955. Energies of replacement of calcium and potassium in soils, *Soil Sci. Soc. Am. Proc.*, **19**: 167–171.

Yariv, S., and Cross, H., 2002. *Organo-Clay Complexes and Interactions.* New York: Dekker, 688 pp.

Cross-references

Acidity
Adsorption
Buffers, Buffering
Chemical Analyses
Electrochemistry
Electro-osmosis
Exchange Phenomena
Flocculation
Lime
Nutrient Potentials
Soil Chemistry
Soil Physics
Soil Solution
Thermal Regime
Thermodynamics of Soil Water

PHYSICAL PROPERTIES

The intensive and extensive properties of a soil that are physical in nature as opposed to chemical or biological. Volume, mass, density, humidity, porosity are examples.

PHYSICAL WEATHERING

See *Mechanical Weathering*.

PHYTOLITH

Microscopic solid body, most commonly composed of opaline silica, laid down within the tissues of a plant as a means of expelling unwanted elements originally absorbed with nutrients obtained from the soil. After Si, the most common element is Al. As with pollen grains, phytoliths are useful in determining the historical sequence of plants in a given area. They are especially important as indicators of the beginnings of agriculture since the cultivated grasses we use as our crops produce distinctive phytoliths (Piperno, 2006).

Bibliography

Piperno, D.R., 2006. *Phytoliths: A Comprehensive Guide for Archaeologists and Paleoecologists*. Lanham, MD: AltaMira Press. 238 pp.

PINGO

A perennial, ice-cored conical or dome-shaped mound (often fissured or cratered on top), with a covering of soil or peat, found in regions of permafrost.

Bibliography

French, H.M., 2007. *The Periglacial Environment*, 3rd edn. Chichester, England: Wiley, 478 pp.

Cross-reference

Ice Erosion

PLANOSOLS

Planosols have bleached, light-colored, eluviated surface horizons that show signs of periodic water-logging on account of the immediate subsoil being significantly more clay-rich and hence less permeable, and abruptly overlie dense, slowly permeable subsoil with significantly more clay than the surface horizon. This article is based on the descriptions in FAO (2001).

Connotation. Soils with a degraded, eluvial surface horizon abruptly over dense subsoil, typically in seasonally waterlogged flat lands; from L. *planus*, flat.

Synonyms. Formerly Planosols were labeled ‘pseudogley soils’. The USDA first used the name planosol in 1938, but in Soil Taxonomy the current USDA usage is to include most of the original planosols in the Great Soil Groups of the albaqualfs, albaquults and argialbolls. In most soil classification systems the term planosol is used.

Definition. Planosols are soils with

1. an eluvial horizon of loamy sand or coarser texture, with a lower boundary (no deeper than within 100 cm of the surface) marked by abrupt textural change to a more clay-rich composition. Stagnic soil properties occur above this boundary, and
2. an absence of albeluvic tonguing.

Parent material. Mostly clayey alluvial and colluvial deposits.

Environment. Planosols are found predominantly on low, flat landforms but can also occur in the border between upland and lowland terrain. On the upland side they may be associated with Acrisols or Luvisols, and on the lowland side with Vertisols. At higher topographic levels Planosols occur also on terraces or plateaus, where they may be associated with Acrisols or other soils with an argic subsurface horizon, or (as in the Ethiopian Highlands) with Vertisols below them in the landscape and Nitisols above.

Distribution. Most of the world’s 130 million ha of Planosols are in subtropical and temperate zones with alternate wet and dry seasons (Figure P43). Major areas are found in Latin America (southern Brazil, Paraguay, Argentina), southern and eastern Africa (Sahel, East and Southern Africa), the eastern United States, Southeast Asia (Bangladesh, Thailand) and Australia.

Characteristics. Typically a Planosol has an ochric or umbric surface horizon with an albic horizon below. The latter lies abruptly over an argic B horizon. In more arid occurrences the surface horizons are poor in organic matter. Planosols in wetter climates are richer in O.M. while in very wet locations, the surface horizon may contain enough to qualify as a dystric histic horizon. The albic horizon is a grayish sand or loam and has a weak structure of low stability. The low permeability of the argic B may result in water stagnation during the wet season, and the consequent development of redox features such as gleying and mottling.

The surface soil of a mature Planosol is strongly, chemically degraded. This manifests itself as a low clay content leading to a low cation exchange capacity, a relatively acid and a low capacity for the retention of soil water. The poor structural stability of the topsoil commonly causes a hard surface in the dry season, which may be temporarily cemented where the texture is silty. This and the compact nature of the subsoil impair the rooting of crops.

Planosols support light forest (shallow rooted species, capable of withstanding both drought and seasonal waterlogging) and/or herbs or grasses. Biodiversity of the soil fauna, and its density, are low.

Origin. A typical Planosol profile has the horizon sequence AEBC, the significant physical feature being the abrupt increase in clay content at the base of the E and top of

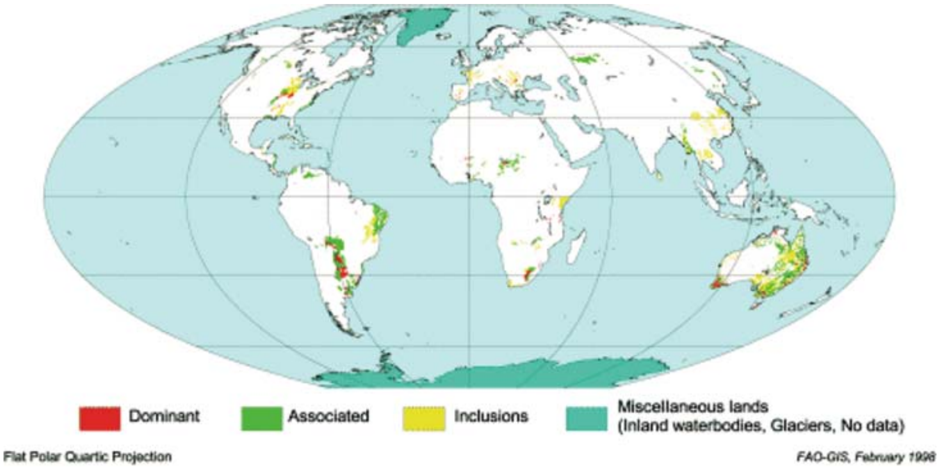


Figure P43 Global distribution of Planosols.

the B horizons. This may be an inherited geological feature resulting from the sedimentary deposition of sandier over more clay rich beds, or it may signal a post-depositional episode of erosion whereby the finer clay fraction has been winnowed out of the coarser material. Alternatively, the abrupt transition may be pedogenetic in origin, and two processes have been invoked. The first is the physical process of eluviation-illuviation: the movement of clay particles in suspension in water from the albic to the B horizon, under the influence of gravity. The second is a physical process proposed by Brinkman (1970) under the name ferrolysis. This is a two-stage reduction-oxidation process, fueled by energy derived from the bacterial decomposition of O.M., and leading to the acidification and destruction of clays.

If a significant population of termites is present, the abrupt textural change cannot develop or persist since the activity of the termites leads to a homogenization of the soil material. Such a process may be capable of transforming a Planosol into a Phaeozem (FAO, 2001).

Use. Planosols are poor soils. In regions with a warm summer season they are mostly under wetland rice. Elsewhere, Planosols are sown to dryland (e.g., fodder) crops or used for extensive grazing. Many Planosol areas are not used for agriculture.

Otto Spaargaren

Bibliography

Brinkman, R. 1970. Ferrolysis, a hydromorphic soil forming process. *Geoderma* **3**: 199–206.

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science*. 2nd edn. Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World*. Heidelberg, Berlin: Springer-Verlag. 130 pp.

Cross-references

Acid Soils
Albeluvisols
Biomes and their Soils
Eluviation
Ferrolysis
Classification of soils: World Reference Base (WRB) for soil resources

PLANT NUTRIENTS

Substances plants require for successful growth and completion of their life cycles are referred to as *plant nutrients*. They consist of oxygen, carbon dioxide, water, and various mineral elements. Some nutrients are absorbed by plants in their elemental forms, and others as various compounds.

Essential elements

Definition of essentiality

The following criteria for the essentiality of an element are generally accepted by the scientific community (Arnon and Stout, 1939):

1. the plant cannot complete its life cycle in the absence of the element;
2. the function of the element must be specific, and no other element can wholly substitute for it;
3. the element must be directly involved in the nutrition of plants as a constituent of a metabolite, a cofactor of an enzymic reaction etc. A certain element may replace an essential element in some functions and may even be more efficient. Nevertheless, it is not considered essential, because the plant can fulfill its life cycle in its absence. It is also clear from this definition that non-essentiality can never be proven, since a potential element might always be present in small quantities that are beyond detection by available analytical methods.

Essential elements

The 16 elements listed in Table P11 have been shown to be essential for the growth of higher plants. Some mineral elements (nitrogen, potassium, phosphorus, calcium, magnesium and sulfur) are required in rather large amounts and are therefore called *macronutrients*. Others (chlorine, boron, manganese, iron, zinc, copper, and molybdenum) are required in relatively small amounts and are referred to as *micronutrients*, *trace elements* or *minor elements*. The optimum levels of individual nutrient elements in plants have a wide range. On an

Table P11 Elements essential for plant growth

Element		Atomic number	Atomic weight	Principal forms for uptake	Plant concentrations		
					%	µMol g^{-1}	Range %
Macronutrients							
Hydrogen	H	1	1	Water	6	60 000	
Carbon	C	6	12	Air-CO_2 (Soil-CO_2)	45	40 000	
Oxygen	O	8	16	H_2O, O_2,	45	30 000	
Nitrogen	N	7	14	NH_4^+. NO_3^-	1.5	1 000	0.5–5
Potassium	K	19	39.1	K^+	1.0	250	0.5–5
Calcium	Ca	20	40.1	Ca^{2+}	0.5	125	0.005–5
Magnesium	Mg	12	24.3	Mg^{2+}	0.2	80	0.1–1
Phosphorus	P	15	31	$H_2PO_4^-$ (HPO_4^{2-})	0.2	60	0.1–0.5
Sulfur	S	16	32.1	SO_4^{2-}	0.1	30	0.05–0.5
Micronutrients					µg g^{-1}		µg g^{-1}
Chlorine	Cl	17	35.5	Cl^-	100	3	100–10 000
Boron	B	5	10.8	H_3BO_3	20	2	2–100
Iron	Fe	26	55.9	Fe^{2+} (Fe^{3+})	100	2	50–1 000
Manganese	Mn	25	54.9	Mn^{2+}	50	1	20–200
Zinc	Zn	30	65,4	Zn^{2+}, Zincate	20	0.3	10–100
Copper	Cu	29	63.5	Cu^{2+}	6	0.1	1–20
Molybdenum	Mo	42	96	MoO_4^{2-}	0.1	0.001	0.1–10

equivalent basis, the ratio is about 1 for molybdenum and 60 million for hydrogen (Epstein and Bloom, 2005; Gauch, 1972). Lower plants (algae, fungi, bacteria) seem to have different nutritional requirements. Present evidence suggests that not all 16 elements essential for higher plants are required by lower forms. For example, it has not been possible to demonstrate that lower plants generally need boron. Moreover, the element calcium, which is a macronutrient for higher plants, becomes a micronutrient for many lower forms.

Beneficial elements

Elements capable of stimulating growth and development even in presence of adequate supplies of essential elements are called *beneficial* or *functional* (Asher, 1991). It is possible that some of these elements might some day be recognized as essential as analytical and purification techniques improve. *Sodium* seems to be necessary for some halophytic plants such as the salt bush (*Atriplex vesicaria*) (Brownell, 1968) and some bluegreen algae (*Anabaena cylindrica*). It is not certain if sodium is generally essential for C4 plants. Stimulating effects have been reported for many plant species, and in some cases such as sugar beet it may even be profitable to use Na fertilizers. Beneficial effects of *silicon* have long been known. This element is definitely essential for diatoms. It strengthens cell walls in higher plants and confers resistance to fungal diseases, insect pests, manganese toxicity, salinity and lodging. Rice and *Equisetum* show specific leaf symptoms in low-Si cultures. Sugarcane suffers from a reduction of growth and from leaf freckles on soils low in extractable Si. Fertilization with Si compounds relieves this problem (Fox et al., 1967). No cases of *aluminum* essentiality are known. Aluminum reduces the uptake of certain elements such as copper or zinc; this is beneficial if these ions are present in toxic concentrations. It is a constituent of the blue pigment in *Hydrangea*. Some plants like tea (*Camellia sinensis*) accumulate large quantities of Al. Stimulatory effects of Al have been reported for tea as well as for some non-accumulating plant species. Brown et al. (1987) observed that grains of barley containing virtually no nickel did not germinate and that the% germination increased as the nickel concentration in grains rose to 100 ng g^{-1}. Such data require that in future nickel be included in the list of essential elements. It has already been demonstrated that urease of a number of sources was a Ni-containing enzyme (Walker et al., 1985). *Cobalt* is essential for the growth of at least some nitrogen-fixing microorganisms (e.g., *Rhizobium* in legumes and *Actinomycetes* in *Alnus*), and the requirement seems to be higher when the organisms are actually fixing nitrogen than when they are relying on an external source of bound nitrogen such as NH_4^+ (Kliewer and Evans, 1963). Some stimulation of growth on higher plants, non-legumes such as *Hevea*, *Triticum* or legumes in the absence of biological nitrogen fixation (clover), has been reported but no proof of essentiality has been forwarded as yet. Although *selenium* can be accumulated to very high levels in accumulator plants there is no evidence that it is essential. Broyer et al. (1972) demonstrated a stimulation of plant growth by selenium in the presence of toxic levels of phosphates. At normal phosphate concentrations selenium had no effect. A number of other elements have been shown to be essential or beneficial in specific cases. Iodine is essential for some marine algae, *vanadium* for some freshwater algae. Stimulation with halides other than Cl have been reported and more research should be conducted on *titanium*, *chromium*, *arsenic* and perhaps even *lanthanum* and *cerium*, the latter two being widely used as fertilizers in China.

Essential elements in animals

Plants stand at the beginning of the food chain and their composition is relevant for animals and humans. Some of the elements are not needed by the plants themselves but are essential to animals. Of the 16 elements universally accepted to be essential to plants, 15 are also required by animals. The optimum concentration for plant growth may not necessarily correspond to the best supply for animals. Molybdenum, for example can cause toxicity problems in animals at levels at which the plant is not injured. Deficiency problems in animals are usually corrected by supplementing feed sources with additional mineral nutrients rather than by fertilizing soils (see *Fertilizers, inorganic*). Until recently, *boron* was believed to be essential only for plants and not for animals. However, Nielsen (1986) found that boron might be essential in regulating parahormone activity. Animal scientists are faced with much greater difficulties in investigating essentialities, because complicated feeds have to be purified, whereas in plant nutrition it is sufficient to refine water and some inorganic nutrients. In addition to the essential plant nutrients, the animals and humans require *sodium*, *iodine*, *chromium*, and *selenium*. There is also strong evidence for an essentiality of *arsenic*, *nickel* and *silicon*. *Boron*, *lithium*, and *vanadium* might also be essential, whereas *fluorine* is probably non-essential in spite of its beneficial effects. The elements *bromine*, *cadmium*, *lead*, and *tin* are not considered essential today although they had previously been on the list.

Minimum requirement for plant growth

Figure P44 shows what is essential for plant growth: (*a*) an adequate light source for energy and for certain regulatory actions, (*b*) CO_2 for photosynthesis, (*c*) oxygen for respiration, (*d*) water, and (*e*) essential mineral nutrients. The solid phase of the soil is not essential, but its importance as a matrix for pores and as a storage for nutrients cannot be overemphasized (see *Soil Fertility*).

Historical development of current knowledge

Ancient and Medieval periods

Scholars of the classical period in Greece were very interested in and puzzled by plant nutrition. Theophrastus (372–287 B.C.), for example, devised a classification of plants and suggested the use of manures to improve poor land. Growing of legumes and the use of saltpeter (KNO_3) were also practiced. Existing knowledge of farm management, including plant nutrition, was summarized by Columella (ca. A.D. 60) in a book that was relied upon for many centuries and was a source of information for later writers as well. Much of the information assembled by Columella was restated and expanded by an Italian, Peter Crescentius (1230–1307) in a book that was also a prime guide for several centuries.

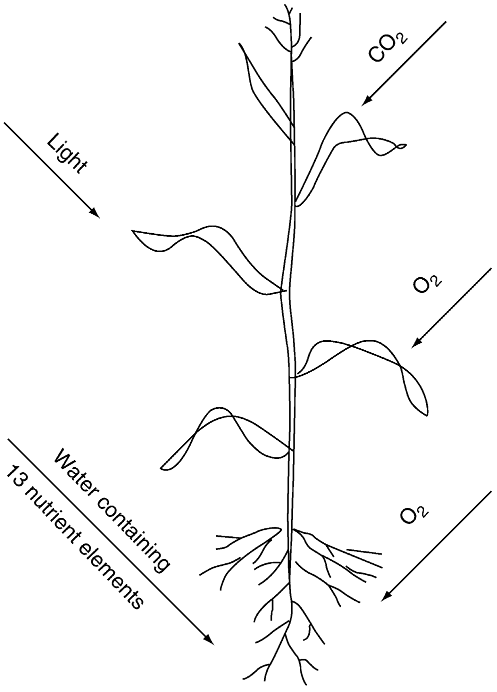


Figure P44 Conditions, which must be met for growth and development of higher plants: a suitable source of light, presence of carbon dioxide and oxygen, presence of water containing the essential nutrients.

The period of 1500 to 1800

During these three centuries, numerous investigators searched for the "principle of vegetation". Discoveries were also made of the chemical and physiological bases of plant growth. As early as 1563, Palissy reported that salts were taken up by plants and returned to the soil in the form of ash, but his findings were not accepted. Water, potassium nitrate, and other substances were at one time or other considered to be the "principle of vegetation". Gradually, experiments demonstrated that plants require several substances, but former beliefs disappeared slowly. In the early part of the nineteenth century, for example, Thaer, Davy, and Berzelius still held that plants fed on the humus in soils (Gauch, 1972; Russell, 1973).

Founding and growth of agricultural chemistry

Boussingauit (1802–1887) showed in pot experiments that the dry weight of growing plants was much higher than the loss of soil organic matter. Plants must use something other than humus. It remained for Liebig (1803–1873), however, through his trenchant and sarcastic writing, to discredit the theory of humus as plant food and to gain acceptance of ideas formulated much earlier by de Saussure and others, namely, that carbon dioxide supplies carbon and oxygen, water supplies hydrogen and oxygen, the air supplies oxygen and that all other nutrients were derived from the soil. The needs of non-leguminous plants for a soil source of nitrogen were established in long-time experiments at Rothamsted in England. Fixation of gaseous nitrogen in root nodule bacteria was discovered as late as 1886 by Hellriegel. A few years earlier it had been learned that oxidation of ammonia to nitrite and then to nitrate was mediated by bacteria (Russell, 1973). By the end of the nineteenth century, 10 elements (carbon, oxygen, hydrogen, nitrogen, phosphorus, sulfur, potassium, calcium, magnesium and iron) were known to be essential for plant growth. Six more, all micronutrients, were added in the twentieth century (manganese, boron, zinc, copper, molybdenum and chlorine) (Glass, 1989). Knowledge of the physical chemistry of soils, including ion exchange and the fixation of nutrient elements, has increased greatly during the twentieth century. Mechanisms of nutrient transport in soils and plants and of nutrient absorption by plants have been subjects of intensive research.

Plant composition

The composition of plants differs with growing conditions, especially the nutrient supply. The composition also differs among plant parts, plant species and varieties, leaf position, and even time of the day (Table P12). For example, water contents can range from less than 10% in some seeds to more than 90% in some roots and leaves. Ash contents of plants tend to vary with the supply of nutrients in the soil. Thus, halophytes characteristically have high ash contents, because they grow on saline soils. On a dry-weight basis, ash contents are relatively high in leaves, moderately low in seeds, tubers and roots, and very low in wood. Young leaves are usually high in most

Table P12 Examples of plant composition. FW = Fresh Weight; DW = Dry Weight

Plant/Organ	Water content (% FW)	Ash (% DW)	N (% DW)	P	K	Ca	Mg	S	Fe (mg kg^{-1} DW)	Mn	B	Zn	Cu	Mo
Cereals straw	75–90	6–11	0.5	0.1	1	0.3	0.1	0.07	50	40	5	30	5	0.2
Cereals grains	12–15	1–5	2	0.4	0.5	0.05	0.15	0.02	100	40	5	30	5	0.5
Cereals leaves	75–90	5–14	2–5	0.3–0.6	3–6	0.3–1	0.15–0.35	0.17	200	25–150	5–12	20–70	5–15	0.1–0.3
Potato leaves	75–90	6–14	5–6.5	0.36–0.6	5–7	0.6–2	0.25–0.8	0.33	180	40–200	25–70	20–80	7–15	0.2–0.5
Potato tuber	75	2.2–5.8	1.5	0.2	2	0.05	0.1	0.1	40	10	7	15	5	0.3
Sugar beet top	2–7	8–30	3	0.3	3	3	1	0.3	100	60	50	50	10	1
Sugar beet root	75–80	2–6.6	0.8	0.22	1.5	0.2	0.2	0.06	25	20	30	25	7	1
Alfalfa top 15 cm	75–90	6–14	4	0.45	3.2	1.7	0.55	0.27	90	90	50	50	10	1.2
Needles spruce			1.4–1.7	0.1–0.2	0.5–1	0.4–0.7	0.1–0.2			50–500	10–30	15–50	5–12	0.04–20
Wood spruce	40	0.15–0.2	–	0.002–	0.025	0.05–0.005	0.04	0.09	5	–	–	–	–	–

Table P13 Compositions in the major plant nutrients of the lithosphere[a], ocean water[b], soil solution[c], food and forage plant organs[d], and the human body[b] (all values in g kg^{-1})[e]

Element	Lithosphere	Ocean	Soil solution	Wheat flour (whole)	Potato tuber	Tomato fruit	Forage grasses	Human body
Nitrogen			0.110	21	15	30	26–40	79
Phosphorus	0.5		0.00008	3.7	2	5	3.5–6	28
Potassium	19	0.4	0.045	3.2	20	55	20–30	9.5
Calcium	50	0.4	0.080	0.4	0.5	2	6–15	50
Magnesium	23	1.3	0.075	1.2	1	3	2–6	1
Sulfur		0.9	0.040	1.2	1	3.5	3.3	6.5

[a] From Scheffer and Schachtschabel (2002).
[b] Calculated after Loffler and Petrides (1988), aussuming a water content of 60% for a human body.
[c] Estimated from Asher (1978), Reisenauer (1966).
[d] Estimated from Bergmarm, 1983, Schilling (1990) and others.
[e] Dry weight per kg water.

nutrients, whereas old leaves contain more of the immobile elements such as calcium, boron and iron. Grains are high in nitrogen and phosphorus; roughly half of the amounts found in the wheat plant are present in seeds. Dicotyledons require more boron than monocotyledons.

Table P13 compares the dry matter composition of a human (Loffler and Petrides, 1988) body with some food sources for humans and animals, typical soil solution concentrations and the Earth's crust. Although plants take up nutrients from the soil solution the relative composition of the two are different and again the composition of the animal body does not reflect that of its feed, namely the plant. Of course the plant supplies building material and energy to the food chain and different compositions would be expected. Moreover, plant and soil compositions are highly variable (see *Soil Fertility*).

Some plants accumulate very large amounts of specific elements, which can result in problems if the plants are being consumed by animals or humans. The content of molybdenum in healthy plants may be excessive and cause disease in animals. The content of fluorine is 0.2 to 2 mg kg^{-1} (DW) in most plants. Yet black tea may contain 100 to 200 mg kg^{-1}. Crop plants generally contain only 0.1 to 2 mg kg^{-1} of selenium, whereas species of certain wild plants such as *Astragalus racemosus* and *Stanleya bipinnata* may contain up to 15 000 mg kg^{-1}. These "converter plants" are able to use forms of selenium not available to other species. After such plants die and decay, the selenium is much more available to other species and can then cause diseases in animals such as the "alkali" disease.

Plants take up solutes from the soil irrespective of actual needs. Hence plant composition does not reflect metabolic needs, nor does it reflect directly the composition of either the soil as a whole or of the soil solution at any given moment.

Nutrient transport and uptake

Water and most nutrients are taken up by the roots of plants. Exceptions among nutrient elements are carbon and part of the oxygen, which are absorbed by leaves. The efficiency of nutrient uptake depends on the root morphology and physiology. The entire root surface of a single plant can reach hundreds or even thousands of square meters, considering the major roots, rootlets, and root hairs. To be absorbed by a leaf cell, nutrient elements in soils must first reach the root in a form suitable for uptake, then cross the outer or free space, and move radially across the root into a conductive tissue, the xylem in which they are transported upward (Figure P45). In the leaf, the nutrient enters the cell wall region (the apoplast) and is transported through the plasmamembrane into the cell. Within the cell, various additional systems may be traversed (cytoplasm, membranes of organelles).

Laws governing transport

There are three fundamental types of transport (Mitchell, 1961), namely "*diffusion of the chemical species in a fluid or solid relative to the local center of gravity according to thermodynamic laws, or, in other words, by thermally activated bounces down an electrochemical gradient; convection of the chemical species with the local center of gravity of a surrounding fluid, moving according to hydrodynamic laws, or in other words, by carriage with a fluid moving down a hydrostatic pressure gradient; propulsion of the chemical species with the local center of gravity of a solid, according to the laws of mechanics*." Propulsion plays no role in nutrient and water transport in the soil–plant system, and, therefore, we are concerned here with diffusion and convection only and with combinations of the two. This includes active transport, carrier mediated transport etc. Diffusion is described by Fick's Laws:

- for steady state (Fick's First Law)

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -D\frac{\mathrm{d}c}{\mathrm{d}x}$$

- for a transient state (Fick's Second Law)

$$\frac{\delta c}{\delta t} = \frac{\delta}{\delta x}\left(D\frac{\delta c}{\delta x}\right)$$

for constant D

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta x^2}$$

Convection, in a simple form, can be described

for steady state: $q = \text{const.}\dfrac{\mathrm{d}p}{\mathrm{d}x}$

for transient state: $\dfrac{\delta\theta}{\delta t} = \dfrac{\delta}{\delta x}\left(D_0\dfrac{\delta\theta}{\delta x}\right)$

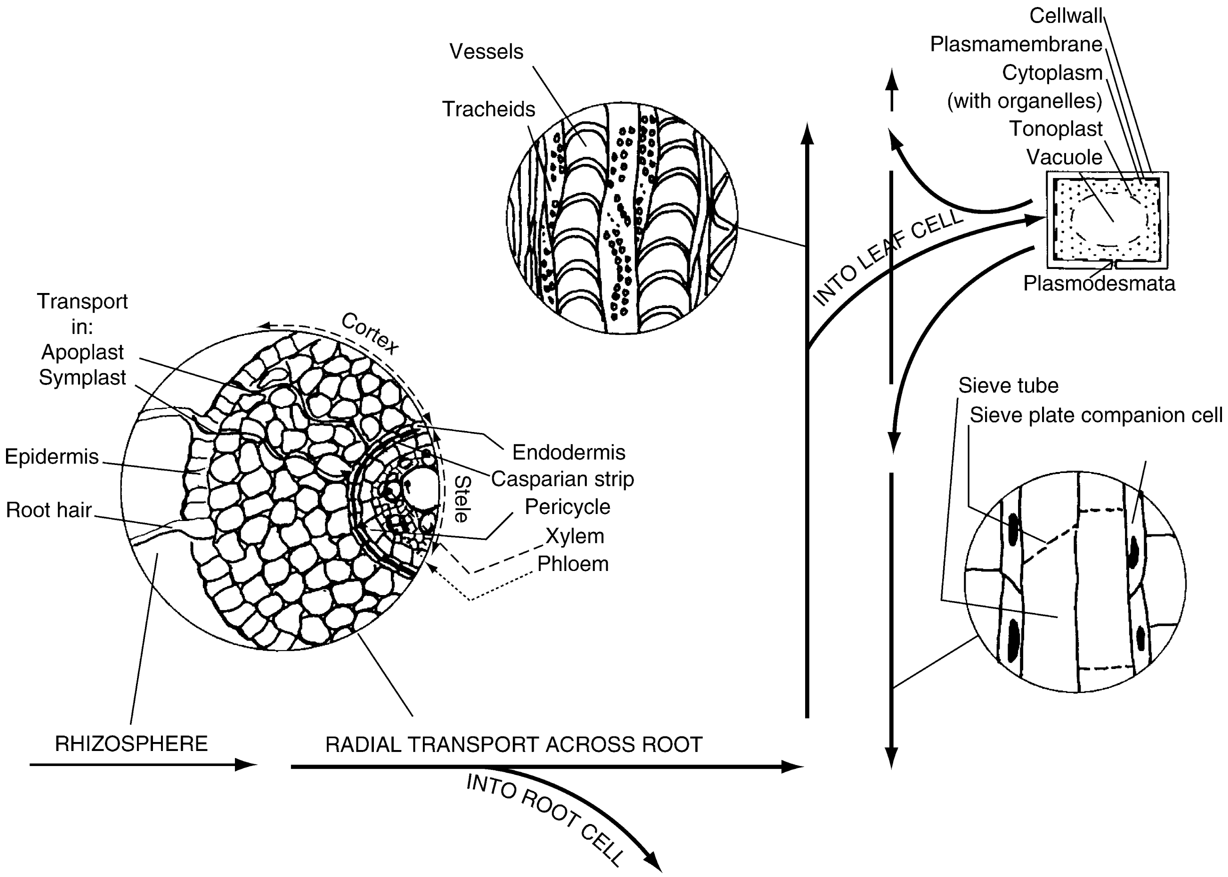


Figure P45 Schematic representation of the transport of nutrients across the rhizosphere, the root, in the xylem and into leaf cells. Mobile elements are retranslocated in the phloem. The apoplast of the root cortex may correspond to the free space.

where n is the substrate of concentration c that is transported in the (horizontal) direction x, t the time, D the diffusion constant, q the rate of solution flow, D_0 the diffusivity (equal to $-K(\delta P/\delta\theta)$), θ the water (solution) content, P the pressure, K the hydraulic conductivity.

For water and solute fluxes in plants, two particularly valuable equations have been derived from thermodynamics of irreversible processes:

$$J_v = L_p(\Delta P - \sigma\Delta\Pi)$$

and

$$J_s = \omega\Delta\Pi + J_v(1 - \sigma)C_s + J^*$$

(J_v the volume flow, J_s the solute transport, L_p the hydraulic conductivity, a the reflection coefficient with values between -1 and $+1$, ΔP and $\Delta\Pi$ the hydrostatic and osmotic pressure differences, ω the solute permeability, c_s the mean solute concentration, e.g., of two solutions between which the transport occurs, and J^* the solute transport not linked directly to water transport sometimes referred to as an active transport of solutes). The equation for J_v, shows that hydrostatic and osmotic gradients are usually not able to induce solution flow to the same degree. Solution may flow along a decreasing hydrostatic gradient and against a much larger osmotic gradient, i.e., in upward direction of the total water potential gradient. The equation for J_v holds for simultaneous diffusive and convective flows, and the steady state diffusion and convection are contained in it as special cases.

Transport across the rhizosphere to the plant roots

Movement of the soil solution to the surface of a root occurs by diffusion and mass flow. Dominance of one mechanism or the other depends on the given situation, i.e., on the ion species, the rate of its uptake, the rate of water flow, and various soil characteristics. Mass flow prevails for nutrients that are present in relatively high concentrations (calcium, magnesium) and for those that are neither exchangeable nor stored otherwise except in the soil solution (NO_3). In contrast, transport by diffusion is more important for ions present in low concentrations such as phosphates and iron. Because roots continue to grow and thus penetrate new regions of the soil, changes in actual possibilities for absorption are continuous. During the transport across the rhizosphere, ion exchange processes occur, and nutrients may be dissolved through the action of exudations of roots and microorganisms. The composition of the soil solution in the rhizosphere (a boundary zone at the root surface) differs from the bulk soil solution, a fact that limits interpretations of soil analyses with respect to plant nutrition. Mineral nutrition, especially that of phosphorus, is also affected by the presence of mycorrhiza.

Transport in the free space

The free space has mainly been studied as a compartment (volume), and few data are available to characterize transports. A fraction of ions taken up can easily be washed out of roots, and further fractions are easily removed through ion exchange processes, especially with cations. It is assumed that these easily removable nutrients did not enter cells across the plasmamembrane and are present in the cell walls, i.e., in the "outer" or "free" space of the root. The *water free space* refers to the region from which nutrients are readily leached, the *Donnan free space* to the region from which nutrients are removed by ion exchange. The extent of the respective free spaces is calculated by dividing the quantities of removed ions by the external concentration. The results are referred to as magnitudes of *apparent free spaces* since the values do not represent true volumes. Values reported in the literature range between 0.1 to 0.15 ml per gram fresh weight of roots (Epstein and Bloom, 2005). The transport across the free space probably resembles that across the rhizosphere. In addition to ion exchange, complexing and chelation of certain nutrients at fixed sites may play a more important role than in soils, whereas dissolution of nutrients from the solid phase will be negligible.

Radial transport across roots

Diffusion and convection are again the transport mechanisms. There are a number of different pathways, all of which are probably used to some extent. Which is most important is not clear, and views change rapidly (Oertli, 1991). One path, the apoplastic, occurs in cell walls only. Another path requires uptake into the cytoplasm and transfer from cell to cell via plasmodesmata (the symplast) or alternately transfer from cell to cell across the cell wall. Finally, the vacuole may participate in nutrient transports, and transfers between cells may occur again via plasmodesmata or through cell walls. There is strong evidence that in the endodermis of the roots all substances have to enter the cells, thus giving the plant an opportunity to exert some metabolic control on the transport.

Xylem flow. In a transpiring plant nutrients are rapidly flushed out of the root xylem, and the solution will always be dilute. In the absence of transpiration, as occurs during a humid night, nutrients accumulate in the root xylem, increasing the osmotic pressure which stimulates water uptake from the soil, resulting in an increase in the hydrostatic pressure which is the cause of root pressure and leads to exudations of solution from the leaves (guttation, bleeding). The flow in the xylem is essentially a convection along a gradient of hydraulic heads.

Transport in the leaf apoplast

What has been said for the root apoplast is also valid here.

Transport into cells

This transport is usually designated "short range" in contrast to "long range" which describes the transport from the soil across the plant into the leaf. It is characterized by a transport across an outer membrane, the plasmamembrane, and possibly by other membrane transports into organelles including across the tonoplast into the vacuole.

Kinetics of membrane transport

Numerous short-term absorption experiments have shown that nutrient uptake obeys saturation kinetics (Figure P46) when the uptake during a given time is plotted over the concentration

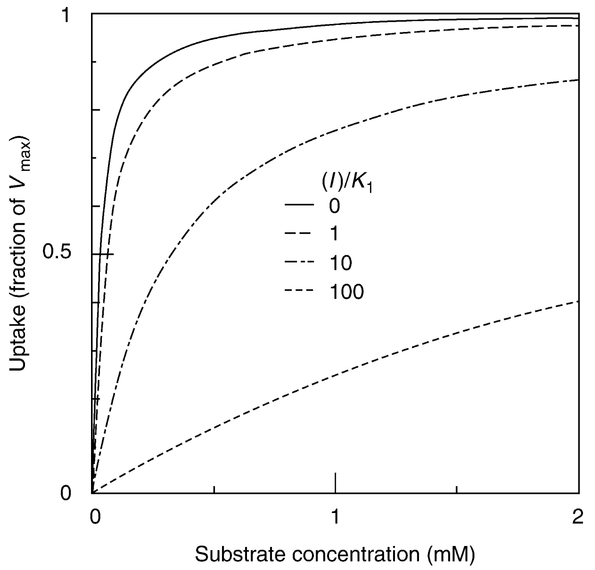


Figure P46 Absorption isotherms (plot of uptake rates versus concentration of substrate in the external solution) in absence and in presence of a competitor *I* at three concentrations ($I/K = 1$, 10, and 100).

in the root medium. The curve can be described by an equation that is mathematically equivalent to Michaelis-Menten enzyme kinetics or to a Langmuir adsorption isotherm. The model assumes the formation of a carrier-substrate (carrier-nutrient) (*CS*) complex between substrate *S* and carrier *C* at the outer surface of the membrane and diffusion of this complex to the inner surface of the membrane where it again dissociates. The substrate can cross the membrane only as a complex, and no reverse transport occurs:

$$S + C \leftrightarrow CS \rightarrow S + C^1$$

Figure P46 is then closely described by

$$v = \frac{V_{\max}[S]}{K_m + [S]}$$

where v is the rate of uptake, $V_{\max}$ the highest possible uptake rate, $[S]$ the substrate concentration, K_m a constant analogous to the Michaelis-Menten constant and C the carrier. In the presence of a competitor I one has:

$$I + C \leftrightarrow CI \rightarrow I + C$$

and for the uptake rate

$$v = \frac{V_{\max}[S]}{[S] + K_m\left[1 + \frac{[I]}{K_I}\right]}$$

where I stands for the competitor and K for its Michaelis-Menten constant. The treatments of the two substances are equal, and each of them can be designated substrate or inhibitor.

Numerous reports on K_m determinations have appeared. Most values fall into the narrow range of 0.01 to 0.03 mM (Epstein and Bloom, 2005). The good fit between Michaelis-Menten kinetics and observed data holds only for the range of low concentration up to a few tenths of a mM. Beyond that concentration deviations become clearly noticeable, and an increased uptake is observed at higher nutrient supply concentrations. This phenomenon has been explained by a multiplicity of carriers functioning simultaneously but having different K values (Epstein and Bloom, 2005) or by changes in phase of either the carrier or the membrane with a change in the external solution concentration (Nissen et al., 1980). The good agreement in the low concentration range between observed data and the mathematical treatment, with and without competitors, is not proof for carriers; the data could equally well be explained by diffusion through a porous membrane. Better evidence is obtained from demonstrations of counter current phenomena. A simple version of the model assumes simultaneous influxes and effluxes of a carrier. Carrier complex formations and dissociations, obeying Michaelis-Menten kinetics, occur at the outer (o) and inner (i) sides of the membrane:

$$S_o + C_o \leftrightarrow CS_o \text{ diffusion } CS_i \leftrightarrow S_i + C_i$$

The rate-limiting step is assumed to be the diffusion step:

$$v = -D(CS_o - CS_i)$$

The analogy to enzyme kinetics is no longer present. Substituting CS_o and CS, one obtains in the presence of a competitor:

$$v = K\left[\frac{[S_o]}{[S_o] + K_m\left[1 + \frac{[I_o]}{K_I}\right]} - \frac{[S_i]}{[S_i] + K_m\left[1 + \frac{[I_i]}{K_I}\right]}\right]$$

According to this equation, an inward transport is possible, even if $[S_o] < [S_i]$, i.e., a transport against the decreasing free energy gradient of the substrate S is possible, if the concentration of the inhibitor I at the inner side of the membrane is sufficiently high. It can be shown that in this case the inhibitor is transported from the inner to the outer side (Oertli, 1964). The energy for pumping S uphill in the energy field originates from the downhill transport of I in an outward direction. An outward flow of hydrogen ions generated within the cell could, for example, implement an uphill inward transport of nutrient cations such as potassium. This counter current transport model has been much investigated by animal and human physiologists but largely neglected in plants. This concept is also applicable to channels in which a substrate leaps from one fixed carrier site to another.

In recent years evidence has accumulated that hydrogen ions are generated through H^+-ATPases and are involved in ion transport. H^+-ATPases are enzymes that couple the hydrolysis of ATP to a transmembrane movement of protons (Serrano, 1989). These ATPases are believed to be located in membranes and they show some specificity for particular membranes. The free energy, which becomes available from the dissociation of ATP, is used to establish a proton gradient. This is the reverse reaction of the chemiosmotic theory in which a proton gradient is used to synthesize ATP. This proton gradient can be used for a counter transport another positive ion (an antiport transport). In addition the electrical potential difference which results from the separation of charges by the action of the ATPase can drive positively charged ions through specific channels in the direction of a decreasing electrochemical potential gradient (a uniport transport) (Flowers and Yeo, 1992, Hedrich and Schroeder, 1989). Moreover the proton or another ion of the same charge can be taken up together with an anion (a symport transport). Thus, the hydrogen ion assumes a central role in ion transport across plant membranes. Much progress is currently being made through "patch clamping", a method that permits the measurement of electrical currents passing through single channels. These channels can be opened and closed, i.e., they are gated, and their permeability is variable. The gating is controlled by the magnitude of the transmembrane electrical potential difference, by chemicals such as plant hormones, perhaps by turgor pressure and it may be intimately connected with many physiological processes such as stomatal regulation, cell elongation, the homeostasis of cellular nutrient concentrations and of turgor pressure. Recently, an attempt was made to explain saturation kinetics of nutrient uptake by changing electrical potential differences across membranes causes by ion fluxes at different external concentrations (Schroeder and Fang, 1991). Many aspects of this relatively new field of research are still poorly understood. The molecular mechanisms causing the specificity of channels remain unknown. If channels contain electrical charges (Serrano, 1989), interactions between ions and channels must be expected and the transport kinetics would again involve fixed carriers. A central and still unsolved problem is the mechanism of functioning of the proton pump. During the establishment of a proton gradient through hydrolysis of ATP a scalar property (the chemical reaction) is linked to a vectorial property (the proton gradient). The mechanism of this link must be explained without violating the Curie principle. Suggestions have been made by Serrano (1989) and Briskin and Hanson (1992).

Energetics of membrane transport

The criterion whether a transport is uphill or downhill is the total Gibbs free energy gradient (gradient of free enthalpy in some countries). An uphill transport, often called *active*, requires an input of metabolic free energy. Considering concentration and electrical potential differences, one has:

$$\Delta\mu = \mathrm{R}T \ln\frac{C_i}{C_o} + zF\Delta E$$

where μ stands for the chemical potential, R the universal gas constant, T the absolute temperature, z the valence of an ion, F the Faraday and ΔE the electrical potential difference, 'o' for the outside and 'i' for the inside of a cell. (The differences here are taken inside minus outside). A $\Delta\mu = 0$ indicates equilibrium, a $\Delta\mu > 0$ a higher internal chemical potential. An uptake taking place with a higher internal chemical potential is, by definition, *active*. In order to determine whether a transport is active or passive, the electrical and the concentration differences must be measured. For example, Higginbotham et al. (1967) measured electrical potential differences of –110 mV between root cells of pea and external medium and –84 mV between oat roots and their medium. The external concentrations were 1 mM in KCl, $Ca(NO_3)_2$, and NaH_2PO_4. From these data they calculated a theoretical internal concentration at equilibrium. The results (Table P14) show that no equilibrium was present except perhaps with potassium in pea roots, that anions must have been taken up actively and that the cations Na, Ca, Mg were either transported actively in an outward direction (after a passive influx) or penetrated the roots extremely slowly.

Numerous models for carrier and active transport have been suggested in the literature, but the compounds have not yet

Table P14 Test for active ion transport

Ion	Pea roots ($\Delta E = -110$ mV)		Oat roots ($\Delta E = -84$ mV)	
	Calculated (mM)[a]	Measured (mM)	Calculated (mM)[a]	Measured (mM)
K^+	74	75	27	66
Na^+	74	8	27	3
Mg^{2+}	2 700	3	350	17
Ca^{2+}	10 800	2	1 400	3
NO_3^-	0.027	28	0.076	56
Cl_3^-	0.014	7	0.038	3
$H_2PO_4^-$	0.014	21	0.038	17
SO_4^{2-}	0.000094	19	0.00071	4

[a] Calculated hypothetical concentration assuming equilibrium between external and internal concentration at the measured electrical potential difference.

been isolated. The input of energy could occur in various ways, namely counter current transport has already been discussed above. Active transport does not violate thermodynamic laws, and the overall process can always be reduced to a combination of individual processes, each of them occurring in a downhill direction.

In concurrence with active transport, the requirement for energy has been clearly established:

- Nutrient uptake by roots requires oxygen. The energy is apparently derived from respiration.
- No oxygen is required in green leal tissues, because photosynthetic energy can be utilized directly. However, in this case light is required.
- Inhibitors of the tricarbonic acid (Krebs) cycle and uncouplers in respiration also inhibit salt uptake.
- A high sugar content in roots stimulates nutrient uptake.

Additional characteristics of membrane transport of nutrients

Selectivity. Ions are taken up at different rates. If a cation is taken up faster than an anion, electroneutrality in the soil solution is maintained by an increase in protons. An excess anion uptake leads to a decrease in protons, i.e., a rise in pH. This phenomenon is important when the soil is fertilized with ammonium nitrogen. Most nutrients are then taken up as cations, and the pH of the rhizosphere drops.

The pH *of the solution.* Uptake rates of nutrients are decreased at low and at high solution pHs. At low pH, the decrease is more pronounced for cations, at high pH more so for anions. This indicates possible competition between cations and protons at low pH and between anions and hydroxyl ions at high pH, but all the pH effects cannot be explained by competition.

Temperature effects. A high rate of flow for the absorption process cannot be interpreted as evidence of a metabolic uptake process, because diffusion through a barrier such as a membrane can easily have a high temperature response.

Effect of the counter ion. A counter ion taken up rapidly stimulates nutrient uptake; a counter ion taken up slowly retards ion uptake. For example, potassium as chloride is taken up faster than as sulfate, and chloride is known to be taken up much faster than sulfate. Chloride is taken up more rapidly when associated with potassium than with calcium, the latter being taken up only slowly. This effect seems to be absent at low substrate concentrations.

Organic acids in roots. An excess cation uptake leads to an increase in organic acid anions in roots, an excess anion uptake to a decrease. Malate is often the anion.

The role of calcium. Over certain concentrations ranges of potassium (and other ions), calcium (and other polyvalent cations) stimulates the net uptake (Viet's effect). One explanation may be that ions taken up can again leak out of cells passively. Calcium may affect membrane properties and thus reduce this leakage, resulting in an increased net uptake. Calcium also reduces the injurious effect of low pH, and is suspected to play a role in the proper functioning of potassium and sodium carriers.

Plant species. Uptake characteristics vary with plant species and physiology such as age of the species.

Internal salt concentration. Observed rates of uptake are usually lower in tissues of high solute contents. This may be due to an increased efflux, giving a lower net uptake, an exhaustion of energy required for the uptake and the maintenance of higher internal solute activities or to some regulatory mechanism that senses the high internal concentration and gives a signal for a reduction of the uptake.

Uptake along the root. It is necessary to distinguish between the location of maximum content in the root and the location through which most nutrients pass when translocated into the plant top. The latter process appears to be most important at some distance (2 to 3 cm in barley) beyond the root tip (Wiebe and Kramer, 1954), but it can remain significant over a long distance from the tip. This uptake behavior varies with plant species, ion species, age of plant and other physiological conditions (Marschner, 1986).

Mobility of nutrients after absorption

Some nutrients remain in a tissue such as a leaf after they have been deposited. These nutrients are called *immobile*. Other nutrients are readily removed from a tissue and transported to another. These are *mobile* elements. The efflux from a tissue occurs in the phloem, which, in contrast to the xylem, is a living tissue. The nutrients are classified as follows:

- mobile elements: N, K, Mg, P, S, Cl,
- immobile elements: Ca, B,
- intermediate: Fe, Mn, Zn, Co, Mo.

Non-essential elements such as Sr and Ba are immobile like Ca, while Na, Rb and Cs are mobile. Sr and Cs are of special interest, because they are important fallout products.

Losses of nutrients from plants

Mobile elements can be transported from leaves into roots and returned to the soil. This loss is usually minor. Leaching of leaves by rain and leaf drop, especially by trees in the fall, are major pathways by which losses occur. Some nutrients are lost with guttation fluids and through special salt glands. Many of these nutrients are returned directly to the soil, a process of special importance in many tropical rain forests where relatively small amounts are stored in soils. A different type of loss – not from a plant but from a site – is removal with a crop during harvest or by erosion.

Symptoms of nutrient deficiencies

Plants, which suffer from shortage of an essential nutrient, develop visible symptoms, which are more or less characteristic of the deficiency. However, in the field, many factors such as simultaneous presence of several deficiencies, environmental pollution and plant diseases may interact, and it is difficult and sometimes impossible to identify accurately the problem visually. Symptoms vary with plant species and growing conditions (see special publications for detailed descriptions and color photos: Bergmann, 1983; Sprague, 1964; Wallace, 1961; Bould et al., 1984, Robinson, 1983, 1987). Some aspects of nutrient deficiencies are general for many plant species. Deficiencies of mobile elements almost always start in older leaves from where the nutrient is removed to the actively growing region, whereas deficiencies of immobile elements are observed around the growing points.

Nitrogen. Often a general yellowing of old leaves, blades of cereals tend to be stiff and erect, tip necrosis, in maize extending in basal direction along midrib. Phosphorus. Often purplish discoloration or darker leaves due to anthocyanin formation (purplish discolorations are occasionally observed with other deficiencies [N, B, Mg, Zn]). Stiffness of leaf blades with tips bent outward. First symptoms more often in older leaves.

Potassium. Symptoms first in old leaves: yellowing, followed by necrosis, at tip and margin of leaves. Wilting of foliage, tendency toward lodging of cereals. In some legumes (e.g., clovers) white speckling of leaf blades.

Calcium. Death of growing points and root tips (an immobile element), buckling of stems, dark foliage, shedding of blossoms and buds, water-soaked, discolored areas on fruits (blossom-end rot of tomatoes, peppers, melons; bitter pit or cork spot of apples).

Magnesium. Characteristic interveinal chlorosis, later necrosis of mature leaves. Upward curling of leaves along margins.

Sulfur. Light green to yellow color of young leaves (slow mobility), sometimes affecting the entire plant. Plant spindly and small.

Chlorine. Bronzing of leaves, wilting, chlorosis and even necrosis. Excessive branching of lateral roots. Hardly observed under field conditions.

Iron. Interveinal chlorosis of young leaves, veins remain green. In severe cases, the entire leaf turns chlorotic and changes from yellow to whitish. Leaves of some plants turn necrotic. Injury to terminal bud causes development of shoots from dormant side buds.

Manganese. Interveinal chlorosis in youngest leaves, with gradual color change toward green veins (in contrast to iron deficiency).

Boron. Stunted growth, chlorosis, bronzing, curling and wilting of new leaves, death of terminal bud, cracking of stems and roots.

Zinc. Mottled leaves, interveinal chlorosis, decrease in stem length causing resetting of terminal leaves, dieback of twigs, small leaves ("little leaf disease").

Copper. Wilting, death of leaf tips, dieback of terminal shoots in trees, poor pigmentation, gum formation, e.g., on trunks on almond trees.

Molybdenum. Cupping or rolling of leaves, reduced development of leaf blades (whiptail) in some plants (cauliflower), some symptoms similar to nitrogen deficiency.

Some nutrient deficiencies have been given special names, especially where micronutrients are concerned. Examples are: Fe: lime-induced chlorosis; Mn: grayspeck of oats, mouse ear of pecans; B: heart rot of sugar beet, cracked stem of celery, white top of alfalfa, brown rot of cauliflower; Zn: little leaf and rosette diseases of fruit trees; Cu: exanthema (gums exuded from barks); Mo: whiptail of cauliflower, yellow spot of citrus.

Functions of nutrients

Carbon and hydrogen are present in essentially all organic compounds, whereas oxygen, nitrogen, sulfur and phosphorus are constituents of important metabolites. The major functions of the remaining nutrient elements are as constituents or activators of enzymes. A few elements such as potassium and chlorine play important roles in osmoregulation. Others have buffering effects on pH. The ionic environment also strongly affects the colloidal properties, especially membrane characteristics within the cells of plants. The major functions of nutrients are summarized as follows (Marschner, 1986; Mengel, 1991).

Nitrogen. A constituent of a great number of important compounds such as proteins (e.g., enzymes), nucleic acids, porphyrins (chlorophyll, cytochromes, etc.), also of alkaloids. Nitrate induces the formation of the enzyme nitrate reductase.

Phosphorus. Plays a key role in energy metabolism. Many intermediates in the breakdown of sugars to water and carbon dioxide (in glycolysis) and in the dark reaction of photosynthesis are phosphorylated. Adenosine triphosphate (ATP) functions universally in energy transfer. Phosphorus is also a constituent of hydrogen carriers such as di- and triphosphopyridine nucleotides (NAD, NADP). It is contained in nucleic acids and it is a constituent of phospholipids, which are major constituents of membranes. Phytic acid is a storage form of phosphorus in plants.

Potassium. Not known as a constituent; it contributes to activation of some enzymes, probably through effects on enzyme conformation. Examples are the synthesases: acetyl-CoA-synthesase, NAD-synthesase, and malic enzyme; the dehydrogenases: glycerindehydrogenase, malic acid dehydrogenase, and succinic acid dehydrogenase; and kinases such as pyruvate kinase, fructokinase, and phosphohexokinase. It is required for protein synthesis and for the activation of membrane-bound ATPases. Osmotic effects include a role in operation of guard cells of stomata; a role in opening and closing of leaflets of some plants (nyctinastic and seismonastic movements); perhaps a function in phloem transport; and a role in osmotic adjustment to salinity. Potassium accelerates movement of photosynthates from leaves.

Sulfur. A constituent of the amino acids cystine, cysteine, methionine, homocysteine; of coenzymes thiamine and biotin and of coenzyme A. Formation of disulfide bond

$$-\mathrm{SH} + \mathrm{HS}^- \rightleftharpoons -\mathrm{S}-\mathrm{S}^- + 2\mathrm{H}^+$$

important for tertiary structure of proteins and for redox reactions. Ferredoxins, compounds that function in photosynthesis, contain sulfur. Some special compounds, often volatile and sometimes with disagreeable odors, contain sulfur, e.g., mercaptans in radish roots and onions, disulfides in onions, polysulfides and sulfoxides in garlic and mustard oils.

Calcium. A constituent of phytin and pectin (important for mechanical strength); present in the enzyme amylase and as precipitates (Ca-oxalates, -carbonates, and to a lesser extent as -sulfates and -phosphates). Calcium activates some enzymes (α-amylase, phospholipase, ATPases) and can act as a competitive inhibitor for magnesium. It stabilizes membranes, regulates ion transport mechanisms and is a chemotropic factor in pollen germination. In its absence cell elongation is inhibited, but it stabilizes cell walls. A number of enzymes are inhibited by Ca (hexodiphosphatase, PEP carboxylase).

Magnesium. A constituent of chlorophyll, phytin and pectin. The element is an activator of many enzymes, especially phosphorylating enzymes (connected with energy metabolism), bridging enzymes (synthesis of RNA). It is antagonistic to potassium absorption.

Iron. A constituent of many compounds: iron porphyrins (heme compounds) such as cytochromes, cytochrome oxidases, catalases and peroxidases. The element plays a major role in electron transport through valence change between di- and trivalent forms. Hemoglobin plays a role in biological nitrogen fixation by root nodule bacteria. Non-porphyrin compounds are ferredoxin and ferritin. Iron is an activator of enzymes such as aconitase.

Manganese. An activator of many enzymes, similar to magnesium for enzymes in energy metabolism (phosphorylation), arginase, in photosynthesis, formation of chlorophyll, in a superoxide dismutase. Role in synthesis of proteins, carbohydrates, lipids, and synthesis of vitamin C.

Boron. Functions not well understood. Participation in carbohydrate metabolism and transport and interaction with growth hormones has been suggested. Stimulates germination of pollen and tube growth.

Zinc. A constituent of some dehydrogenases (alcohol dehydrogenase, lactic dehydrogenase), superoxide dismutase (in association with Cu); the element also functions in the formation of auxins, in carbonic anhydrase and in peptidases.

Copper. A constituent of enzymes (oxidases, functions through change in valence) such as laccases, phenolases, ascorbic acid oxidases and cytochrome oxidase, superoxide dismutase, amine oxidases. It is also a constituent of plastocyanin, a compound that functions in photosynthetic electron transport. Copper may also function in nitrite reductase, and it may have an effect on lignification.

Molybdenum. A constituent of enzymes involved in nitrogen fixation (nitrogenase) and nitrate reduction (nitrate reductase). It functions through a change in valence.

Chlorine. This element functions in photosynthesis and as an activator of enzymes involved in splitting water. It also functions in osmoregulation of plants growing on saline soils.

Cobalt. Required for biological nitrogen fixation and a constituent of vitamin B_{12}.

J. J. Oertli

Bibliography

Arnon, D.I., and Stout, P.P., 1939. The essentiality of certain elements in minute quantity for plants with special reference to copper. *Plant Physiol.*, **14**: 1460–1470.

Asher, C.J., 1978. Natural and synthetic culture media for Spermatophytes. *CRC handb. Ser. Nutr. Food, Sect.*, **G3**: 575–609.

Asher, C.J., 1991. Beneficial elements, functional nutrients, and possible new essential elements. In Mortvedt, J.J., Cox, F.R., Shuman, L.M., and Welch, P.M., eds., *Micronutrients in Agriculture,* 2nd edn. Madison, WI: Soil Science Society of America, pp. 703–723.

Bergmann, W., 1983. *Ernahrungsstbrungen bei Kulturpflanzen.* Stuttgart: Gustav Fischer Verlag, 614 pp.

Bould, C., Hewitt, E.J., and Needham, P., 1984. *Diagnosis of Mineral Disorders in Plants.* New York: Chemical Publishing Co. Inc.

Briskin, D.P., and Hanson, J.B., 1992. How does the plant plasma membrane H^+-ATPase pump protons? *J. Exp. Bot.*, **43**: 269–289.

Brown, P.H., Welch, P.M., and Gary, E.E., 1987. Nickel: a micronutrient essential for higher plants. *Plant Physiol.*, **85**: 801–803.

Brownell, P.F., 1968. Sodium as an essential micronutrient element for some higher plants. *Plant Soil*, **28**: 161–164.

Broyer, T.C., Johnson, C.M., and Huston, P.P., 1972. Selenium and nutrition of Astragalus. I. Effect of selenite or selenate supply on growth and selenium content. *Plant Soil*, **36**: 635–649.

Epstein, E., and Bloom, Arnold J. 2005. *Mineral Nutrition of Plants: Principles and Perspectives.* (2nd ed.) Sunderland, Mass.: Sinauer Associates. 400 pp.

Epstein, E., 1972. *Mineral Nutrition of Plants: Principles and Perspectives.* New York: Wiley, 412 pp.

Flowers, T.J., and Yeo, A.R., 1992. *Solute Transport in Plants.* London: Blackie Academic & Professional, 176 pp.

Fox, R.L., Silva, J.A., Younge, O.R., Plunknet, D.L., and Sherman, G.D., 1967. Soil and plant silicon and silicate response by sugar cane. *Soil Sci. Soc. Am. Proc.*, **31**: 775–779.

Gauch, H.G., Jr., 1972. *Inorganic Plant Nutrition.* Stroudsburg, PA: Dowden, Hutchinson & Ross, 488 pp.

Glass, A.D.M., 1989. *Plant Nutrition. An Introduction to Current Concepts.* Boston: Jones and Bartlett Publishers, 234 pp.

Hedrich, R., and Schroeder, J.I., 1989. The physiology of ion channels and electrogenic pumps in higher plants. *Annu. Rev. Plant Physiol.*, **40**: 539–569.

Higginbotham, N., Etherton, B., and Foster, R.J., 1967. Mineral ion contents and cell transmembrane electropotentials of pea and oat seedling tissue. *Plant Physiol.*, **42**: 37–46.

Kliewer, M., and Evans, H.J., 1963. Identification of cobamide coenzyme in nodules of symbionts and isolation of the B_{12} coenzyme from Rhizobium meliloti. *Plant Physiol.*, **38**: 55–59.

Loftier, G., and Petrides, P., 1988. *Physiologische Chemie.* Berlin: Springer, 1036 pp.

Marschner, H., 1986. *Mineral Nutrition of Higher Plants.* London: Academic Press, 674 pp.

Mengel, K., 1991. *Ernahrung und Stoffwechsel der Pflanze*, 7th edn. Jena: G. Fischer, 466 pp.

Mitchell, P., 1961. Biological transport phenomena and the spatially anisotropic characteristics of enzyme systems causing a vector component of metabolism. In Kleinzeller, A., and Kotyk, A., eds., *Membrane Transport and Metabolism.* New York: Academic Press, pp. 22–34.

Nielsen, F.H., 1986. Other elements: Sb, Ba, B. Br, Cs, Ge, Rb, Ag, Sv, Sr, Ti, Zr, Be, Bi, Ga, Au, In, Nb, Sc, Te, TI, W. In Mertz, W., ed., *Trace Elements in Human and Animal Nutrition.* 5th edn. New York: Academic Press, pp. 415–463.

Nissen, P., Fageria, N.K., Rayar, A.J., Hassan, M.M., and van Hai, T., 1980. Multiphasic accumulation of nutrients by plants. *Physiol. Plant.*, **49**: 222–240.

Oertli, J.J., 1964. Betrachtungen zum Tragertransport bei der pflanzlichen lonenaufnahme. *Z. Pflanzenernahr., Bodenkd.*, **104**: 25–38.

Oertli, J.J., 1991. Transport of water in the rhizosphere and in roots. In Waisel, Y., Eshel, A., and Kafkafi, U., eds., *Plant Roots, The Hidden Half.* New York: Marcel Dekker, pp. 559–587.

Reisenauer, H.M., 1966. Mineral nutrients in soil solution. In Altman, P.L., and Dittmer, D.S., eds., *Environmental Biology.* Bethesda: Federation of American Societies for Experimental Biology, pp. 507–508.

Robinson, J.B.D., ed., 1983. *Diagnosis of Mineral Disorders in Plants*, Vol. 2. New York: Chemical Publishing Co., 96 pp.

Robinson, J.B.D., ed., 1987. *Diagnosis of Mineral Disorders in Plants*, Vol. 3. New York: Chemical Publishing Co., 168 pp.

Russell, E.W., 1973. Soil Conditions and Plant Growth, 10th edn. London: Longemans, 849 pp.

Scheffer, F., and Schachtschabel, P., 2002. *Lehrbuch der Bodenkunde.* Stuttgart, Germany: Enke Verlag, 528 pp.

Schilling, G., 1990. *Pflanzenernahrung und Dungung*, Teil 1. Berlin: Deutscher Landwirtschaftverlag, 248 pp.

Schroeder, J.I., and Fang, H.H., 1991. Inward-rectifying K^+ channels in guard cells provide a mechanism lor low-affinity K^+ uptake. *Proc. Natl Acad. Sci. USA*, **88**: 11583–11587.

Serrano, R., 1989. Structure and function of plasma membrane ATPase. *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, **40**: 61–94.

Sprague, H.B., ed., 1964. *Hunger Signs in Crops*, 3rd edn. New York: McKay, 461 pp.

Walker. C.D., Graham, R.D., Madison, J.T., Cary, E.E., and Welch, R.M., 1985. Effects of Ni deficiency on some nitrogen metabolites in cowpeas (*Vigna unguiculata* L. Walp). *Plant Physiol.*, **79**: 474–479.

Wallace, T., 1961. The Diagnosis of Mineral Deficiencies in Plants, 3rd edn. London: H.M. Sta. Office, 125 pp.

Wiebe, H.H., and Kramer, P.J., 1954. Translocation of radioactive isotopes from various regions of roots of barley seedlings. *Plant Physiol.*, **29**: 342–348.

Cross-references

Fertilizers, Inorganic
Macronutrients
Micronutrients
Nitrogen Cycle
Phosphorus Cycle
Potassium Cycle
Soil Fertility
Sulfur Transformations and Fluxes
Trace Elements

PLANT ROOTS AND SOIL PHYSICAL FACTORS

Plant roots interact with soil physical factors. A complete understanding of the nutrient requirements of plants needs to take this fact into account. Soil-plant relationships have been reviewed in a number of publications, which except for those by Arkin and Taylor (1981) and Russell (1977) devote little attention to the physical aspects of the problem. All aspects of the relationship of soil physical conditions to plant roots relations based on knowledge up to 1988 are described in a special monograph by Gliński and Lipiec (1990) and supplemented with the *Proceedings of the Polish-French Colloquium* (*Conditions Physiques des Sols et Fonctionnement Racinaire*, 1990). More recently, approaches for controlling and measuring the physical environment in root growth experiments were described by Whalley et al. (2000).

Soil physical factors

The main aspect of soil physics for plant productivity is the requirement for suitable proportions between solid, liquid, and gaseous phases. These proportions are found to be optimal only in some soils and when climatic conditions and human activity are appropriate.

Soil physical properties can be divided into 3 groups:

- relatively stable (texture, mineralogy, cementing agents, profile development, topography), resulting from geological and pedological processes,
- dynamic (structure, bulk density, pore size, aggregation, profile characteristics),
- highly variable (water, air, temperature, mechanical resistance).

Every physical property and process in question is modified by natural conditions (mainly weather phenomena such as precipitation and radiation) and human manipulations (management practices such as tillage, plowing, chemical additives, irrigation and drainage), which drastically change physical properties of upper soil layers.

Soil physical properties and processes are more or less closely interconnected, which is shown on Figure P47. A very good relationship exists between soil, water, air, temperature and mechanical resistance, which directly affect plant roots. They are by turn, affected by texture, structure, bulk density, aggregation, pore size distribution and profile characteristics.

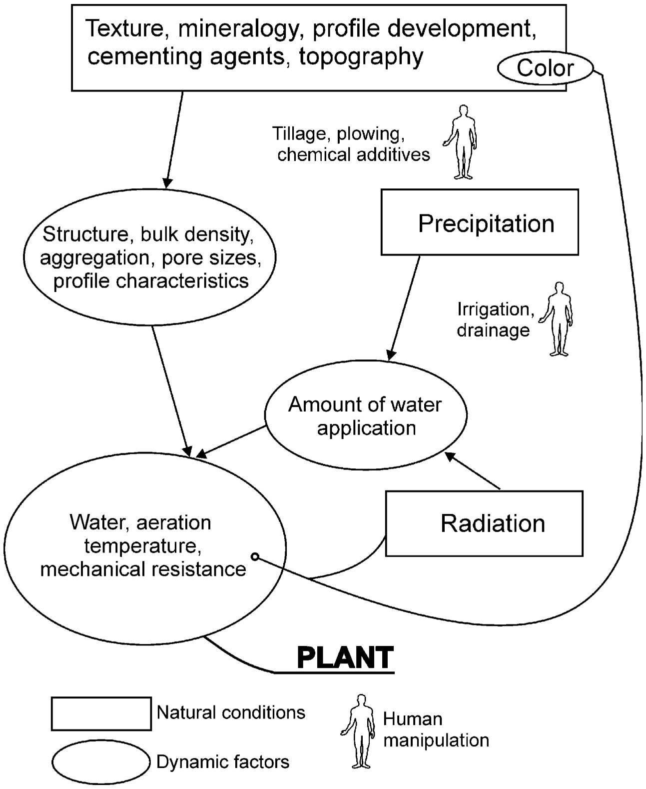


Figure P47 Relationship between climatic and soil physical conditions and human manipulation in affecting plant growth and yield (adapted from Letey, 1985).

Soil-root relations are very complex and dynamic. These relations occur at the soil-root interface, which is defined as a boundary between the outermost root tissues and the particles of soil, which are closest to them. Within this boundary is a zone of microbial activity called rhizosphere. Root environment is rapidly changing especially in respect to soil physical conditions such as mechanical properties, moisture, aeration and temperature.

Soil mechanical impedance

Soil materials constitute mechanical obstacles to growing roots. The pressure available for roots to accomplish work against external constraint is termed root growth pressure and is written as:

$$\frac{F_t - F_{\mathrm{ew}}}{A}$$

where $F_{\mathrm{t}} - F_{\mathrm{ew}}$ are respectively, the summation of the longitudinal forces in the root that arise from turgor pressure and the longitudinal forces in cell walls which resist cellular elongation and A is the cross-sectional area of the root at the plane where force is determined. The maximum axial root growth pressures range for a number of species from 0.9 to 1.3 MPa and maximum radial growth pressures are around 0.5 MPa (Gliński and Lipiec, 1990).

Pore size and aggregate size largely affect root penetration. The data on the growth of various roots through porous sinters show that roots of most plants are incapable of decreasing in size to enter pores of smaller diameter than they are. The growth in such media usually causes morphological changes, such as larger diameter of roots due to a great enlargement in the cortex in which cells became shorter in longitudinal direction and wider across, while the cell volume was unaffected. Roots, which are unable to penetrate the strong layer, are deflected to grow horizontally along the interface between the loose and strong layer until they encounter vertical cracks (Dexter, 1986). The proportions of roots, which entered cracks, were found to decrease strongly with decreasing crack width and increasing angle of incidence between the root and the crack (Figure P48).

Roots of some grasses (Italian ryegrass, *Lolium perenne*), however, are able to penetrate into pores of a lower diameter than themselves. This ability is considered as an alternative mechanism to the exertion of radial pressure by which the root may penetrate compressed soil layers (Gliński and Lipiec, 1990).

A soil matrix with cracks and other macropores will offer greater potential for undisturbed root growth because the roots can by-pass the zones of high mechanical impedance and increase the percentage of roots in deeper and stronger layers. The preferential root growth into macropores will lead to increasing critical limits of soil compactness and soil strength (Håkansson and Lipiec, 2000; Whalley et al., 2000). The critical lower limit set of macropore volume at 5 m^3/100 m^3 for cropped sites on poorly drained soil was suggested (McQueen and Shepherd, 2002). The relationship between the distribution of macropores and roots can be described numerically using fractal analysis (Hatano and Sakuma, 1990; Lipiec et al., 1998). This analysis indicated the occurrence of the relationship between distribution patterns of the pores and roots in loose and moderately compacted soil.

Lower growth rate, greater diameter, greater deflection, and increased percentage of forked beets characterize roots grown in beds of large compared with small aggregates. Large aggregates reduce greatly the proportion of roots that penetrate them. Nutrient uptake, e.g., P, is lower from large aggregates. The response of roots to aggregate size is closely related to the type of roots.

Parameters commonly used to relate the mechanical impedance of the soil to root growth are bulk density and penetrometer pressure (penetration resistance, cone index, and strength). Soil mechanical impedance is closely connected with soil and subsoil compaction. Dry bulk density and soil strength measurements such as penetrometer resistance, shear strength, aggregate strength and precompression stress are widely used to assess soil mechanical impedance following compaction (Horn and Rostek, 2000; Lipiec and Hatano, 2003). To quantify soil compaction effects on pore and aggregate structure, images of resin-impregnated soils are used (Horn et al., 1995; Pagliai et al., 2000). Morphological analysis of the images revealed that compaction of loamy soil by tractor pass reduced larger pores but mainly the elongated and continuous transmission pores (50 to 500 µm) and to lesser extent those <50 µm (Pagliai et al., 2000). New CCD cameras and scanners of high resolution (<10 µm) are being developed and provide potential for more detailed quantification of soil structure (Young et al., 2001; Gantzer and Anderson, 2002). Recent developments in computer assisted tomography (CAT) scanning based on generating transmission images (Perret et al., 1999) and detecting nuclear radiation emitted from the soil (single photon emission computed tomography – SPECT) (Perret et al., 2000; Young et al., 2001) can be used to 3-D quantification of macropore network (set of interconnected macropores) at the scale of soil core or column.

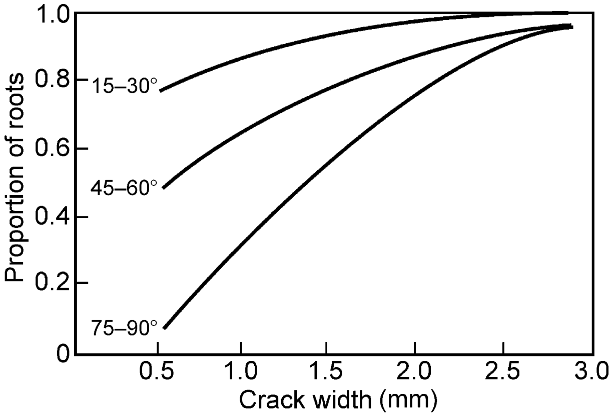


Figure P48 Proportions of seminal roots of wheat, which enter cracks of various width and angle of incidence (adapted from Dexter, 1986).

Field experiments showed that (Lipiec et al., 1991; Håkansson and Lipiec, 2000) an increase in soil compactness resulted in lower root growth rate, greater concentration of roots of spring barley in the surface layer and in a lower rooting depth (Figure P49). It is generally accepted that roots grown in mechanically impeded materials are thicker and are characterized by a higher degree of flattening, tortuous growth, distorted epidermal cells and radially enlarged cortex cells. The effect of soil compaction on root growth was also less inhibited in beds of 4–8 mm aggregates than those with structural units of <2 mm although penetration resistance was higher in the former (Busscher and Lipiec, 1993). This implies the presence of inter-aggregate pores larger than growing roots.

Changes in the root system and soil conditions due to soil compaction affect uptake of water. In laboratory conditions Lipiec et al. (1992) showed this with spring barley (Figure P50). The cumulative water use by plants during the whole experimental period was lowered with increasing soil compaction. Root uptake rate was highest, however, in medium compacted soil (bulk density 1.45 Mg m^{-3}) and lowest in loose soil (bulk density 1.30 Mg m^{-3}). Simultaneously, higher proportion of fine roots was recorded in compacted soil. This can be due to a decrease of the number of large pores. The highest total water use in loose soil was attributed to the highest total root size and more uniform root distribution in the soil. The higher root uptake rate in compacted soil compared with loose soil could be explained as a result of increasing contact area between the roots and soil and higher unsaturated hydraulic conductivity at that water potential. Approaches with split root systems in soil of varying bulk density and soil water potential are useful to study the effect of spatial distribution of mechanical impedance and aeration on root growth and function (Whalley et al., 2000).

Soil water

Rooting of a plant is directly affected by soil water status. It is generally considered that the water potential in the root zone of about −50 kPa causes root growth to start to decrease and to continue slowly until about −1 500 kPa. In wet soil, root

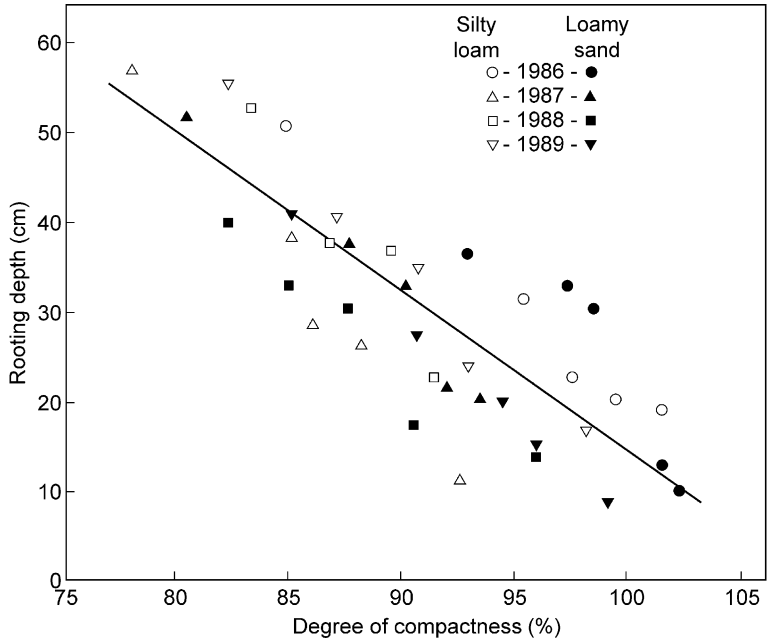


Figure P49 Rooting depth of spring barley at heading time in relation to the degree of compactness (Lipiec et al., 1991, reprinted by permission of the publisher).

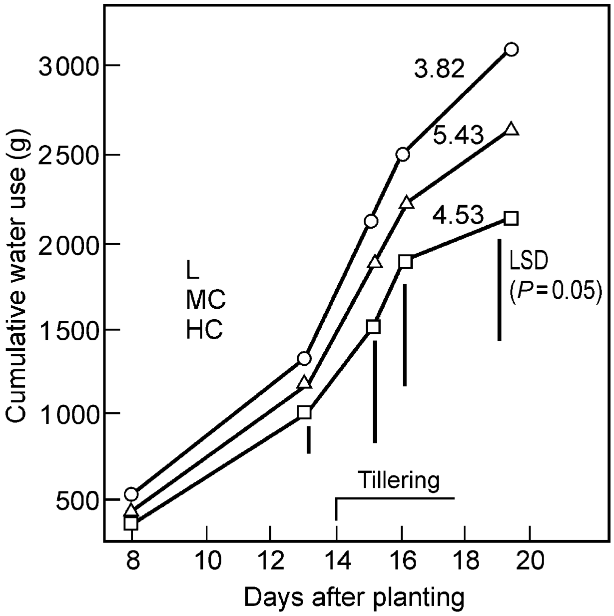


Figure P50 Cumulative water use for treatments with three dry bulk densities: *L* (1.30 Mg m^{-3}), *MC* (1.45 Mg m^{-3}) and *HC* (1.60 Mg m^{-3}). Root uptake rate (mm^{-3} H_2O/mm root/day) is indicated by 3.82, 5.43 and 4.53 (Lipiec et al., 1992, reprinted by permission of the publisher).

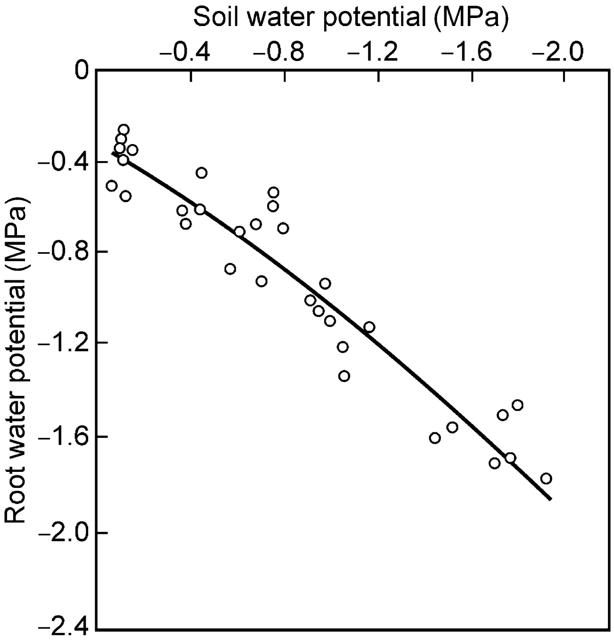


Figure P51 Relation between soil water potential and root water potential of loblolly pine seedling (adapted from Kaufmann, 1968).

growth can be limited unless aeration is adequate. A relationship between soil water potential and root water potential was also found (Figure P51) as well as between root moisture stress and soil moisture stress (Figure P52). Supplying a root system with water in the soil depends not only on the water potential at the different depths, but also on the rate at which water moves through the soil to the root. The amount of water available to the roots varies widely in soils as affected by their texture,

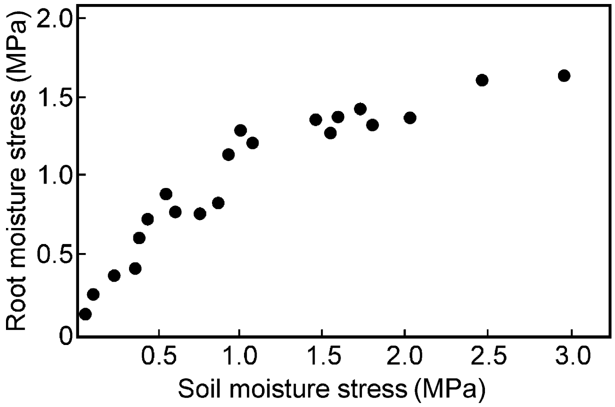


Figure P52 Root moisture stress of tobacco plants as related to soil moisture stresses in sandy loam (adapted from De Roo, 1969).

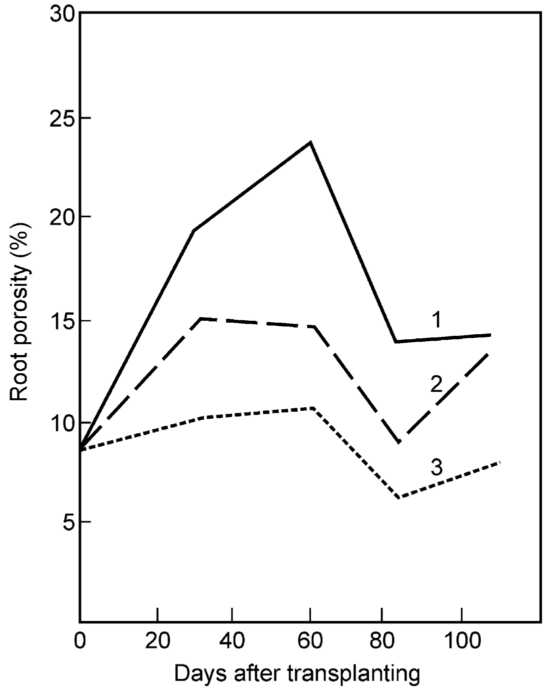


Figure P53 Changes in root porosity of rice at different stages of growth under different soil moisture regime: (*1*) flooding, (*2*) alternate flooding, and (*3*) no flooding (adapted from Das and Jat, 1997).

organic matter content, soil density, soil temperature, and soil aeration. In general, soils with smaller water-holding capacity have deeper roots, while those with a larger capacity have a shallower root zone.

Soil water significantly influences root morphology, root porosity (Figure P53), water (Figure P54) and nutrient uptake by roots and root diseases and affects the mobility of ions moving from the soil to the plant root by diffusion. This is determined by the effective diffusion coefficient (D_c).

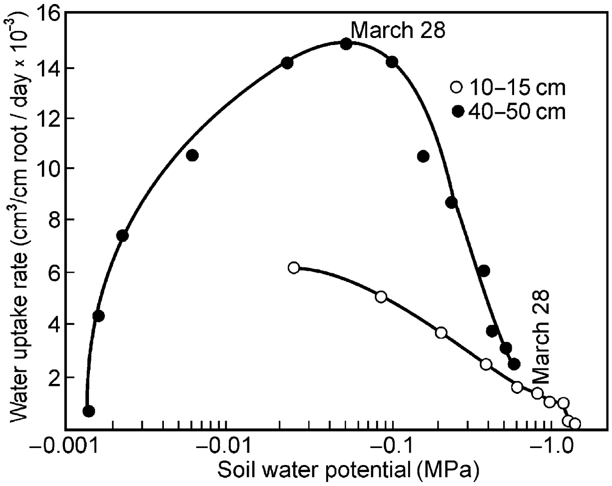


Figure P54 Water uptake rate by rice roots as a function of soil water potential for two soil layers (Hasegawa and Yoshida, 1982, reprinted by permission of the publisher).

$$D_c = D_1 \theta f \frac{dC_1}{dC}$$

where D_1 is the diffusion coefficient in water; θ is the volumetric water content; f is the impedance factor; C_1 is the concentration of the nutrient in the solution; C is the quantity of the nutrient participation in diffusion; and dC_1/dC is the reciprocal of the buffer capacity.

Soil aeration status

The main components of soil air affecting plant roots are oxygen and carbon dioxide. They have direct and indirect effects on roots (Figure P55). Soil oxygen plays a fundamental role for plant root functioning, through its availability to the root system, its direct effects connected with the physiological events, occurring within the plants and through its indirect effects changing soil properties (Gliński and Stępniewski, 1990). Most of the negative phenomena connected with oxygen deficiency in soil are caused solely and directly by the lack of oxygen for metabolic processes. Indirect effects appear only when there is a long-lasting shortage of oxygen in the soil. They comprise the influence of both O_2 and CO_2 on redox processes in the soil, on its acidity and on the living organisms within it. All these factors influence the availability of nutrients to plants, and to their well being in general. The state of soil anaerobiosis has two levels: a short term lack of oxygen in soil air which is directly connected with plant roots, and is distinguished from a long-term lack of oxygen causing more persistent consequences in soil.

Plants vary widely in response to oxygen stress in the soil. The most sensitive are tobacco and legumes for example, with cereals and sugar beets resistant examples. The example of the effect of oxygen on root growth force is shown on Figure P56. As it can be seen root growth force decreased drastically at oxygen concentrations below 3–5%. In general, the critical oxygen level in soil for plants begins in the range of 5 to 10% O_2 by volume. Root growth of most plants is limited when less than 0.1 of the pore spaces in soil are filled with air and the oxygen diffusion rate (*ODR*) is less than 35 μg m^{-2} s^{-1}

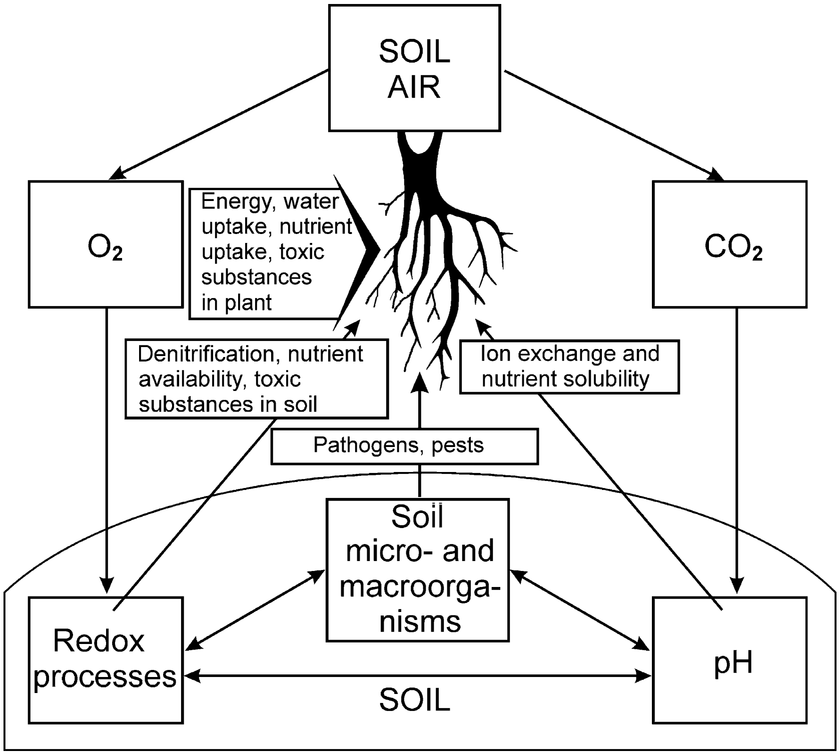


Figure P55 A scheme of direct and indirect effects of soil air on plants (adapted from Gliński and Stępniewski, 1985).

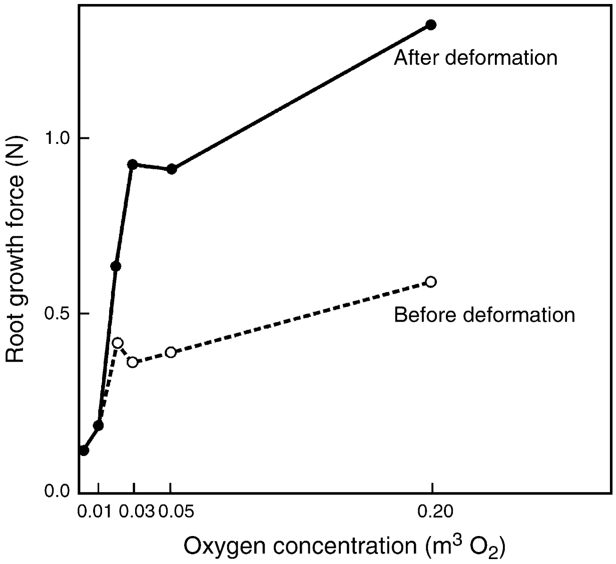


Figure P56 The dependence of growth force of maize seminal roots before and after their deformation due to facing the obstacle on oxygen concentration in the gas mixture surrounding the radicle (adapted from Gliński and Stępniewski, 1990).

(Gliński and Lipiec, 1990). It is widely agreed that the best indicator of soil oxygen availability for plant roots is the *ODR*. The reaction of roots of different plants to *ODR* is shown in Figure P57. In general, this critical value for other plants is differentiated from 8 (Kentucky blue grass) to 42 μg m^{-2} s^{-1} (maize).

Plants subjected to long-lasting atmospheric stresses in the soil form some adaptive mechanisms, which allow them to grow, develop and yield. Three different kinds of such adaptation were identified: anatomical and morphological adaptations to internal transport T, shallow rooting, metabolic and physiological adaptation. One of the most common anatomical adaptations is the formation of increased intercellular air spaces in root cortex that provide canals parallel to the axis of the roots to a distance of 2 to 3 mm from the root tip through which gases can diffuse longitudinally. They are found in the suberized adventitious root tissue known as aerenchyma. These roots also have porosity much greater than in the primary roots. Shallow rooting is explained by the death of the top roots after reaching the anoxic layer followed by stimulation of lateral root growth and by aerotropic root growth. Roots growing in an environment with restricted oxygen supply are thicker, shorter, less branched, of light color, have larger cells, and in the case of legumes, posses fewer nodules. In some cases the roots become aerotropic and emerge from the soil. Metabolic and physiological adaptation involves a decrease of Pasteur effect, ethanol removal from roots and alternative metabolic path leading not to ethanol but to less toxic end products such as malate, lactate, shikimate, glutomate, the amino acids or glycerol.

Temperature

Temperature is the most important factor regulating water and nutrient absorption by roots. It affects water absorption by increasing permeability of the cell membrane and metabolic activity (Figure P58). It is a general tendency for nitrogen,

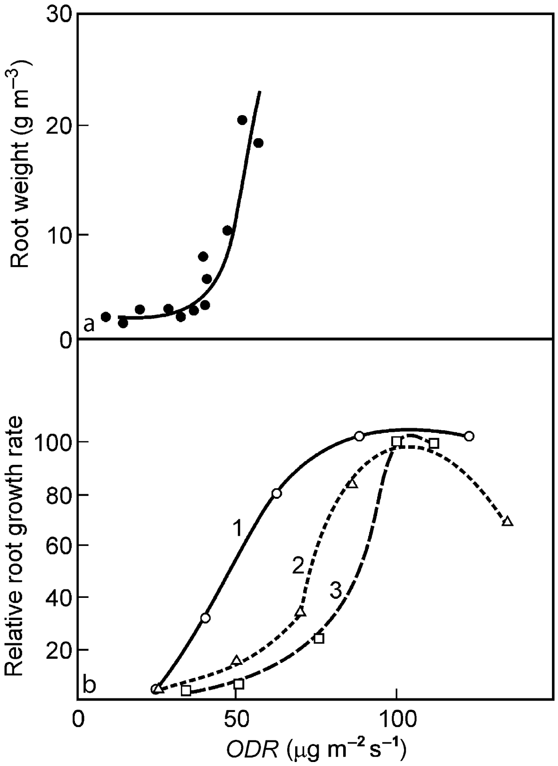


Figure P57 Root response to *ODR*; (**a**) population of wheat roots in soil under field conditions, (**b**) relative root growth rate of three desert shrubs: *Fransera dumosa* (*1*), *Larrea tridentata* (*2*), *Artemisia tridentata* (*3*) (adapted from Gliński and Stępniewski, 1985).

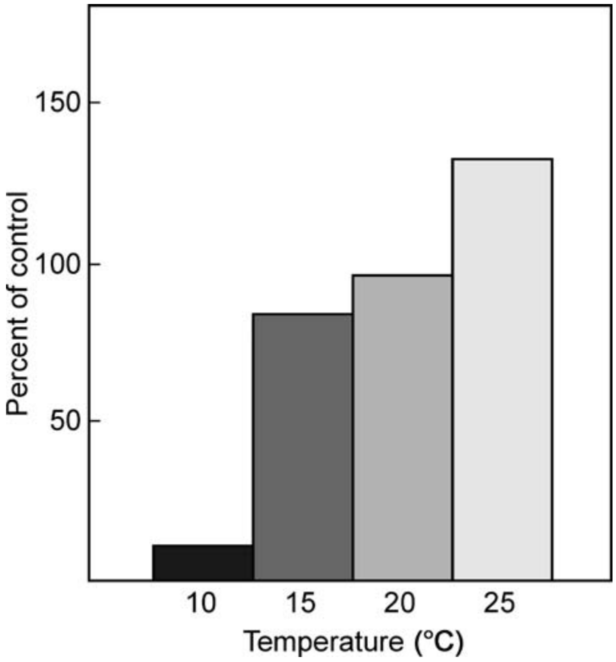


Figure P58 Water content (percent of control) in root of maize at different temperatures (adapted from Frossard, 1985).

potassium, phosphorus and magnesium absorptions to increase in roots with temperature. Also root nodulation, nitrogen fixation and root rot diseases have their optimum temperature, e.g., maximum nitrogen fixation was found at 24 °C for *Medicago tribuloides* Desr. and at 27 °C for *Vigna sinensis*. When soil temperature decreases with depth, commonly deeper root system in loose soil may experience a lower temperature than shallow root system in compacted soil.

Effect of all soil physical factors on root growth and functions is closely related to climatic conditions, soil management, and the stage of plant development. For example, in wetlands, the factor most correlated with root growth may be soil aeration while in the northern latitudes it is soil temperature. Complex interactions result in no universal factor affecting root growth and functions. In most conditions, soil water content or soil water potential appears to be of particular importance since it directly affects both root growth and functions and indirectly influences other significant factors, such as aeration, mechanical resistance, and soil temperature. The importance of this property is enhanced by the fact that it can to some degree be manipulated and predicted by means of climatic factors. The interrelationships between soil water and other physical factors are expressed by the indicators called a non-limiting water range (Letey, 1985) or least limiting water range (da Silva et al., 1997) at which soil aeration and mechanical resistance do not restrict root growth or is minimal.

Influence of roots on soil properties

Plant roots alter the chemical, physical and biological nature of the soil adjacent to the root. Plant roots influence such physical properties as structure stability, bulk density, porosity, soil mineralogical and mechanical composition and water characteristics of soil.

The role of plant roots in soil structure formation consists mainly in soil aggregation. Root and root hairs penetrating the soil produce lines of weakness along which the clod or soil mass may break into granules. Also the pressure exerted by developing roots may induce aggregation. Root secretions may flocculate colloids and stabilize or cement aggregates. The use of moisture by roots may cause dehydration of colloids, thus resulting in shrinkage and finally in cementation of soil aggregates. The effect of living roots on soil structure stability, apart from the nature of the mineral substrates and climatic conditions, depends on the plant species. Lucerne may be an example of a plant capable of improving structural stability of soil, while maize, on the other hand, generally decreases this stability. Callot et al. (1982) and Jaillard (1987) presented the effects of plant roots on the physical and physicochemical environment of calcareous soil. Water flux toward the roots and acidification of root environment formed various types of soil structure due to dissolution, movement, and re-precipitation of soil carbonates.

Extending roots are able to displace individual soil aggregates from their path in a loose seed bad. Roots of plants producing mucilages can form bridges between primary clay particles themselves and between these particles and the root surface forming the so-called, root soil aggregates, during the process of soil desiccation and moistening (Figure P59). Roots growing in the soil, increasing their diameter increase the bulk density of the soil near the root (Dexter, 1987; Bruand et al., 1996). This increase, according to Greacen et al. (1968), may reach value of 0.1–0.2 Mg m^{-3}. Dexter (1987) indicated that the soil density around roots decreases exponentially with distance

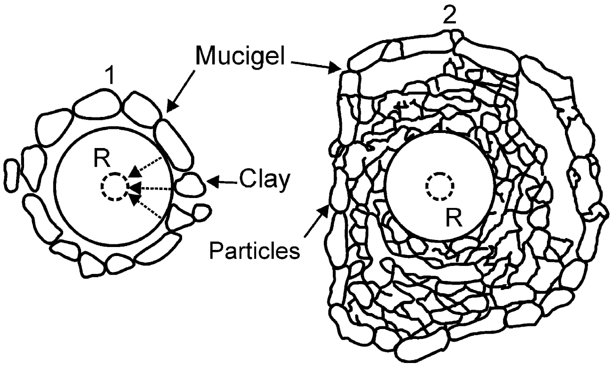


Figure P59 Model of aggregates formation at root surface: (*1*) function of clay particles by mucigel bridges at the root (*R*) surface, (*2*) root aggregate (adapted from Tinker, 1976).

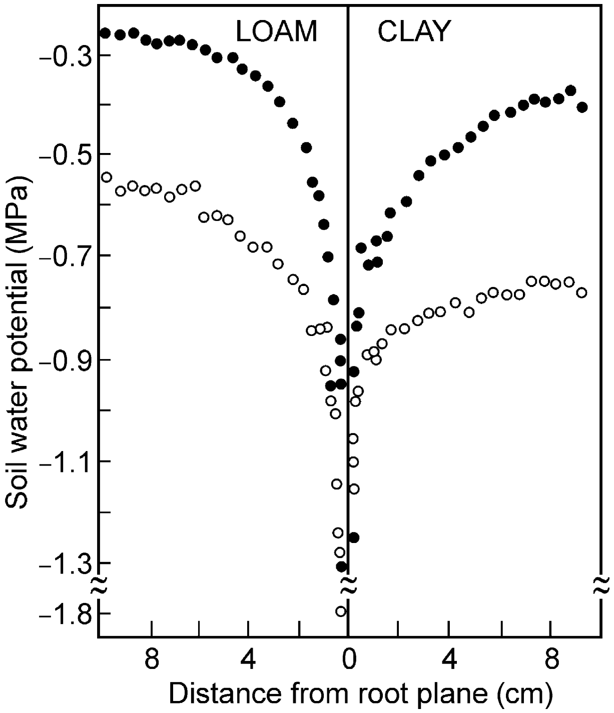


Figure P60 Soil water potential gradients in clay and loamy soils with a distance from soybean root plane. Moist treatment (full circles), dry treatment (open circles) (Hasegawa and Sato, 1985, reprinted by permission of the publisher).

from the root surface with an exponent, which is a constant multiple of the root diameter. This can be enhanced in compacted soil where roots are typically shorter and thicker (Lipiec and Simota, 1994). Dual-source γ-CT scanning was used with satisfactory precision to monitor changes non-destructively in spatial distribution of bulk density and water content close to the root (Phogat et al., 1991; Asseng et al., 2000).

Certain taprooted plants, e.g., pigeon pea, lucerne or robust wild plants, can perform compact layers and create easily accessible pathways for the roots of succeeding crops (Cresswell and Kirkegaard, 1995). On the above basis, proposals are made to screen suitable species and cultivars for their ability to penetrate and loosen compact semi-rigid soils and therefore to become potential tillage tools.

Plant roots penetrating soil leave macropores (channels) that improve water and gas movement. Due to the death of the appropriate fraction of the root system before plant maturity and the decrease of root diameter through degradation of their cortex due to invasion by microorganisms or dessication their contact area with soil decrease and soil porosity increases. The uptake behavior of roots changes water movement and the accumulation profile in the rhizosphere (Figure P60).

Jan Gliński, Jerzy Lipiec, and Witold Stępniewski

Bibliography

Adeoye, K.B., and Rawlins, S.L., 1981. A split-root techniques for measuring root water potential. *Plant Physiol.*, **68**: 44–53.

Arkin, G.F., and Taylor, H.M., 1981. Systems, considerations and constrainsts. In Arkin, G.F., and Taylor, H.M., eds., *Modyfying the Root Environment to Reduce Crop Stress.* ASAE Monogr. No. 4. St. Joseph, MI: American Society of Agricultural Engineering.

Asseng, S., Aylmore, L.A.G., MacFall, J.S., Hopmans, J.W., and Gregory, P.J., 2000. Computer-assisted tomography and magnetic resonance imaging. In Smit, A.L., Bengough, A.G., Engels, C., van Noordwijk, M., Pellerin, S., van de Geijn, S., eds., *Root Methods A Handbook.* Berlin, Heidelberg: Springer pp. 343–363.

Bruand, A., Cousin, I., Nicoullaud, B., Duval, O., and Begon, J.C., 1996. Backscattered electron scanning images of soil porosity for analyzing soil compaction around roots. *Soil Sci. Soc. Am. J.*, **60**: 895–901.

Busscher, W., and Lipiec, J., 1993. Early growth of maize in compacted soil with fine and coarse structure. *Int. Agrophys.*, **7**: 77–83.

Callot, G., Chamayon, H., Maertens, C., and Salsac, L., 1982. *Soil-Root Interactions. Aspects of Mineral Nutrition.* Paris: INRA (in French).

Conditions Physiques des Sols et Fonctionnement Racinaire, 1990. *Zesz. Probl. Postępów Nauk Roln.* Vol. 385. Warsaw: PWN.

Creswell, H.P., and Kirkegaard, S.A., 1995. Subsoil amelioration by plant roots, the process and the evidence. *Aust. J. Soil Res.*, **33**: 221–239.

Das, D.K., and Jar, R.L., 1977. Influence of three soil-water regimes on root porosity and growth of four rice varieties. *Agron. J.*, **69**: 197–200.

Da Silva, A.P., Kay, B.D., and Perfect, E., 1997. Management versus inherent soil properties effects on bulk density and relative compaction. *Soil Till. Res.*, **44**: 81–93.

De Roo, H.C., 1969. Water stress gradients in plants and soil-root systems. *Agron. J.*, **61**: 511–515.

Dexter, A.R., 1986. Model experiments on the behavior of roots at the interface between a tilled seed-bed and a compacted sub-soil. III. Entry of pea and wheat roots into cylindrical biopores. *Plant Soil.*, **95**: 149–161, 1986.

Dexter, A.R., 1987. Compression of soil around roots. *Plant Soil*, **97**: 401–406.

Frossard, J.S., 1985. Root temperature effect on root respiration and growth in maize seedlings of two grain types. *Agronomie*, **5**: 719–725.

Gantzer, C.J., and Anderson, S.H., 2002. Computed tomographic measurement of macroporosity in chisel-disk and no-tillage seedbeds. *Soil Till. Res.*, **64**: 101–111.

Gliński, J., and Lipiec, J., 1990. *Soil Physical Conditions and Plant Roots.* Boca Raton, FL: CRC Press.

Gliński, J., and Stępniewski, W., 1985. *Soil Aeration and Its Role for Plants.* Boca Raton, FL: CRC Press.

Gliński, J., and Stępniewski, W., 1990. Influence of soil oxygen supply on root growth and functioning (review of the literature). *Zesz. Probl. Post. Nauk Roln.*, **385**: 7–72.

Greacen, E.L., Barley, K., and Farrell, D.A., 1968. In Whittington, W.J., ed., *The Mechanics of Root Growth in Soils with Particular Reference to the Implications for Root Distribution in Root Growth.* London: Butterworth.

Håkansson, I., and Lipiec, J., 2000. A review of the usefulness of relative bulk density values in studies of soil structure and compaction. *Soil Till. Res.*, **53**: 71–85.

Hasegawa, S., and Sato, T., 1985. Soil water movement in the vicinity of soybean roots determined by root plane experiment. *Trans. Jpn. Soc. Irrig. Drain Reclam. Eng.*, **17**: 22–24.

Hasegawa, S., and Yoshida, S., 1982. Water uptake by dryland rice root system during soil drying cycle. *Soil Sci. Plant Nutr.*, **28**: 191–204.

Hatano, R., and Sakuma, T., 1990. The role of macropores on rooting pattern and movement of water and solutes in various field soils. *Trans 14th Int. Congr. Soil Sci.*, **II**: 130–135.

Horn, R., Domżał, H., Słowińska-Jurkiewicz, A., and Van Ouwerkerk, C., 1995. Soil compaction processes and their effects on the structure of arable soils and the environment. *Soil Till. Res.*, **35**: 23–36.

Horn, R., and Rostek, J., 2000. Subsoil compaction processes – state of knowledge. In Horn, R., van den Akker, J.J.H., Arvidsson, J., eds., *Subsoil Compaction – Distribution, Processes and Consequences.* Advances in geoEcology 32, Catena, Reiskirchen, Germany, pp. 44–54.

Jaillard, B., 1987. Rhizomorphic Carbonate Structure: Model of Rearrangement of Soil Minerals by Roots. Ph.D. thesis, Montpellier p. 221 (in French).

Kaufmann, M.R., 1968. Water relations of pine seedlings in relation to root and shoot growth. *Plant Physiol.*, **43**: 281–288.

Letey, J., 1985. Relationship between soil physical properties and crop production. *Adv. Soil Sci.*, **I**: 277–295.

Lipiec, J., Håkansson, I., Tarkiewicz, S., and Kossowski, J., 1991. Soil physical properties and growth of spring barley as related to the degree of compactness of two soils. *Soil. Till. Res.*, **19**: 307–317.

Lipiec, J., and Hatano, R., 2003. Quantification of compaction effects on soil physical properties and crop growth. *Geoderma*, **116**: 107–136.

Lipiec, J., and Simota, C., 1994. Role of soil and climate factors influencing crop responses to compaction in Central and Eastern Europe. In Soane, B.D., van Ouwerkerk, C., eds., *Soil Compaction in Crop Production.* Amsterdam: Elsevier, pp. 365–390.

Lipiec, J., Szustak, A., Bennicelli, R., and Kania, W., 1992. The influence of soil compaction on water use and growth of spring barley. *Zesz. Probl. Post. Nauk Roln.*, **397**: 40–44.

Lipiec, J., Hatano, R., and Słowińska-Jurkiewicz, A., 1998. The fractal dimension of pore distribution patterns in variously-compacted soil. *Soil Till. Res.*, **47**: 61–66.

Lowery, B., and Morrison, Jr., J.E., 2002. Soil penetrometers and penetrability. In Dane, J.H., Topp, G.C., eds., *Methods of Soil Analysis, Part 4. Physical Methods.* Soil Sci. Soc. of Am. Book Series, vol. 5. Madison, WI, pp. 363–388.

McQueen, D.J., and Shepherd, T.G., 2002. Physical changes and compaction sensitivity of a fine-textured, poorly drained soil (Typic Endoaquept) under varying durations of cropping Manawatu Region, New Zealand. *Soil Till. Res.*, **63**: 93–107.

Pagliai, M., Pellegrini, S., Vignozzi, N., Rousseva, S., and Grasselli, O., 2000. The quantification of the effect of subsoil compaction on soil porosity and related physical properties under conventional to reduced management practices. In Horn, R., van den Akker, J.J.H., and Arvidsson, J., eds., *Subsoil Compaction – Distributionm, Processes and Consequences.* Advances in geoEcology 32, Catena, Reiskirchen, Germany, pp. 305–313.

Perret, J.P., Prasher, S.O., Kantzas, A., and Langford, C., 1999. Three-dimensional quantification of macropore networks in undisturbed soil cores. *Soil Sci. Soc. Am. J.*, **63**: 1530–1543.

Perret, J.P., Prasher, S.O., Kantzas, A., and Langford, C., 2000. Preferential flow in intact soil columns measured by SPECT scanning. *Soil Sci. Soc. Am. J.*, **64**: 469–477.

Phogat, V.K., Alymore, L.A.G., and Schuller, R.D., 1991. Simultaneous measurement of the spatial distribution of soil water content and bulk density. *Soil Sci. Soc. Am. J.*, **55**: 908–915.

Russell, R.S., 1977. *Plant Root Systems: Their Function and Interaction with the Soil.* London: Mc Graw-Hill.

Souty, N., and Stępniewski, J., 1988. The influence of external oxygen concentration on axial root growth force of maize radicals. *Agronomie*, **8**(4): 295–300.

Tardieu, F., 1994. Growth and functioning of root systems subjected to soil compaction. Towards a system with multiple signalling? *Soil Till. Res.*, **30**: 217–243.

Tinker, P.B., 1976. Transport of water to plant root in soil. *Phil. Trans. R. Soc, London Ser. B.*, **273**: 445–461.

Whalley, W.R., Lipiec, J., Stępniewski, W., and Tardieu, F., 2000. Control and measurement of the physical environment in root growth experiments. In Smit, A.L., Bengough, A.G., Engels, C., van Noordwijk, M., Pellerin, S., van de Geijn, S.C., eds., *Root Methods A Handbook.* Berlin, Heidelberg: Springer, pp. 76–112.

Young, I.M., Crawford, J.W., and Rappoldt, C., 2001. New methods and models for characterising structural heterogeneity of soil. *Soil Till. Res.*, **61**: 33–45.

PLASMA

The combination of inorganic, clay-sized materials, made up of clay minerals, iron oxides and hydroxides, amorphous phases, and organic matter, that provides support for the larger grains and components that comprise the skeletal elements of the soil. In thin-section it is seen as the background to the larger constituents.

Cross-reference

Micromorphology

PLASTIC

Capable of permanently changing shape under the influence of stress, without rupturing. The minimum water content in a soil that allows it to act this way is the plastic limit.

Cross-reference

Particle Size Distribution

PLAYA

A flat, unvegetated, basin in a desert plain that becomes a temporary lake (playa lake) after rain. It contains silty or sandy sediment, and salts produced by evaporation. The prevalence of salts is conducive to the development of Solonchaks in playa depressions.

Cross-reference

Solonchak

PLINTHITE

Name originally given to the brick-red, clay-rich alteration product of weathered basaltic rocks in Northern Ireland and Western Scotland. Now used to mean the ferric iron and clay-rich material occurring as mottles in soil, and that irreversibly hardens to a hardpan (petroplinthite) on repeated cycles of wetting and drying.

Cross-references

Duricrusts and Induration
Plinthosol
Soils of the Coastal Zone
Tropical Soils

PLINTHOSOLS

Plinthosols are soils with ‘plinthite’ – a firm but soft, iron-rich, red-mottled clay, made up of a humus-poor mixture of kaolinite, quartz and other constituents that irreversibly hardens to petroplinthite when exposed to repeated wetting and drying. Hard Plinthosols are equivalent to laterite, as originally used by Buchanan (1807) for an iron-rich, humus-poor mixture of kaolinitic clay and quartz that was cut into bricks (laterite comes from the Latin word ‘later’ for brick) in western India, and used for building. The term plinthite was introduced when laterite became compromised by many meanings. Petroplinthite may exist as a continuous layer, or occur in ‘skeletic’ form as discrete concretions. This account is taken from FAO (2001).

Connotation. Soils with ‘*plinthite*’; from Gr, *plinthos*, brick.

Synonyms. ‘Lateritas hydromorficas’ (Brazil), ‘sols gris latéritiques’ (France), ‘plinthaquox’ (Soil Taxonomy) or as Plinthosols (FAO). Generally known as ‘groundwater laterite soils’.

Definition. FAO (2001) defines Plinthosol as soils with

- a *petroplinthic* horizon starting within 50 cm from the soil surface, or
- a *plinthic* horizon starting within 50 cm from the soil surface, or
- a *plinthic* horizon starting within 100 cm from the soil surface underlying either an *albic* horizon or a horizon with *stagnic* properties.

Identification of plinthite may present a problem since not all red mottled clay is plinthite. True plinthite satisfies the following field criteria. (*a*) Red mottles are firm or very firm when moist and hard or very hard when dry. (*b*) They *can be cut with a knife* but only with difficulty. (*c*) They *have sharp boundaries*. (*d*) They *hardly stain the fingers* when rubbed. (*e*) They *do not slake in water.*

Petroplinthite (known also as ‘ironstone’, ‘laterite’, ‘murram’ or ‘ferricrete’) takes two forms. It occurs as massive iron pans, or as discontinuous segregations.

Parent material. Plinthite is more common in weathering material from basic rocks than from acidic rocks. In any case it is crucial that sufficient iron is present, originating either from the parent material itself or brought in by seepage water from elsewhere.

Environment. Plinthosols with soft plinthite form under hot, humid conditions and are indigenous to the tropical rain forest. The formation of plinthite is associated with level to gently sloping areas with fluctuating groundwater. Bottomlands are a favored locale. ‘*Petroplinthic*’ soils with continuous, hard ‘*ironstone*’ form where plinthite becomes exposed to the surface, e.g., on erosion surfaces that are above the present drainage base. They are Soils with petroplinthite are especially abundant in the transition zone from rain forest to savannah, notably in dry areas that were once much wetter (for example, the Sahel, and southern Sudan). ‘*Skeletic*’ soil units having a layer of hardened plinthite concretions, occur mostly in colluvial or alluvial deposits.

Distribution. Globally there are about 60 million ha of Plinthosols. Soft plinthite occurs mostly under hot, wet climates, for example in the eastern part of the Amazon basin, the central Congo basin and parts of Southeast Asia. There are large areas of hardened plinthite in the Sahel, and similar soils are found in India, and in drier parts of Southeast Asia and northern Australia. The global distribution of the Plinthosols is shown in Figure P61.

Characteristics. Profiles are mostly A(E)BC sequences. The plinthite segregates at the depth of groundwater fluctuation. Hardening of plinthite to *petroplinthite* takes place upon repeated drying and wetting, commonly after geological uplift of the terrain and/or change to a drier climate, or simply by removal of vegetation.

Chemically Plinthosols have high Fe and Al contents and this shows up in the mineralogy. The common minerals are quartz (inherited from the parent material), eucrystalline kaolinite, and various hydroxy and oxy phases of Fe and Al, for example: *goethite* (FeOOH) and *hematite* (Fe_2O_3), and less commonly *lepidocrocite* (FeOOH), often taken to be an indicator of vegetation fires; and *gibbsite* ($Al(OH)_3$) and/or *boehmite* (AlOOH). Iron minerals are the cementing agents in hardened forms of plinthite.

Water circulation may be hindered by the presence of plinthite or petroplinthite, especially in bottomlands, and gleyic or stagnic features can form.

Origin. The characteristic genetic feature of Plinthosol is the formation of plinthite, which requires a wet, tropical climate so

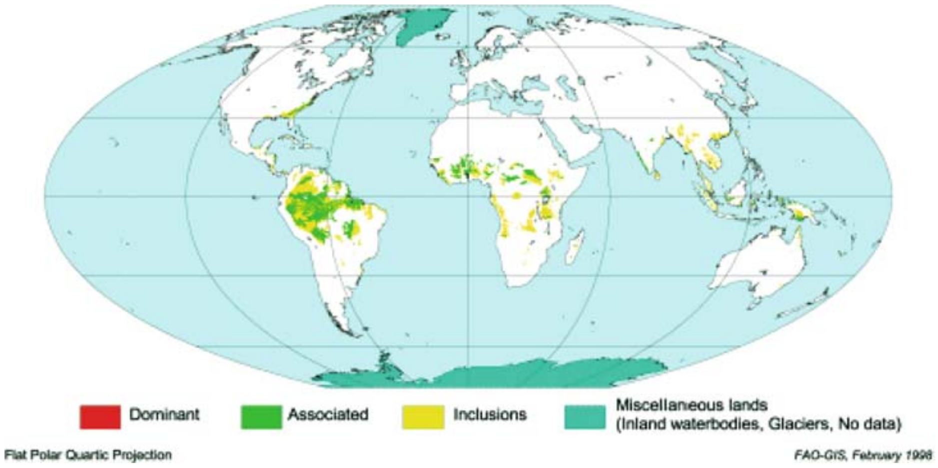


Figure P61 Global distribution of Plinthosols.

that the solum is perennially moist. The following processes are involved:

1. *Accumulation of iron and aluminum by* (*a*) the *removal of silica and base cations* through hydrolysis and leaching over a long period of time. Typically a quartz-kaolinite assemblage is produced. Or (*b*) *absolute accumulation* of iron and aluminum through enrichment from outside.
2. *Segregation of iron* (mottles) by alternating reduction and oxidation, typically producing a pattern of red mottles in a platy, polygonal or reticulate configuration. Reduction (when water saturated) mobilizes iron in ferrous form. Oxidation, when dry, immobilizes it as ferric oxides and hydroxides. Re-dissolution on wetting again is only partial, so that the oxides and hydroxides accumulate with time.

Eluviation is found in some Plinthosols and an *albic* horizon may be present, commonly beneath an *umbric* surface horizon. Plinthosols in bottomlands may develop *gleyic* or *stagnic* properties.

Unaltered, plinthite is soft enough to be cut with a spade. If climate becomes drier or if drying is induced by the removal of vegetation and erosion of the topsoil, plinthite hardens to petroplinthite by

1. *crystallization of amorphous iron phases* to crystalline forms, especially *goethite*, thereby forming continuous aggregates, and
2. *dehydration of goethite* (*FeOOH*) *to hematite* (Fe_2O_3) and, in Al-rich Plinthosols, the dehydration of gibbsite ($Al(OH)_3$) to boehmite (AlOOH).

Both may be inherited from pre-existing materials.

Petroplinthite is resistant to weathering and erosion, so that, on exposure, it becomes a caprock on the landscape, protecting the subjacent formations from further erosion. Meanwhile, the surrounding, unprotected landscape continues to waste away and an inversion of topography may take place.

Where petroplinthite has been eroded and broken up, it may collect as rounded concretions (pisoliths) in alluvium or colluvium and become part of a new soil-forming event. Plinthic soil units in other Reference Soil Groups may form in this way.

Use. Where farmed at all, Plinthosols are mostly used for low volume grazing. Arable cropping is hindered by poor rooting conditions associated with frequent water logging and/or excessive stoniness and low chemical soil fertility.

Limitation for agricultural use is severe. Both plinthite and petroplinthite obstruct the percolation of water and the penetration of plant roots, penetration of plant roots. Hydrodynamic properties are better in skeletic forms, which are cropped for cocoa in West Africa, and cashews in India. However, water-holding capacity is poor, and drought is a problem in the dry season. By contrast, waterlogging hinders their use in the bottomlands, which constitute the more favored situation for Plinthosol formation.

In construction, plinthite is a useful material for making bricks, while the more massive forms of petroplinthite are also cut into building blocks. In addition ironstone gravel is used in foundations for surfacing roads.

Some plinthite is exploited as ores of iron, aluminum, manganese, titanium and other metals. The Ni-bearing laterites of New Caledonia are a notable example.

Otto Spaargaren

Bibliography

Buchanan, F., 1807. A journey from Madras through the Countries of Mysore, Canara and Malbar. Volume 2. East India Company, London, 436–460 pp.

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science*, 2nd edn. Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag. 130 pp.

Cross-references

Acid Soils
Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Tropical Soils

PLOW

Also plough. An agricultural implement, used to prepare soil for sowing or planting. The essential action is to cut a furrow by means of a metal blade, and to turn the soil over with a mold board. In the most primitive examples, a wooden stick, which eventually evolved into a hardwood blade, serves to make the furrow. The transition to an iron blade essentially opened all soils, including heavy clay soils, to cultivation. The plow has been arguably the most important human artifact in modifying the planetary surface.

PLOW LAYER

The total depth of the soil affected by plowing. Commonly designated as the Ap horizon.

Cross-references

Bulk Density
Compaction
Profile

PODZOLS

Podzols have a distinctive ash-gray subsurface horizon, from which iron and aluminum has been leached by organic acids and complexants to be deposited in a dark horizon immediately below. The following account is from FAO (2001).

Connotation. From the Russian *pod,* under, and *zola,* ash.

Synonyms. Podzol is the term used in most national systems, the USDA's Soil Taxonomy, in which these soils are classified as spodosols, being a notable exception.

Definition. Podzols are soils with a *spodic* horizon starting within 200 cm of the soil surface, underlying an *albic, histic, umbric* or *ochric* horizon, or an *anthropedogenic* horizon less than 50 cm thick.

Parent material. Podzols form on unconsolidated, siliceous materials such as quartz-rich sands and sandstones, and on the

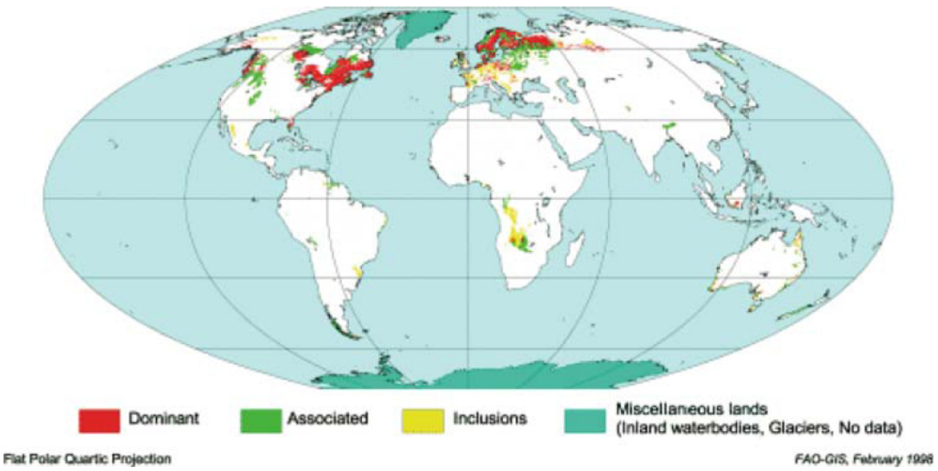


Figure P62 Global distribution of Podzols.

sedimentary debris derived from granitoid rocks and gneisses, originating from glacial and post-glacial processes in particular. If rainfall is high enough, and flow-through rapid, Podzols may occur on almost any materials, as for example in the temperate rainforest of British Columbia. In the tropics Podzols form largely on iron-poor materials.

Environment. Mainly, but not exclusively soils of temperate and boreal regions in the northern hemisphere. Found there, on level or hilly land under ericaceous vegetation and/or coniferous forest. In the humid tropics Podzols occur under light forest.

Distribution. There are about 485 million ha of podzolic soils globally, mainly in the temperate and boreal zones of the Northern Hemisphere. No more than 10 million ha occur in the tropics. Figure P62 shows the global distribution.

Characteristics. Commonly in profiles with O(Ah)EBhsC sequences, with the Ah horizon absent in most boreal Podzols. A layer of organic litter (H horizon) is common at the surface. The O horizon, contains partly humified organic matter mixed with mineral matter, and is very dark in contrast to the eluviated, E (albic) horizon below it. The latter is granular, and overlies a horizon of illuviation (Bhs or spodic horizon) which is subangular blocky to very hard and massive. In the tropics E horizons may reach thicknesses of several meters (Giant Podzols), and (rarely) transported Fe and Al may form mottles of soft concretion-like accumulations in the spodic horizon.

Quartz is the predominant mineral in Podzols, and is an especially obvious, unstained feature of the albic horizon. Where derived from granitoid materials (as in glacial deposits of northern Shield regions) alkali feldspar is a common accompaniment. In the spodic horizon, these primary minerals are normally stained brown or reddish brown by translocated organic matter and Fe. The iron and aluminum deposited in the illuvial horizon may form amorphous or short-range order phases (allophane, imogolite and ferrihydrite for example), though crystalline secondary phases of the hydroxy-interlayered 2 : 1 type are common and beidellite and even kaolinite are known to occur.

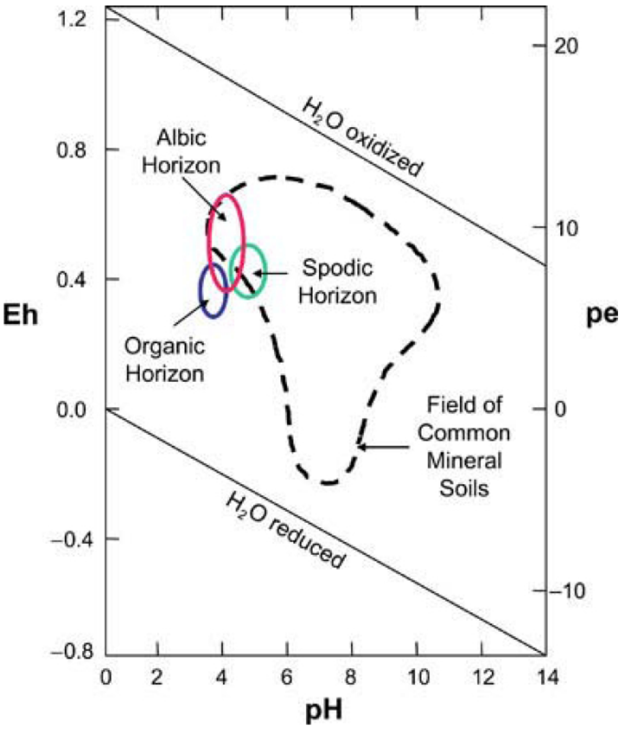


Figure P63 Approximate redox-pH conditions in organic, albic and spodic horizons (after Chesworth and Macias-Vasquez, 1985).

Podzols have a sandy texture, too low in clay to produce well-formed aggregates. They are usually well drained, and may be droughty, even in regions with a high rainfall. If drainage is restricted the B horizon may become weakly cemented in an irregular fashion. When the cemented horizon is hard and continuous, the hardpan is called ortstein or orterde. Podzols of this type are sometimes referred to as groundwater Podzols.

Redox-pH characteristics are shown in Figure P63. Organic matter is concentrated at the surface and below the albic horizon, in the spodic horizon. Earthworms tend to be uncommon and biodiversity is not as great as in less acid soils. Biological activity increases on fertilization.

Origin. The distinctive feature in podzolization is the mobilization of Al, Fe and organic compounds from the A to the B horizon, in percolating water under the influence of gravity. Organic acids in solution, at pH as low as 3.5 attack all primary minerals except quartz, which is left behind in a bleached albic horizon. Organic complexes carry Al and Fe into the B, where humic material as well as amorphous, inorganic compounds of Al and Fe precipitate in an illuvial '*spodic*' horizon.

Podzolization, which is specifically defined as the formation of a spodic horizon, combines two processes among others:

- *cheluviation:* the movement of metal-humus chelates down from surface soil; and
- *chilluviation:* the subsequent accumulation of Al- and Fe-chelates in a *spodic* horizon. The more soluble organic compounds may continue to move to even greater depths.

A rudimentary Podzol morphology may appear in about a century on highly quartzose sands, but on more compositionally complex materials, the time of formation is from one to a few thousand years.

The depth to which water-borne materials are carried is variable. Metal-organic complexes in solution precipitate either through saturation (usually within one meter of the surface), or where the waterfront stops. Other organic components may travel deeper than the illuvial horizon, if the waterfront is deeper. On materials poor in components other than quartz, or after a very long period of pedogenesis, accumulation horizons may extend to even greater depths.

In *hydromorphic situation,* dissolved organic matter with bound Al, can move laterally for considerable distances. When the water reaches the surface it contributes to the 'black water' found in the rivers and lakes in boreal, temperate and tropical regions. The limited depth of the phreatic zone usually restricts vertical transport in the soil.

If water unsaturated in organic substances reaches the top of an illuviation horizon formed earlier under slightly different conditions, the existing, solid Al,Fe-humus complexes can redissolve. With time, the entire spodic horizon can slowly be remobilized to greater depth.

Giant Podzols with the illuvial horizon several meters down, form in hot climates with high precipitation rates (the humid tropics for example) on base-poor, quartzose sands. The spodic horizon may be entirely lacking if the mobile humus is removed by lateral flow of groundwater.

Use. Podzols suffer from major limitations for arable agriculture. Fertility is low by virtue of a high degree of leaching. Plant nutrients are concentrated in the surface soil, though phosphate tends to accumulate in the B horizon where it is fixed by Al and Fe. Also, the soils drain rapidly in most cases and have a low available water capacity. High acidity, Al-toxicity and P-fixation are common. The presence of hardpan may be a further complication. In addition Podzols usually occur in regions of colder climate – the boreal forest for example.

If the climate allows, they may be prepared for cropping by deep plowing, and by chemical fertilization. Otherwise they are best left to forestry, or to low intensity grazing.

Otto Spaargaren

Bibliography

Chesworth, W., and Macias-Vasquez, F., 1985. pe, pH and podzolization. *Am. J. Sci.*, **285**: 128–146.

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science*. 2nd edn. Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Acid Soils
Biomes and their Soils
Classification of soils: World Reference Base (WRB) for soil resources
Classification of soils: World Reference Base (WRB) Soil Profiles

POINT OF ZERO NET CHARGE

The pH of a solution in equilibrium with a mineral, at which the total positive and negative charges are equal. It marks the point at which a mineral changes from the possibility of acting as an anion adsorber to cation adsorption.

POLLUTION

The presence in the environment, or the introduction into it, of products produced by human activity, which have harmful effects on environmental quality from the standpoint of the living organisms there, including human beings, and not excluding aesthetic considerations. Note that certain natural processes have deleterious effects on environmental quality similar to those of pollution (volcanic eruptions for example). Use of the word pollution for such instances is improper, since human agency is not involved.

POLYCYCLIC

Said of a landscape or soil produced by more than one cycle of weathering.

POLYGENETIC

Said of a landscape that has been subjected to a wide variation in one of its principal formative factors, climate for example. Used also of a soil the profile of which is a composite of horizons from more than one soil-forming event.

POLYGONAL

Many sided closed geometric figure, commonly six-sided in polygonal features in soil. Polygonal patterns of cracks are common in soils with swelling clays (Vertisols for example), and hexagonal features such as arrangements of pebbles on a soil surface, are common on periglacial landscapes (patterned ground), and are caused by freeze-thaw processes. Vertical polygonal columns occur in the B horizons of salt affected soils, Solonetz in particular.

Cross-references

Ice Erosion
Solonetz
Vertisols

POLYPEDON

A group of similar pedons in lateral gradation, for example as part of a catena, and generally mapped as a single cartographic unit.

PORE

A void-space in soil, saturated (filled) with water in the phreatic zone below the water table, and with insufficient (if any) water to completely fill the void, in the vadose zone. In the vadose zone of a soil, pores contain mainly gases from the atmosphere, with an admixture of gases (particularly CO_2) produced by respiration and the decay of organic matter.

Cross-reference

Soil Pores

PORE SIZE DISTRIBUTION

See *Soil Pores*.

PORE SPACE, DRAINABLE

See *Soil Pores*.

POROSITY

The property of being porous. Operationally, the total volume in a soil or sediment, not occupied by solid materials. The interconnectivity of pores is a principal determining factor in hydraulic conductivity.

Cross-reference

Soil Pores

POTASSIUM CYCLE

Potassium is one of the major nutritional elements in soil, Sparks and Huang (1985) describe its role in the biosphere as ‘prodigious’. Its chemical symbol K is taken from Kalium, the German term for the element, derived from the word alkali. K influences the osmotic relations between plant and soil, functions in respiration and photosynthesis, and is an enzyme activator.

The word alkali was introduced by the Arabs to signify the ash of vegetable matter. Incineration of marine vegetation yields predominantly sodium carbonate, while terrestrial vegetation gives potassium carbonate. It was not until the eighteenth century that the two were distinguished from each other. Together they were considered fixed alkali, by contrast to ammonium carbonate, which was called volatile alkali. A further distinction was made by the Arabs between mild alkali (carbonate) and caustic alkali (hydroxide). Davy isolated the element potassium electrochemically in 1807 and derived its name from “pot ashes”, adding the Latinate suffix “ium”. The term “potash” survives in the literature of agriculture and the fertilizer industry to refer to the oxide, K_2O.

Occurrence

Potassium is the 7th most abundant element in the Earth’s crust, occurring principally as potassium feldspar and mica, in acid igneous rocks and their metamorphic equivalents. In the form of quartzo-feldspathic rocks, these make up about two thirds of the continental crust. The less common potassium-rich silicates that belong to the feldspathoid and zeolite groups, are only of local significance.

In the sedimentary realm, the common K-bearing silicate is illite. It may form as a weathering product of feldspar, via the intermediate product of hydrothermal alteration, sericite, or by the degradation of the white mica muscovite. Alternatively, illite may be produced during the process of diagenesis of clay-rich clastic sediments. Glauconite is a sheet silicate that forms authigenically in the sedimentary realm, and is taken as an indicator of an originally marine environment.

All the major geological sources of K in commercial fertilizer are from the sedimentary deposits known as evaporites. In Europe the classic examples are deposits in Germany (particularly at Stassfurt) and France (Alsace). Currently, the most productive are in Saskatchewan, Canada.

The formulae and occurrences of K minerals are summarized in Table P15.

The potassium cycle

Figure P64 provides a general idea of the movement of K on a global scale. Details of its movement in soils require a consideration of the weathering of the primary minerals.

Weathering of quartzo-feldspathic rocks causes the slow release of structural potassium in primary minerals. The agent of change is the slightly acid water of CO_2-charged atmospheric precipitations (pH about 5.7), in which the acidity may be augmented in soil by two orders of magnitude (in Podzolic soil waters for example) by virtue of the presence of organic acids in the upper parts of the solum. Rates of alteration of the acid rocks are generally in the range of one micron thickness per 10^3 to 10^4 years.

The stabilities of potassium feldspar and its low temperature breakdown products are shown in Figure P65. Projection of the

Table P15 Potassium bearing minerals and their occurrence

Mineral	Formula	Occurence
1. Aluminosilicate minerals		
Potassium feldspar	$KAlSi_3O_8$	Acid igneous and metamorphic rocks. Polymorphs: adularia, orthoclase, microcline
Mica	Biotite: $K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$ Muscovite: $KAl_2(AlSi_3O_{10})(F,OH)_2$	Acid igneous and metamorphic rocks. Clastic sedimentary rocks
Glauconite	$(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$	Marine sedimentary rocks
Sericite	Between muscovite and illite	Hydrothermal alteration of K feldspars
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	Alteration of sericite. Diagenesis of clays
Feldspathoids	Kalsilite: $KAlSiO_4$ to Nepheline $NaAlSiO_4$ Leucite: $KAl(SiO_3)_2$	Alkaline vocanics and rare plutonics
Zeolites	Clinoptilolite: $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36} \cdot 12H_2O$ Mordenite: $(Ca,Na_2,K_2)Al_2Si_{10}O_{24} \cdot 7H_2O$ Chabazite: $(Ca,Na_2,K_2,Mg)Al_2Si_4O_{12} \cdot 6H_2O$	Low grade metamorphic rocks. Hydrothermal to low temperature alteration of feldspars
2. Evaporite minerals. All occur in natural deposits produced by evaporation of hydrothermal waters or seawater		
Sylvite		KCl
Saltpeter nitre		KNO_3
Carnallite		$KMgCl_3 \cdot 6(H_2O)$
Kalinite		$AlK(SO_4)_2 \cdot 12H_2O$
Kainite		$MgSO_4 \cdot KCl \cdot 3H_2O$
Polyhalite		$K_2Ca_2Mg(SO_4)_4 \cdot 2(H_2O)$
Sylvinite		Mixture of sylvite (KCl) and halite ($NaCl$)

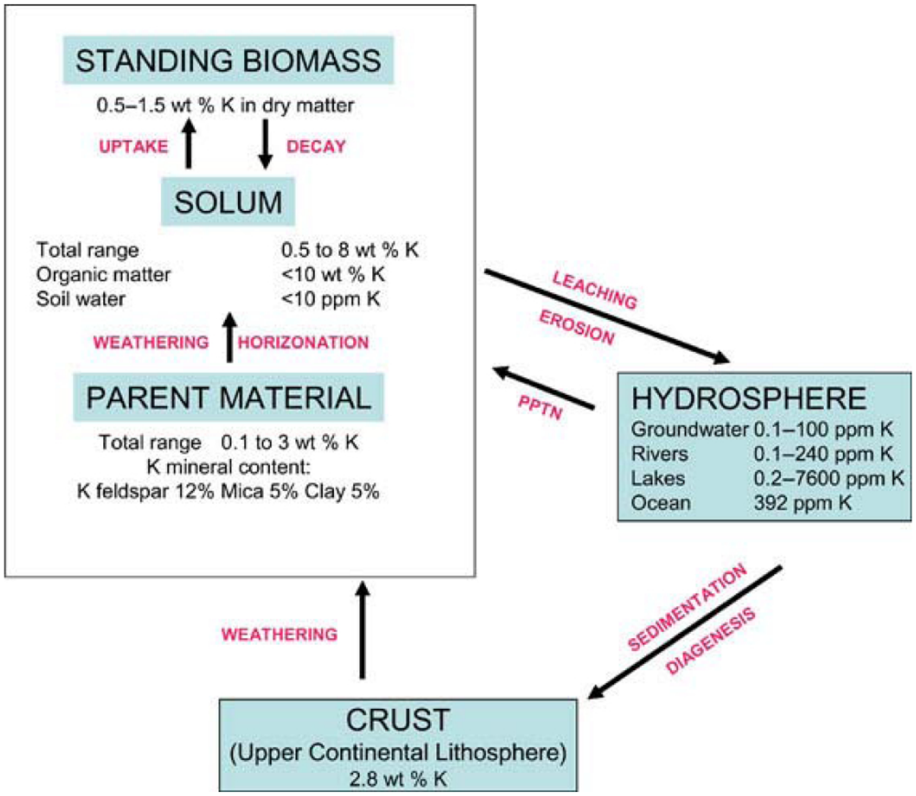


Figure P64 A general view of the potassium cycle, emphasizing the soil. Within the soil, K is shown in three compartments. K in the soil solution is instantly available to organisms as K^+. Fixed K is structurally incorporated into primary minerals such as the feldspars and micas, inherited from lithospheric parent materials, as well as K in interlayer structural positions in 2:1 clays such as illite and sericite. In fact ‘fixed’ K is very slowly released by weathering. Exchangeable K is K^+ adsorbed on negatively charged exchange sites on clay minerals and organic matter. It is readily available. In agriculture, where K is removed in the crop, K is replaced as soluble fertilizers, or as exchangeable K in manures and composts.

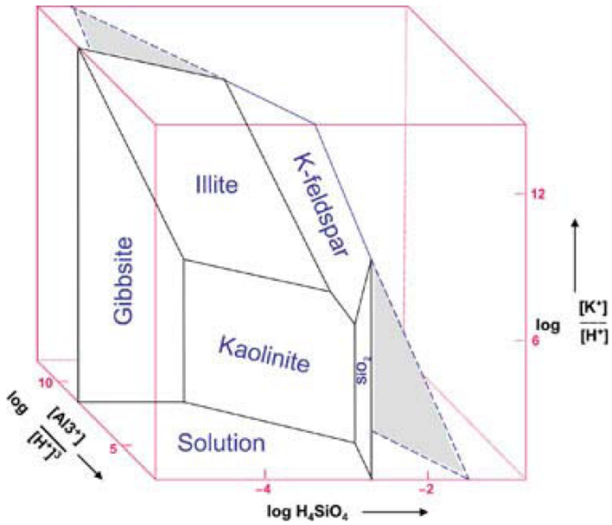


Figure P65 The stability of potassium feldspar under Earth-surface conditions. The *shaded portion* of the K-feldspar surface lies behind the precipitation surfaces of the secondary minerals and represents conditions under which the feldspar would dissolve incongruently when equilibrium prevails. The *unshaded portion* would allow K-feldspar to dissolve congruently.

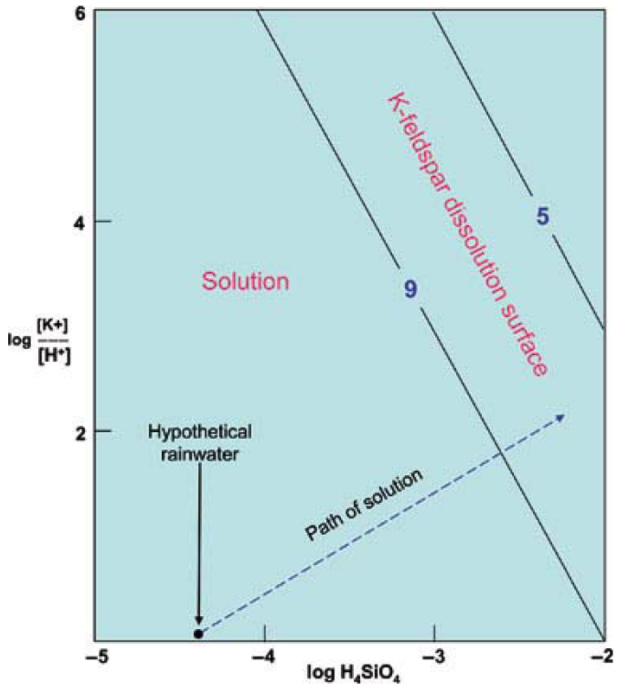


Figure P66 Projection of Figure P65 along the log$[Al^{3+}]/[H^+]^3$ axis. The K-feldspar solution surface is shown between the values of log$[Al^{3+}]/[H^+]^3$ between 5 and 9. A path of congruent solution is marked by the *dashed arrow*.

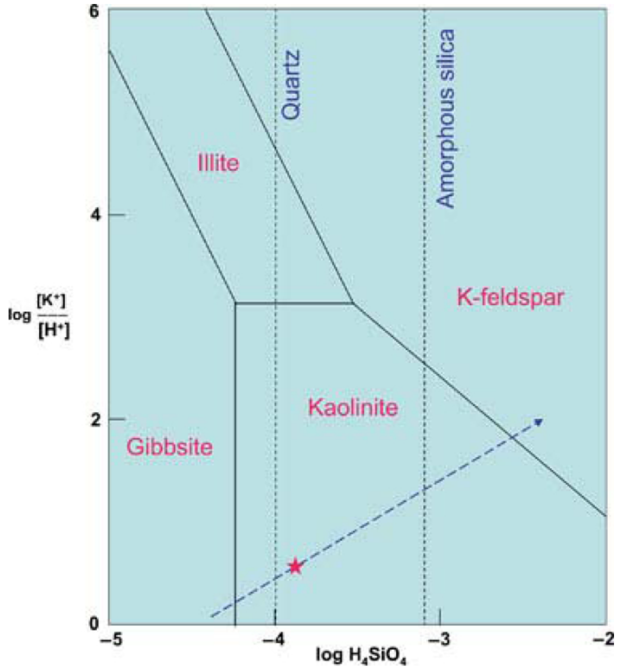


Figure P67 Projection of the solution-present volume of Figure P65 along the log$[Al^{3+}]/[H^+]^3$ axis, with the solution path of Figure P66 added. The star is the mean composition of podzolic soil waters recorded in Macias-Vazquez et al. (1987). Kaolinite would be the expected secondary product.

feldspar dissolution surface down the log $[Al^{3+}]/[H^+]^3$ axis gives Figure P66. The simplest reaction for the breakdown of K feldspar during weathering is one of congruent dissolution by the hydrolytic reaction:

$$\overset{\text{K-feldspar}}{KAlSi_3O_8} + 4H_2O + 4H^+ \rightleftharpoons K^+ + Al^{3+} + 3H_4SiO_4 \quad (1)$$

Figure P66 shows a solution path according to Reaction (1). The actual path is dictated by the starting point and the stoichiometry of the dissolving feldspar (i.e., the extent to which Na and Ca substitute for K in the orthoclase, microcline or adularia structures).

Projection of Figure P65 gives Figure P67, on which the general composition field for soil water is shown. The solution path from Figure P66 is also shown. This indicates that the path for most likely conditions at the surface of the earth intersects the fields of the secondary minerals in Figure P65, before it reaches the saturation surface of K-feldspar. Commonly the reaction proceeds as far as to produce kaolinite as in the example shown in Figure P67 from a region of podzolization in northwestern Spain. Assuming equilibrium is established the reaction involved is:

$$\overset{\text{K-feldspar}}{2KAlSi_3O_8} + 4H_2O + 2H^+ \rightleftharpoons 2K^+ + \overset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 4H_4SiO_4$$

This is a reaction of incongruent solution, that is, one that results in the production of a secondary solid phase in addition to species in solution. In this case the remaining solution contains K^+ and the neutral species H_4SiO_4. The K^+ is available for uptake by plants or for adsorption onto exchange sites on clays or organic matter. Alternatively a portion may stay in solution to be leached away in humid climatic zones, whereas

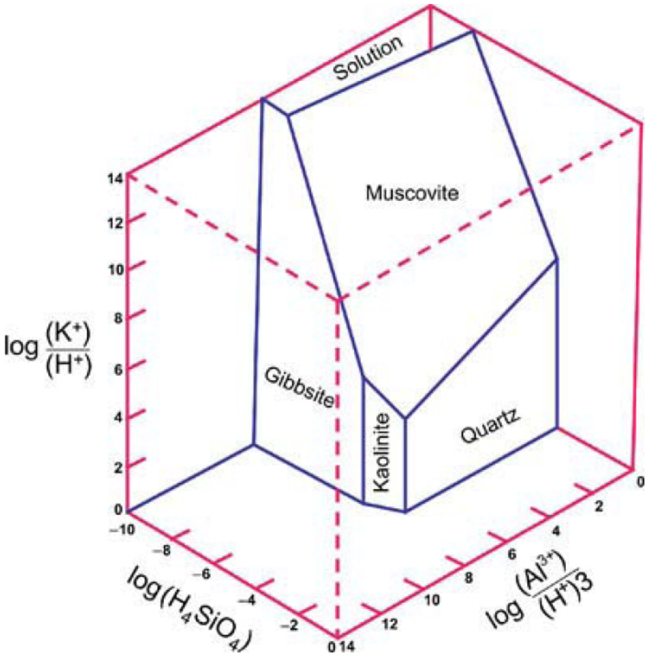


Figure P68 Muscovite and secondary phases in equilibrium with aqueous solution under Earth-surface conditions. The solution volume is constructed from data in Bowers et al. (1984).

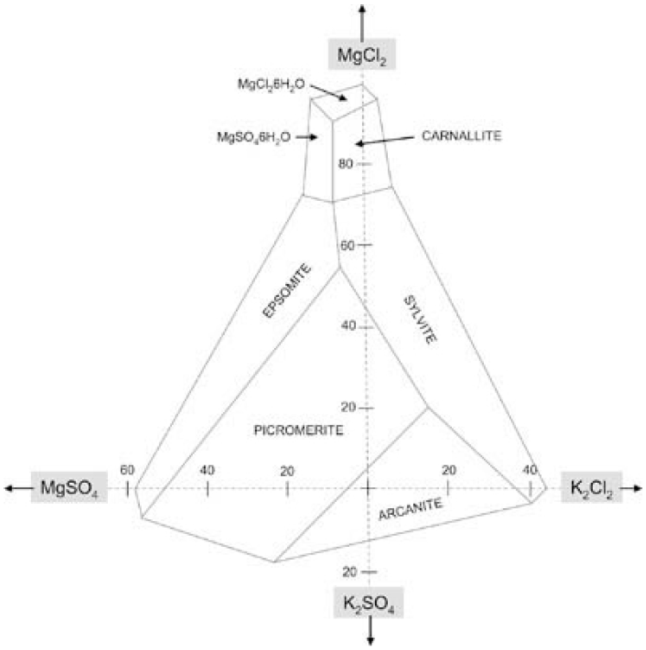


Figure P69 The solution volume for evaporite minerals in the system K–Mg–Cl–SO_4, under earth-surface conditions.

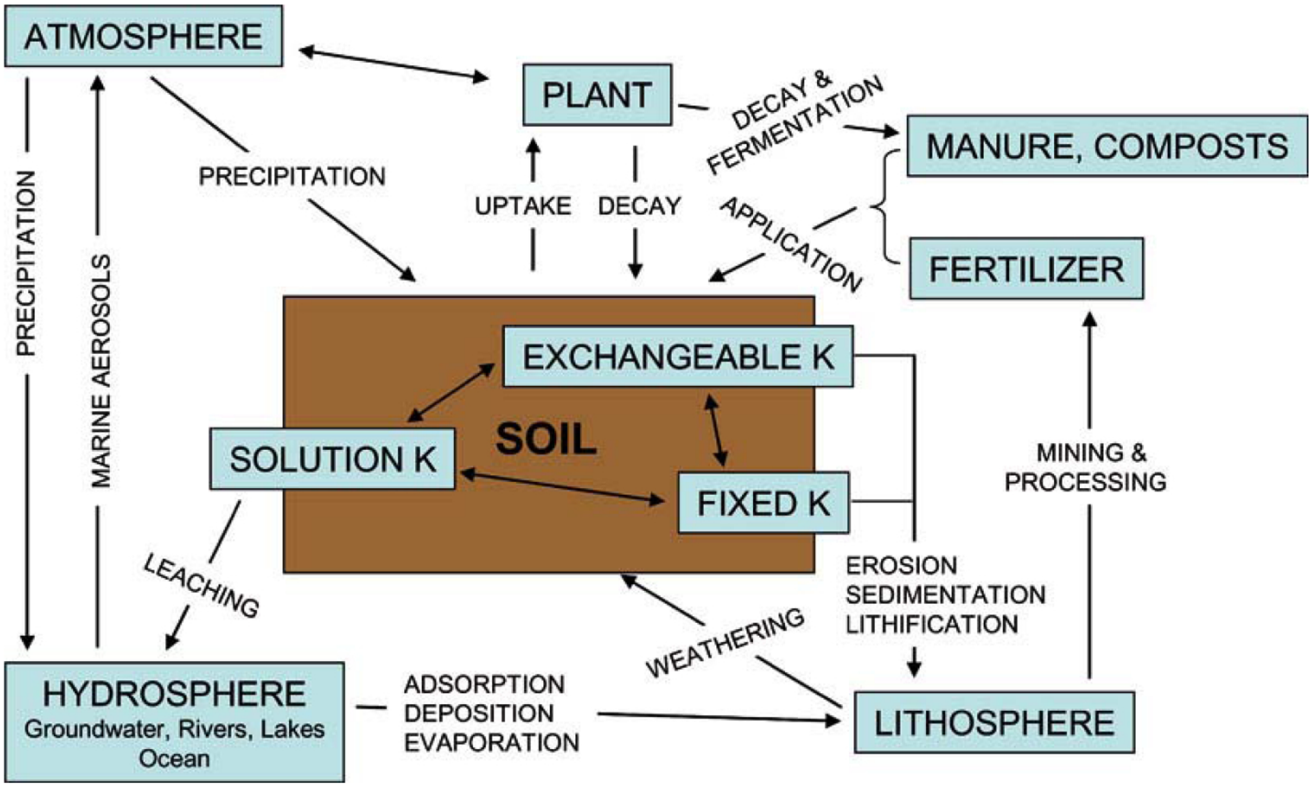


Figure P70 The potassium cycle emphasizing the centrality of the soil compartment at the earth’s surface.

in arid and semi-arid regions with a net water deficit, it may be deposited in the solum in various sodium salts or even in zeolites, (with K isomorphously substituting for Na).

K^+ may also be released by the weathering of muscovite. Figure P68 shows the equilibrium limits of the solution surface for muscovite. Again kaolinite is likely to be the ultimate product in most weathering systems.

The final geochemical fate of any K^+ that is leached from soil is to be carried to the ocean, or in regions with internal drainage, into saline lakes. Evaporation in the latter, and in the marine environment along coastal sabhkas or salars, can then remove K from solution, commonly with Na, Mg and Ca as various salts. Figure P69 illustrates conditions under which carnallite and sylvite form in a Mg-containing brine.

Figure P70 is a version of the potassium cycle at the surface of the Earth, with the emphasis on the soil environment. Within the soil, the availability of K as a nutrient varies widely. In the soil solution (as K^+) it is immediately available, as is the so-called exchangeable K^+ adsorbed on negatively charged sites on clay minerals and organic matter. At the other extreme, structural K incorporated into primary minerals, and clay phases such as illite, is essentially unavailable, at least to the higher plants.

In farmed soils, the K removed by harvesting, is not replaced fast enough by the natural process of weathering to sustain an annual cropping system, hence the need for fertilizer or manure application, composting, or crop rotations that include periods of fallow.

K fertilizer

Production

Evaporite deposits are the main source of fertilizer K. Extraction is normally by underground mining or by solution mining as in Saskatchewan. Solution mining is easier than underground mining, but any economic advantage may be offset by the cost of evaporating the resultant solution, natural gas being the usual fuel. In areas of a hot dry climate, saline lakes such as the Dead Sea in Jordan, are exploited, evaporation being by solar heat. Table P16 shows the FAO statistics for major producers.

Table P16 Major producers of K_2O in million t (data for 2005 from USGS, 2006)

Canada	9.70
Russian Federation	4.09
Belarus	4.07
Germany	3.45
Israel	1.90
Jordan	1.09
USA	1.09
Rest	2.73
World	28.12

Table P17 Regional consumption of K_2O in million t (statistics from the International Fertilizer Industry Association, 2006)

Region	Consumption			
	1975/1976	1985/1986	1995/1996	2005/2006
Western Europe	5.19	5.71	4.33	3.04
North America	4.95	4.98	5.08	4.65
Latin America	0.93	1.70	2.33	4.45
Africa	0.32	0.42	0.40	0.39
Developed	19.32	21.23	11.95	9.62
Developing	2.09	4.40	8.60	16.82
World	21.42	25.63	20.55	26.44

Consumption

In much of the developing world the principal source of potash is manure, and unlike N and P, the K in animal manures is not fixed to other compounds, so that it is readily available to plants. Elsewhere K as chloride or sulfate salts is used in fertilizer formulations. Statistics on K_2O consumption from fertilizer sources are shown in Table P17. In industrialized agriculture 20 to 80 kg K_2O per hectare is the common range of application.

Ward Chesworth

Bibliography

Bowers, T.S., Jackson, K.J., and Helgeson, H.C., 1984. *Equilibrium Activity Diagrams: for Coexisting Minerals and Aqueous Solutions at Pressures and Temperatures to 5 kb and 600 °C.* Berlin: Springer, 397 pp.

International Fertilizer Industry Association. 2006. Accessed at http://www.fertilizer.org/ifa/statistics/indicators/tablek.asp.

Macias-Vazquez, F., Fernandez-Marcos, M-L., and Chesworth, W., 1987. Transformations mineralogiques dans les sols podzoliques de Galice (N.W. Espagne). In Righi, D., and Chauvel, A., eds., *Podzols et Podzolization.* Paris: AFES-INRA, pp. 163–177.

Sparks, D.L., and Huang, P.M., 1985. Physical chemistry of soil potassium. In Munson, R.D., ed., *Potassium in Agriculture.* Madison, WI: Soil Science Society of America, pp. 201–276.

USGS, 2006. *Mineral Commodity Summaries*. Washington, DC: United States Government Printing Office, U.S. Geological Survey. 199 pp.

PRAIRIE

The French word for field adapted in North America to designate the extensive grassland in the center of the continent. The Spanish word Pampas is used for the grasslands in South America (Argentine). Steppe is the equivalent used for the grasslands of Eurasia, puszta is used in Hungary and veldt in South Africa.

Bibliography

Suttie, J.M., Reynolds, S.G., and Batello, C., 2005. *Grasslands of the World.* Rome: Food and Agricultural Organization of the United Nations, 514 pp.

Cross-reference

Biomes and their Soils

PRIMARY MINERAL

Originally a mineral formed by the crystallization of magma in the production of igneous rock. In soil science, essentially any mineral needing a high temperature and/or pressure for its formation, and therefore not capable of originating by weathering, pedogenetic, or sedimentary processes.

PRIMARY PRODUCTIVITY

Net Primary Productivity (NPP) is the net amount of energy a plant accumulates during a specific time period. The unit in the accompanying map is kg carbon per square meter per year. Since the mass of a plant is directly related to the energy accumulated by the plant, the NPP can also be considered as the amount of mass a plant gains (or grows) over some period of time. NPP is (or better yet, how much the plant grows over a given time frame). NPP is calculated by taking the *gross primary productivity* (the total amount of energy/mass taken in by the plant) minus the total amount of energy/mass lost by the plant as it respires.

PRISMATIC

Having a relatively regular enclosed three-dimensional form, such as the polygonal columns found in the B horizons of salt affected soils. See *Polygonal*.

PROFILE

A soil profile is a vertical section through soil. A complete soil profile displays all horizons of a soil down to unweathered material or bedrock. Within the profile, horizons are designated as follows in the American system of Soil Taxonomy. See *Horizon Designations in the WRB* (*q.v.*) for information concerning that system of classification.

1. Capital letters designate the principal horizons as shown in Table P18.
2. Lower case letters indicate the principle formative process of a horizon and qualify the principal horizon designation as a subscript, as shown in Table P19.
3. Numerical subscripts are used to designate the sequence of particular horizons.
4. Transitional horizons are indicated by the two capital letters that pertain to the horizons affected.
5. Lithological discontinuities are indicated numerically with the numbers used as prefixes to the horizons affected.

Diagnostic horizons

A diagnostic horizon is distinctive of a particular class of soils and may therefore be used to distinguish one class of soil from another. It is one of the most important concepts in soil classification and was introduced by the U.S. Department of Agriculture. It has since been adopted in other systems of classification, most notably by the World Resource Base system.

In Soil Taxonomy there are two broad types of diagnostic horizon: those that form at the surface (epipedons) and those that form below the surface (called endopedons by Miller and Donahue, 1990). They are used to distinguish among soil orders, suborders, great groups, and subgroups in the classification. The brief description of each horizon given below derive from Miller and Donahue's text and are meant in the spirit of those authors, to give the reader a rapid grasp of the essential feature of a particular horizon. In other words they are not definitive. For the definitive treatment refer to Soil Survey Staff (1999).

1. Epipedons and other near-surface horizons
   - *Albic horizon:* A strongly leached, commonly whitish, E horizon.
   - *Anthropic epipedon:* A mollic horizon formed by human activity.
   - *Histic epipedon:* An organic surface horizon underlain by mineral soil.
   - *Mollic epipedon:* A dark, friable surface horizon, not strongly acidic.
   - *Ochric epipedon:* A thin or light-colored surface.
   - *Plaggen epipedon:* An anthropic horizon, high in humus due to long term manuring.
   - *Umbric epipedon:* An acidic dark horizon.
2. Endopedon horizons
   These horizons commonly show an accumulation of colloids or are weathered.
   - *Agric horizon:* A tillage-caused clay and humus accumulation horizon.
   - *Argillic horizon:* A horizon of clay accumulation.
   - *Cambic horizon:* A "color" or weakly developed B horizon.
   - *Kandic horizon:* An argillic horizon with 1 : 1 sheet silicates.
   - *Natric horizon:* Like an argillic but with a high exchangeable sodium content.
   - *Oxic horizon:* A highly weathered B horizon.
   - *Sombric horizon*: An acidic, humus accumulation, tropical B horizon.
   - *Spodic horizon:* An acidic, cool area, humus and/or sesquioxide accumulation B horizon.
3. Endopedons from accumulations of solubilized substances
   - *Calcic horizon:* A calcium carbonate accumulation horizon.
   - *Gypsic horizon:* A horizon of gypsum accumulation.
   - *Salic horizon:* A soluble salt accumulation horizon, commonly saline.
   - *Sulfuric horizon:* A horizon high in sulfides (pyrite, the commonest).

Hardpan horizons

- *Duripan:* A hardpan with silica cement, usually with some carbonates.
- *Fragipan:* A brittle pan of relatively high density, with little or no cement.
- *Petrocalcic horizon:* A hard pan with calcite cement.
- *Petrogypsic horizon:* A hard pan with gypsum cement.
- *Placic horizon:* A very hard pan with an iron oxide or hydroxide phase as cement. Mn and organic matter may also be involved.

Carmela Monterroso

Bibliography

Miller, R.W., and Donahue, R.L., with Miller, J.U., editorial assistant, 1990. *Soils: An Introduction to Soils and Plant Growth*. Englewood Cliffs, NJ: Prentice-Hall, 768 pp.

Table P18 Master soil horizons and layers in a profile

New	Old	Description
O	O	Organic horizons of minerals soils. Horizons (*i*) formed or forming in the upper part of mineral soils above the mineral part; (*ii*) dominated by fresh or partly decomposed organic materials; and (*iii*) containing more than 30 percent organic matter if the mineral fraction is more than 50 percent clay, or more than 20 percent organic matter if the mineral fraction has no clay. Intermediate clay content requires proportional organic matter content.
Oi	O1	Organic horizons in which essentially the original form of most vegetative matter is visible to the naked eye. The Oi corresponds to the L (litter) layer in forest soils designations and to the horizon formerly called Aoo or O1.
Oa or Oe	O2	Organic horizons in which the original form of most plant or animal matter cannot be recognized with the naked eye. The Oa corresponds to the H (humification) and Oe to F (fermentation) layers in forest soils designations and to the horizon formerly called Ao or O2.
A	A	Mineral horizons consisting of (*i*) horizons of organic matter accumulation formed or forming at or adjacent to the surface: (*ii*) horizons that have lost clay, iron, or aluminum with resultant concentration of quartz or other resistant minerals of sand or silt size; or (*iii*) horizons dominated by (*i*) or (*ii*), but transitional to an underlying B or C.
A	A1	Mineral horizons, formed or forming at or adjacent to the surface, in which the feature emphasized is an accumulation of humified organic matter intimately associated with the mineral fraction.
E	A2	Mineral horizons in which the feature emphasized is the loss of clay, iron, or aluminum, with resultant concentration of quartz or other resistant minerals in sand and silt sizes.
AB or EB	A3	A transitional horizon between A or E and B, dominated by properties characteristic of an overlying A or E but having some subordinate properties of an underlying B.
AB	AB	A horizon transitional between A and B, having an upper part dominated by properties of A and a lower part dominated by properties of B; the two parts cannot be conveniently separated into A and B.
E/B	A and B	Horizons that would qualify for E except for included parts constituting less than 50 percent of the volume that would qualify as B.
AC	AC	A horizon transitional between A and C, having subordinate properties of both A and C but not dominated by properties characteristic of either A or C.
B	B	Horizons in which the dominant feature or features is one or more of the following: (*i*) an illuvial concentration of silicate clay, iron, aluminum, or humus, alone or in combination: (*ii*) a residual concentration of sesquioxides or silicate clays, alone or mixed, that has formed by means other than solution and removal of carbonates or more soluble salts; (*iii*) coatings of sesquioxides adequate to give conspicuously darker, stronger, or redder colors than overlying and underlying horizons in the same sequum but without apparent illuviation of iron and not genetically related to B horizons that meet requirements of (*i*) or (*ii*) in the same sequum; or (*iv*) an alteration of material from its original condition in sequums lacking conditions defined in (*i*), (*ii*), and (*iii*) that obliterates original rock structure, that forms silicate clays, liberates oxides, or both, and that forms granular, blocky, or prismatic structure if textures are such that volume changes accompany changes in moisture. A sequum is an E horizon and its related B horizon.
BA or BE	B1	A transitional horizon between B and A or between B and E in which the horizon is dominated by properties of an underlying B but has some subordinate properties of an overlying A or E.
B/E	B and A	Any horizon qualifying as B in more than 50 percent of its volume, including parts that qualify as E.
B or Bw	B2	That part of the B horizon where the properties on which the B is based are clearly expressed characteristics, indicating that the horizon is related to an adjacent overlying A or an adjacent underlying C or R.
BC or CB	B3	A transitional horizon between B and C in which the properties diagnostic of an overlying B are clearly expressed but are associated with clearly expressed properties characteristic of C.
C	C	A mineral horizon or layer, excluding bedrock, that is either like or unlike the material from which the solum is presumed to have formed, relatively little affected by pedogenic processes, and lacking properties diagnostic of A or B but including materials modified by (*i*) weathering outside the zone of major biological activity; (*ii*) reversible cementation, development of brittleness, development of high bulk density, and other properties characteristic of fragipans; (*iii*) gleying; (*iv*) accumulation of calcium or magnesium carbonate or more soluble salts; (*v*) cementation by accumulations, as calcium or magnesium carbonate or more soluble salts; or (*vi*) cementation by alkali-soluble siliceous material or by iron and silica.
R	R	Underlying consolidated bedrock, such as granite, sandstone, or limestone. If presumed to be like the parent rock from which the adjacent overlying layer or horizon was formed, the symbol R is used alone. If presumed to be unlike the overlying material, the R is preceded by an arabic numeral denoting lithologic discontinuity, such as 2R.

Soil Survey Staff, 1999. *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys*, 2nd edn. U.S. Dept. of Agriculture Handbook 436, Washington DC: Government Printing Office, 869 pp.

Cross-references

Anthrosols
Horizon Designations in the WRB

PROFILE, PHYSICAL MODIFICATION

Broadly speaking, physical properties are modified by all mechanical and chemical processes that operate in soils, whether natural or human-induced. Naturally occurring processes such as wetting and drying or freezing and thawing are not discussed here; instead, this article focuses on modifications imposed by humans, both intentionally and non-intentionally. Modifications at three different scales are considered, the first two briefly and the third at some length. As used here, modification of physical properties refers to changes in one or more characteristics affecting root growth in the soil profile, chiefly but not entirely below the plow layer or Ap horizon.

Microscale changes are alterations of soil properties in a small volume of soil or over distances of millimeters, centimeters, or a few meters at most. Microscale changes in soil properties occur when a person walks across a garden. Normally, the soil will be compacted slightly in each footprint. Compaction results in a slightly higher bulk density (mass of

Table P19 Suffixes used to indicate subordinate distinctions in master horizons

New	Old	Description	Examples
a	–	High degree of decomposition of organic matter	Oa
b	b	Genetic soil horizon buried under at least 50 cm of sediment	Ab
c	cn	Accumulation of concretions or other hard nodules enriched particularly in Fe and/or Al	Bc
e	–	Intermediate degree of decomposition of organic matter	Oe
f	f	Frozen soil; mostly for permafrost (permanently frozen)	Af
g	g	Strongly gleyed. Anaerobic conditions due to waterlogging. Grey colors indicate reduction and removal of iron. Mottles (brighter orange and yellow colors of oxidized iron) may be present	Cg
h	h	Iluvial humus, usually coating sand particles or as pellets. Particularly applied to B horizons	Bh
i	–	Slight degree of decomposition of organic matter (litter)	Oi
k	ca	Accumulation of carbonates, usually calcite (±Mg)	Bk
m	m	Stronly cemented by various materials	Cm
n	sa	Accumulation of sodium salts	Bn
o	–	Residual accumulation of Fe and/or Al	Bo
p	p	Layer disturbed by plowing	Ap
q	si	Accumulation of silica, usually as a cement	Bq
r	r	Weathered or soft bedrock (saprolite)	Cr
s	ir	Iluvial accumulation of Fe and/or Al, commonly as coatings on sand particles, as pellets, or as cement	Bs
t	t	Accumulation of a usually large amount of clay	Bt
v	–	Plinthite present	B2v
w	–	Weakly developed color or structural B	Bw
x	x	Horizon with fragipan character (firm, brittle, with a high density)	B3x
y	cs	Horizon of gypsum accumulation	C1y
z	sa	An accumulation of salts more soluble than gypsum	B3z

oven-dry soil per unit volume), with lower total and macroporosity and lower saturated hydraulic conductivity. Modifications at this scale usually are of minor importance and will not be considered further.

Tillage modifies physical properties at a larger scale. Some tillage operations affect the *entire surface layer* of soil throughout the field. Moldboard plows shear the uppermost horizons or layers, changing the total porosity and pore size distribution. Secondary tillage, such as disking or harrowing, alters the uppermost part of the plow layer or Ap horizon to break down clods, to ensure adequate seed-soil contact, and, on occasion, to kill weeds. By altering the physical properties of all or part of the Ap horizon, tillage affects aeration, water movement, physical resistance to root penetration, and heat exchange. Although generally beneficial, tillage may also be harmful to plant growth. Plowing wet soils can cause puddling and poor tilth. Disking can loosen the top 10 cm of soil and compress the next deeper 10 cm. Although there is a trend toward elimination or reduction in the number of annual tillage events, tillage remains a common practice in crop production. The effects of tillage have long been studied and are well known, so common tillage practices will not be considered further here. Rather, attention is directed to physically modifying properties of all or much of the soil profile (a vertical section down through the soil). Such efforts date back thousands of years (Crews and Gliessman, 1991) but did not become widespread until powerful tractors and large machines were developed.

Some soils have one or more horizons (individual layers within profiles) with properties that hinder or completely inhibit root penetration and growth. Soils with tillage pans, fragipans, duripans, claypans, and high clay content horizons are examples. The aim of modifying root-restricting horizons is to increase the rooting volume. Such modification has been largely through mechanical means (e.g., subsoiling, deep plowing, and mixing soil layers).

Deep, coarse-textured soils may also benefit from modification, the objective in this case being to provide favorable conditions for water retention and root growth. Additional modification strategies include the addition of chemicals, such as the deep placement of lime or fertilizer, or both, or incorporation of inorganic amendments or sphagnum moss (e.g., Grace et al., 2006).

Soil profile modification

Certainly one of the earliest soil modification projects was the construction of raised fields in Central and South America, which date to as early as 2000 B.C. (Crews and Gleissman, 1991). Low-lying land too wet for crop production was raised to higher elevations using soil material removed from canals that were constructed around the perimeters of each raised field. The higher elevation of the raised field improved the internal drainage of the soil, thus providing a better environment for root growth, and allowed the farmers to grow crops. More recently, methods of modifying soil profiles range from chiseling and subsoiling to adding asphalt barriers at depth and even using dynamite.

Chiseling and subsoiling are used more widely than any other methods to modify the physical properties of soil profiles. The two are alike in that both disturb the soil to some depth without inverting it. Each is performed with a steel beam or shank and requires a large amount of energy. Subsoilers commonly have a shoe or sweep at the bottom and chisels do not. To distinguish the two in this article, chiseling is restricted to disturbance above the depth of 40 cm, whereas subsoiling refers to disturbance below this depth (Cooper, 1971). Each implement is adjusted to penetrate to the desired depth and is then pulled across a field at appropriate intervals. Both are meant to break up a sub-surface layer or layers (see *Pan*), and both are most effective, but require more energy, when the soil is dry. If a soil is wet enough to be plastic, neither operation is effective. Cooper (1971) reports that very compact layers will break up at water contents ranging from field capacity almost to the wilting point, but true “shattering” of the layer into many smaller fragments rarely occurs (see *Field* *water cycle*). Chiseling is an alternative to moldboard plowing in many areas of the world. In the USA the chisels are spaced about 30 cm apart and penetrate to depths of 25 to 30 cm.

In addition to the single blade or shaft, a subsoiler usually has a shoe or sweep at the bottom to increase the loosening of deeper horizons in profiles. Measurements made before and after subsoiling indicate that it reduced bulk density and soil strength and increased infiltration of water (Swain, 1975). These effects are not necessarily reflected in greater yields. Subsoiling or ripping as deep as 2 m has produced positive effects for some soils with poorly or moderately expressed duripans (opal-cemented pans at depths near 60 cm) in southern California.

Deep plowing has been tried in a number of places to improve unfavorable soil conditions. Mostly the efforts have been intended to mix part of a sub-surface layer of clay accumulation, such as a Bt horizon, with a sandy A horizon. Some deep plowing has also been meant to mix, and thus dilute, soil materials with chemical characteristics unfavorable for plant growth, such as horizons high in sodium. Improvement of soils with one or more horizons high in sodium is feasible by deep plowing only if calcium is present in quantity within the depth reached by the plow. Mixing calcium-rich soil materials with those high in sodium can then facilitate sodium removal. In Alberta for example, deep plowing brings gypsum-containing soil materials to the surface, with the potential of providing Ca to replace Na. In NW Texas calcite in lower B horizons has a similar potential. Most deep plowing has been to depths of l m or less, but the maximum is 2 m. In practice, the degree of mixing ranges from poor to good. If horizons are distinct and the soil is not sandy, the sequence of horizons is not completely inverted but tends to be tipped on its side. Multiple passes with a plow increase the amount of mixing. On the whole, experience with deep plowing and mixing of soil horizons in the United States, Canada, and Europe indicates that benefits are obtained in some but not in all instances. For the most part, the practice has not been economical.

Asphalt barriers. Experiments have been conducted with layers of asphalt placed at depth in sandy profiles. The asphalt layer is continuous and forms a barrier to water movement, thus increasing plant-available water. Generally, the asphalt is placed at a depth of 60 cm using a subsoiler with a sweep and a spray attachment. The sweep is moved through the soil at a depth of about 60 cm, lifting the soil material so that an asphalt emulsion can be sprayed on the lower cut surface. Barriers of this type increase the amount of water available for plant growth in sandy soils.

Dynamiting. Most dramatic among attempts to modify soil profiles has been the use of explosives. Dynamite was used with some success in southern California and without benefit in southern Illinois. Begun in the 1880s in southern California, the practice was to use about one fourth of a stick of dynamite to shatter the duripan (see *Pan*) wherever a fig (*Ficus carica* L.) was to be planted (Soil survey Division, 1938). Currently dynamite is not being used in efforts to improve physical properties of soils.

Land forming

Grading or leveling land to shape the surface so that it is smooth and uniform, preferably with a gentle slope in one direction, is called *landforming.* Soil materials from the higher areas are moved into the lower areas. Part or all of the soil profile is thus modified wherever cuts and fills are made. Modification ranges from slight to drastic. Leveling or grading land facilitates uniform water distribution and has long been practiced in irrigated areas (see *Irrigation*). During the last 50 years, however, the practice has spread to humid regions as a water-control measure. Land forming ranges from cutting high spots and filling low ones at one extreme, to precision grading at the other. After precision grading, a field has a uniform gentle slope. Land forming has been most effective where *local relief-differences* in elevation between the high and low points in a field are small and the soils have relatively uniform profiles. If only a portion of the A horizon is removed in land forming operations, the truncated soil will be productive. On the other hand, if the top of the B horizon is rich enough in clay to constitute a Bt, and all of the A horizon is removed, the remaining clay-rich profile retains more water, but initial production may be reduced due to high levels of exchangeable aluminum in the original Bt horizon. Experience from the middle Atlantic Coastal Plain in North Carolina (Thomas and Cassel, 1979) has shown that if all of the A, and E and part of the Bt horizons are removed, it is unlikely that the soil will ever be as productive as it was prior to truncation. If the soils that must be truncated in land forming operations have either or both B and C horizons that are unfavorable for plant growth because of physical or chemical characteristics, removal of the A horizons will result in reduced productivity of some part of a field. In extreme cases, the truncated soils cannot be made as productive as they were previously. Total production from a field as a whole may then be lowered by land forming. One possibility in such instances would be to stockpile the A horizon before grading. Afterward the A horizon materials could be redistributed. Stockpiling is not without disadvantages, however, as it can be detrimental to soil microbial populations and organic matter content (Phelps and Holland, 1987). The soil should be stockpiled during the driest time of the year and remain stockpiled for the shortest possible time. The cost would then be higher than otherwise, but production would increase. Probable benefits would then have to be compared with costs of the two approaches.

Occasionally, grading fields in the western part of the United States has included stockpiling of the uppermost several feet of soil prior to leveling. The gravelly sediments exposed by the stockpiling were then graded, after which the stockpiled soil materials were redistributed. The A and B horizons were mixed in the process of stockpiling and redistribution, but both were rather fine-textured so that the soil materials after the operation were similar. The expense of such an operation is substantial.

Soil profile reconstruction

Soil profile reconstruction is the creation of a new soil from soil and/or overburden materials removed from a former location. Although the procedure has been used to move soil from one locality to another with a better climatic regime for crop production (in the Canary Islands for example, where high value horticultural crops are grown), soil profile reconstruction is most often associated with mineland reclamation as mandated by the Surface Mining Control and Reclamation Act (SMCRA) of 1977 (Office of Surface Mining. 2003). Most literature addressing the physical parameters of soil profile reconstruction deals with mine-soil reclamation. The region-specific soil chemical problems of alkalinity, acidity, heavy metal toxicity, and fertility will not be discussed here. One should be aware that avoiding or ameliorating soil compaction would not enhance crop growth if chemical barriers exist for plant root growth or if nutrients are limiting.

Physical compaction by heavy equipment (Bradford and Peterson, 2000) is the most serious problem in soil profile construction. Compaction reduces the rooting volume, thereby reducing plant-available water and nutrients. Crop yields are greatly reduced on constructed soils with subsoil compaction. Compaction increases soil strength while reducing macropore (water movement) and micropore (water-holding capacity) volumes. Precise compaction evaluation requires the measurements of bulk density (Doll, 1987), soil texture (Wollenhaupt, Doll and Richardson, 1982) and saturated conductivity (Hamblin, 1985). Any of the three measures alone will result in less precise compaction assessment. However, Hooks and Jansen (1986) developed a recording cone penetrometer to measure soil strength and to identify compacted layers restrictive to root growth. Penetrometer readings in conjunction with bulk density measurements allow identification of compacted layers and predict root system performance (Thompson, Jansen and Hooks, 1987).

Compaction is exacerbated on wet soils (Bowen, 1981). Hammer et al. (1991) found bulk densities of 2.3 g cm^{-3} after scrapers replaced wet topsoil in central Missouri. Reclamation cannot always be conducted under ideal soil conditions. However, a "Proctor test" is useful in determining the soil water content for soil reclamation with minimum compaction (Stucky and Lindsey, 1982).

Using rubber-wheeled farm equipment instead of scrapers and dozers can reduce compaction. Soil should be reconstructed by delivering topsoil and subsoil to the face from the graded cast overburden with trucks, or by using a bucket wheel excavator for overburden transport (Smout, 1987). In Illinois, McSweeney and Jansen (1983) used a mining wheel with a belt conveyor to replace minesoil. The belt produced rounded, "fritted" soil structural aggregates, which allowed profuse root growth. Four years of corn and soybean growth were observed on test plots of topsoil over "fritted" subsoil and topsoil over scraper-replaced subsoil. Yields were 4.1 and 3.4 times higher for corn and soybeans, respectively, on "fritted" soils.

Some researchers have suggested that compaction may be reduced by biological amelioration. However, the persistence of dense glacial till in forested and prairie ecosystems through the Pleistocene suggests that biological processes offer limited promise to remedy compaction in constructed soils (Hammer et al., 1992). Plant roots in compacted mine-soils are flattened and are found only in dessication cracks (Dunker et al., 1992). Mycorrhizal inoculation has also been tried as an ameliorative strategy in mine-soils (Ogango and Teyker, 1991), but any benefits appear to be very species-specific. In an Ohio study, earthworms did not penetrate compacted soil, but they improved structure and water-holding capacity of overlying, uncompacted soil, resulting in increased oak root development and seedling growth (Abell and Vimmerstedt, 1985). Biological enhancement of soil structure and aggregate stability, however, is well established for other procedures and techniques. For example, soil characterization after 100 years of cultivation of the Mexico soil (udollic ochraqualfs – wet alfisols with dark surfaces) on Sanborn Field revealed that plots receiving 4 tons manure per year in a rotation of corn, oats, wheat and red clover (*Trifolium pratense* L.) had the strongest surface and subsurface soil structure among all of the treatments. Soils under continuous cultivation of corn by contrast, were nearly devoid of structure (Hammer and Brown, 1990). Also, organic matter additions and crop rotations that include fibrous-rooted small grains and legumes, have led some investigators (Doll, 1987; Grandt, 1981; Hammer et al., 1992) to suggest that reconstructed soils would benefit greatly from incorporation of such practices. In situations where physical amelioration of compacted horizons is too costly, biological enhancement of overlying soil horizons may offer the best option to maximize crop yields.

The mechanical amelioration of constructed soils is best accomplished by subsoiling or deep tillage. Researchers at the University of Illinois have investigated five tillage techniques at the Burning Star Mine. Tillage treatments include: (1) a cut-lift operation which shatters the soils to the 91 cm depth; (2) a vibrating shank method effective to 91 cm; (3) a two-lift solid shank ripper with a 80 cm wide blade on the primary shank, rips and shatters to 122 cm; (4) a commercially available chisel which tills to 45 cm; and (5) a commercially available agricultural chisel plow effective to 25 cm. Corn and soybean yields averaged for three years indicate increasing corn yield response with increasing tillage depth. Soybean yields increased only with the first three tillage treatments. Average soil strength and net water extracted by plants were strongly and positively correlated with increasing tillage depth. Bledsoe et al. (1992) measured increased corn root development in deep-tilled minesoils in southern Illinois and found that root growth was positively correlated with reduced soil strength. The most effective treatment lifts and shatters the massive, compacted soil. Ripping with a blade alone merely "slices" the soil, and can increase compaction adjacent to the blade path (Bowen, 1981). Ripping reconstructed soils increased tree seedling survival and growth in southern Illinois (Philo et al., 1982).

Use of a soil-based productivity index (*PI*)

The concept of the *PI* is that plant root growth is a function of soil chemical and physical properties, and that plant yield will be proportional to root growth (Kiniry et al., 1983). Some scientists (Doll, 1987; Hammer, 1992) have proposed that it would be useful as a method to design and assess soil profile construction. The *PI* is calculated by measuring, for each soil depth increment or horizon, soil properties determined to be significant to the optimization of root development. A given property (soil pH, bulk density, soil moisture, are possible examples) is converted to a sufficiency factor (a level sufficient to avoid adverse effects on root development). Each depth increment is weighted by the fraction of plant roots in that increment of the ideal soil. The original productivity index was

$$PI = \sum_{i=0}^{r} (RI \times A \times C \times \ldots)i$$

where $PI =$ the productivity index; $RI =$ predicted root fraction in the ideal soil; and A through C – sufficiency factors for soil parameters 1 through 3, respectively; $r =$ the total number of depth increments in the rooting profile; and $i =$ the depth increment number ($i = 1, 2, 3, \ldots, r$). The *PI* has been successfully used to assess productivity of unmined soils (Gantzer and McCarty, 1987). Ranjith et al. (2003) provide a recent instance of the use of *PI*.

Conclusion

The examples cited, indicate that where any and all methods for modifying the physical properties of soil profiles are contemplated, the characteristics of the soils of a tract are of the utmost importance to the success or failure of the operation. Remedial measures, when problems arise, may not be completely successful, and there is little doubt that prevention of problems (compaction especially) is better than most attempted cures.

D. K. Cassel and R. D. Hammer

Bibliography

Abell, M.S., and Vimmerstedt, J.P., 1985. White oak *(Quercus alba)* seeding growth in relation to earth *(Lumbricus terrestris)* activity in Ohio surface minesoil. *Ohio J. Sci.*, **85**: 88.

Bledsoe, L., Varsa, E.G., Chong, S.K., Olsen, F.J., Klubek, B.P., and Stucky, D.J., 1992. The effects of deep tillage of reclaimed mine soils on corn root development. In Dunker, R.E., Barnhisel, R.I., and Darmody, R.G., eds., *Proceedings of the 1992 Symposium on Prime Farm land Reclamation. Aug. 10–14.* St. Louis, MO: Dept. of Agronomy, University of Illinois, Urbana, pp. 51–58.

Bowen, H.D., 1981. Alleviating mechanical impedance. In Arkin, G.F., and Taylor, H.M., eds., *Modifying the Root Environment to Reduce Crop Stress, Monograph 4*. St. Joseph, MI: *Am. Soc. Agric. Engin.,* pp. 21–57.

Bradford, J.M., and Peterson, G.A., 2000. Conservation tillage. Section G, chapter 10. In Sumner, M.E., *Handbook of Soil Science,* editor-in-chief. Boca Raton, FL: CRC Press (Various paginations).

Cooper, A.W., 1971. Effects of tillage an soil compaction. In Barnes, K.K., Carleton, W.M., Taylor, H.M., Throckmorton, R.I., and Vanden Berg, G.E., eds., *Compaction of Agricultural Soils.* St. Joseph, MI: American Society of Agricultural Engineering, pp. 315–364.

Crews, T.E., and Gliessman, S.R., 1991. Raised field agriculture in Tlaxcala, Mexico: An ecosystem perspective on maintenance of soil fertility. *Am. J. Altern. Agriculture*, **6**: 9–16.

Doll, E.G., 1987. Regulation, root zone properties, and plant growth on reclaimed land. In Carlson, C.L., and Swisher, J.H., eds., *Innovative Approaches to Mine Land Reclamation.* Proceedings National Mined Land Reclam. Conf., St. Louis, MO, Oct. 23–29, 1986. South 111. Carbondale: Univ. Press, pp. 80–92.

Dunker, R.E., Hooks, C.L., Vance, S.L., and Darmody, R.G., 1992. Effects of deep tillage on surface mined land in southern Illinois. In Dunker, R.E., Barnhisel, R.I., and Darmody, R.G., eds., *Proceedings of the 1992 Symposium on Prime Farmland Reclamation. Aug. 10–14, St. Louis, MO.* Urbana: Dept. of Agronomy, University of Illinois, pp. 59–70.

Gantzer, C.J., and McCarty, T.R., 1987. Predicting corn yields on a clay pan soil using a productivity index. *Trans. ASAE*, **30**: 1247–1352.

Grace, J.M., Skaggs, R.W., and Cassel, D.K., 2006. Soil physical changes associated with forest harvesting operations on an organic soil. *Soil Sci. Soc. Am. J.* **70**: 503–509.

Grandt, A.F., 1981. Problems in reclaiming farm land inIllinois. *Min. Eng.*, **33**: 1347–1350.

Hamblin, A.P., 1985. The influence of soil structure on water movement, crop root growth, and water uptake. *Adv. Agron.*, **38**: 95–158.

Hammer, R.D., 1992. A soil-based productivity index to assess surface mine reclamation. In Dunker, R.E., Barnhisel, R.I., and Darmody, R.G., eds., *Proceedings of the 1992 Symposium on Prime Farmland Reclamation. Aug. 10–14, St. Louis, MO.* Urbana: Dept. of Agronomy, University of Illinois, pp. 221–232.

Hammer, R.D., and Brown, J.R., 1990. 100 years of cultivation on Sanborn field – a pedologist's perspectives. In Proceedings Sanborn June Field Centennial, June 27, 1989. *Univ. Missouri Agric. Exp. Sta. Spec. Pub. 415.* pp 109–123.

Hammer, R.D., Hicks, B.L., and Conkling, B., 1991. Spatial variability of the soil-based productivity index on scraper and dragline reclaimed minesoils. In *Fourth Annu. Pep., Prime Farmland Reclamation After Surface Mining.* Urbana-champaign: University of Illinois, pp. 1111–1122.

Hammer, R.D., Malone, R.A., Coble, D., and Stallman, T., 1992. Ecological succession – its effects on soil properties and implications for surface mine reclamation. In Dunker, R.E., Barnhisel, R.I., and Darmody, R.G., eds., *Proceedings of the 1992 Symposium on Prime Farmland Reclamation. Aug. 10–14. St. Louis, MO.* Urbana: Dept. of Agronomy, University of Illinois, pp. 249–258.

Hooks, C.L., and Jansen, I.J., 1986. Recording cone penetrometer developed in reclamation research. *Soil Sci. Soc. Am. J.*, **50**: 10–12.

Kiniry, L.N., Scrivner, C.L., and Keener, M.E., 1983. A soil productivity index based upon predicted water depletion and root growth. *Res. Bull. 1051*. Agric. Exp. Station, Univ. of Missouri-Columbia.

McSweeney, K., and Jansen, I.J., 1983. Soil structure and associated rooting behavior in minesoils. *Soil Sci. Soc. Am. J.*, **48**: 607–612.

Office of Surface Mining, 2003. *25th Anniversary of the Surface Mining Law.* Washington, DC: U.S. Dept. of the Interior, 44 pp.

Ogango, K.O., and Teyker, R.H., 1991. Mycorrhizal inoculation of newly constructed soil material. In *Fourth Annual Report, Prime Farmland Reclamation After Surface Mining,* Urbana-Champaign: University of Illinois, pp. 1102–1107.

Phelphs, L.B., and Holland, L.J., 1987. Soil compaction in topsoil replacement during mining reclamation. *Environ. Geochem. Health*, **9**: 8–11.

Philo, G.R., Kolar, C.A., and Ashby, W.C., 1982. Effects of ripping on minesoil compaction and black walnut establishment. In *Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation. Lexington, KY, Dec. 5–10, 1982.* Lexington: University of Kentucky, pp. 551–557.

Ranjith P., Udawatta, R.P., and Henderson, G.S., 2003. Root distribution relationships to soil properties in Missouri oak stands: A productivity index approach. *Soil Sci. Soc. Am. J.*, **67**: 1869–1878.

Smout, G.A., 1987. Regulation, root zone properties, and plant growth on reclaimed land. In Carlson, C.L, and Swisher, J.H., eds., *Innovative Approaches to Mined Land Reclamation.* Proceedings of National Mined Land Reclamation Conference, St. Louis, MO., Oct. 28–29, 1986. Carbondale. Southern Illinois Univ. Press, pp. 123–142.

Soil Survey Division, Bureau of Chemicals and Soils, 1938. Soils of the United States. In *Soils and Men. U.S. Department of Agriculture Yearbook of Agriculture*. Washington, DC: U.S. Government Printing Office, p. 1105.

Stuckey, D.J., and Lindsey, T.C., 1982. Effect of soil compaction on growth and yield of soybeans grown in a greenhouse on several reconstructed soil profiles from prime farmland in Southern Illinois. *Reclamation and Revegetation Res.*, **1**: 297–309.

Swain, R.W., 1975. Subsoiling, *In* Soil Physical Conditions and Crop Production. *United Kingdom Ministry Agric., Fisheries, and Food Tech. Bull., No. 29*, pp. 189–204.

Thomas, D.J., and Cassel, O.K., 1979. Land forming Atlantic Coastal Plain soils: Crop yield relationships to soil physical and chemical properties. *J. Soil Water Conserv.*, **34**: 20–24.

Thompson, P.J., Jansen, I.J., and Hooks, C.L., 1987. Penetrometer resistance and bulk density as parameters for predicting root system performance in mine soils. *Soil Set. Soc. Am. J.*, **51**: 1288–1293.

Wollenhaupt, N.C., Doll, E.G., and Richardson, J.L., 1982. A technique for estimating plant available soil moisture capacity from soil texture. *North Dakota Acad. Sci.*, **36**: 53.

Cross-references

Field Water Cycle
Irrigation
Pan

PSEUDOGLEY

The term pseudogley has been used for a type of soil with redoximorphic features (such as mottles, concretions or bleaching) arising from the presence of a perched water table that causes the temporary saturation of the upper part of the soil. Pseudogley is used in several soil classifications for soils that fall into the WRB groups *Stagnosol* (*q.v.*) and *Planosol* (*q.v.*).

PUDDLING

The term *puddling* was defined by Buehrer and Rose (1943) as "*the destruction of the aggregated condition of the soil by* *mechanical manipulation within a narrow range of moisture contents above and below field capacity (0.3 bars), so that soil aggregates lose their identity and the soil is converted into a structurally more or less homogeneous mass of ultimate particles.*" After puddling, a soil is called a *puddled soil*, defined as a "*dense soil with a degraded soil structure; dominated by massive or single-grain structure, resulting from handling the soil when it is in a wet, plastic condition so that when it dries it becomes hard and cloddy.*" (Gregorich et al., 2001).

In most cropping systems, puddling is an unintentional effect of *tillage* (*q.v.*) or traffic at the wrong moisture contents and usually results in severe yield decreases or delays in planting. In flooded rice culture, puddling is an important soil-management practice, conducted with great care for the purpose of destroying the structure of the surface layer. Puddling is almost synonymous with paddy rice culture in Asia (Sanchez, 1976).

Process

The process of puddling in rice culture is accomplished by a series of tillage operations beginning at soil moisture contents above saturation (i.e., flooded) and ending at moisture contents closer to field capacity (see *Field water cycle*). This process is best understood by considering the changes in soil strength *within* aggregates and *between* aggregates. According to Koenigs (1961), the cohesion *within* soil aggregates decreases with increasing soil moisture contents. The individual aggregates become soft and may or may not disintegrate depending on their stability. The cohesion *between* aggregates is very low at low moisture contents but increases rapidly with increasing moisture, peaking at about field capacity, and decreasing sharply as moisture contents approach saturation. The cohesion *between* aggregates depends primarily on the number of contact points between aggregates. The number of contact points is minimal in a dry soil and approaches a maximum at about field capacity because of the increased thickness of water films and the swelling of the aggregates themselves. At higher moisture contents, the thick moisture films act as lubricants and decrease the number of contact points between aggregates. At approximately field capacity the cohesion within the aggregates is very low and the cohesion between the aggregates is maximum. When force is applied by a plow or a foot, the aggregates are easily destroyed because of the combined effects of high friction and low internal aggregate strength.

In practice, rice farmers start their puddling operations at moisture contents above saturation. In this range both the cohesion within and between the aggregates is minimal. Applying force while the soil is saturated does not cause maximum puddling, but it incorporates weeds and starts the aggregate destruction process. Farmers then continue to puddle the soil at progressively lower moisture contents until they reach maximum puddling at moisture tensions close to field capacity. The soil is converted into a uniform mud to a depth of 10 to 20 cm.

The degree of puddling attained differs with soil type and management. High clay contents facilitate puddling and permit more aggregate destruction. Nevertheless, sandy soils with low clay contents can be puddled. Montmorillonitic soils are puddled easier and more thoroughly than kaolinitic or oxidic soils. Sodium-saturated soils are the easiest to puddle because of their dispersed state. In general, the higher the contents of organic matter, iron oxides, or aluminum oxides, the more difficult it is to puddle a soil. Andepts and oxisols are extremely difficult to puddle, and the degree of aggregate breakdown seems lower than in other soils.

Consequences of puddling

Aggregate destruction

The primary consequence of puddling is the destruction of soil aggregates (Sharma and De Datta, 1985). A puddled soil consists essentially of a two-phase or solid-liquid system. Individual clay particles or clusters thereof are oriented in parallel rows and are surrounded by capillary pores saturated with water. Sand and silt particles and some remaining aggregates are also part of the matrix. The degree of aggregate destruction is difficult to quantify because drying is necessary to measure aggregation. Kawaguchi et al. (1956) and others provide evidence of aggregate destruction after puddling and subsequent drying.

Changes in porosity

Noncapillary pores are essentially eliminated in the process of puddling. Bodman and Rubin (1948) found that 91–100% of the volume occupied by such pores was destroyed by puddling a silt loam. Capillary porosity increases drastically. Because most of these pores are smaller than 0.2 μm in effective radii, water may move through pores as a liquid but can be lost only as vapor.

Bulk density

Immediately after puddling a saturated soil, the apparent specific gravity or bulk density is less than that of the original soil because of the larger total pore volume occupied by water. With time, however, the bulk density of the flooded soils increases probably because of a slow settling of the clays. When dried, puddled soils shrink dramatically with resultant large increases in bulk density (Kawaguchi et al., 1956; Sanchez, 1968).

Increased soil moisture retention

As a consequence of the destruction of noncapillary pores, the increase in water-saturated capillary pores, and the decrease in initial bulk density, puddled soils hold more water than unpuddled soils at a given moisture tension. The effect is measurable within a range of 0 to 10 bars of soil moisture tension.

Decreased moisture losses

The changes in porosity and water retention result in sharply reduced soil moisture loss patterns in puddled soils (Sharma and De Datta, 1985). Table P20 shows the effects of puddling on drainage rates of six Philippine rice soils ranging widely in texture and mineralogy. Puddling decreased percolation losses by a factor of 1000 regardless of soil properties.

The benefits of puddling in decreasing the rate of soil *water movement* (*q.v.*) have been previously attributed to the formation of a relatively impermeable "plow pan" just below the puddled layer. These plow pans are found in loamy soils planted to rice for many years, e.g., in well-drained oxisols and as concretionary materials in andepts. Plow pans are absent in sandy and clayey soils, vertisols, and young alluvial and calcareous soils (Sanchez, 1973). Puddling, however, is almost universally practiced in lowland rice farms. With the dikes surrounding the paddy fields and the puddled soil at the bottom, the rainfed fields hold

Table P20 Effects of puddling on the drainage rates of six flooded Philippine soils in pot conditions (After Sanchez, 1973)

Soil	Mineralogy	Clay (%)	Drainage rate (cm day^{-1})	
			Granulated condition	Puddled condition
Psamment	Siliceous	9	267	0.45
Fluvent	Mixed	24	215	0.17
Aquept	Montmorillonitic	30	183	0.05
Aqualf	Montmorillonitic	40	268	0.05
Ustox	Kaolinitic	64	155	0.05
Andept	Allophanic	46	214	0.31
Mean			217	0.18

the maximum amount of water possible for the rice crop growing during the rainy season. Another consequence of puddling is the slow rate of drying. The drying process may take several months in puddled clayey soils as opposed to much shorter periods in well-structured soils.

Reducing conditions

Due to the absence of air, reduction processes can take place as soon as the soil is puddled (Breazeale and McGeorge, 1937). Puddled soils remain reduced regardless of whether they are flooded until cracks begin to form. Lack of oxygen in the soil pores inhibits the growth of most crops except rice and other anaerobic species. Nitrates are lost through denitrification (Aggarwal, 1995).

Organic matter decomposition

Puddling, like any other aggregate disruption process, temporarily hastens organic matter decomposition due to increased accessibility of the substrate by soil microorganisms. Puddling increases the mineralization of soil organic nitrogen during the first month after puddling and flooding (Harada et al., 1964), but the effect disappears at later stages (Briones, 1966).

Nutrient availability

Puddling flooded soils does not *directly* increase the availability of nutrients to the rice plant (Sanchez, 1968, 1973; Obermueller and Mikklesen, 1974). Small increases in iron and manganese availability have been recorded (Naphade and Ghildyal, 1971) but are not large enough to be of practical significance. Puddling often indirectly increases the availability of nutrients by decreasing leaching losses of cations such as NH_4^+ (Sanchez, 1973; DeDatta and Kerim, 1974; Aggarwal, 1995).

Regeneration of structure

Puddling is not an irreversible process. The original structure can be regenerated through the processes of alternate wetting and drying or freezing and thawing. The puddled soil must be dried first, after which aggregates are reformed by these processes. Tillage at the appropriate moisture content facilitates regeneration of structure. This is accomplished most readily in soils high in organic matter or iron and aluminum oxides (Koenigs, 1961).

Effects of puddling on crop growth

The effects of puddling on crops other than rice are clearly detrimental (McGeorge and Breazeale, 1938). For rice, puddling is considered advantageous because it facilitates land leveling, permits the farmers to work the soil regardless of moisture status, reduces initial weed infestations, and, most important, decreases water and leaching losses.

The primary contribution of puddling to rice growth is to decrease water losses (Sanchez, 1973). Puddling is generally beneficial to rice grown on soils subject to leaching losses in irrigated paddy systems. This generalization is of particular relevance to sandy soils and well-aggregated oxisols and andepts, where often puddling is essential to flood such soils. At the other extreme, puddling is probably of little importance in soils having an impermeable layer in the subsoil, a constantly high water table, or in sodic soils that are naturally dispersed. Puddling is not practiced in soils having such properties in the rice-growing regions of the United States. In most rice soils puddling helps in decreasing percolation losses (Kukal and Aggarwal, 2002).

Puddling, however, is a double-edged sword in rainfed paddy systems. In most cases puddling attenuates the increases in soil moisture tension during temporary droughts and increases yields. But when intense droughts take place shortly after transplanting, the puddled soil may shrink, crack, and impede rice root development to a degree from which plants cannot recover afterwards (Sanchez, 1973; De Datta and Kerim, 1974). Another potential detrimental effect of puddling is the time required for the soil to dry and be prepared for aerobic crops grown in rotation with rice. This time interval may be several months in clayey montmorillonitic soils but only several days in clayey kaolinitic, allophanic, or oxidic soils. In continuous paddy rice systems, this effect is irrelevant.

Pedro A. Sanchez

Bibliography

Aggarwal, G.C., Sidhu, A.S., Sekhon, N.K., Sandhu, K.S., and Sur, H.S., 1995. Puddling and N management effects on crop response in a rice–wheat cropping system. *Soil Tillage Res.*, **36**: pp. 129–139.

Bodman, G.B., and Rubin, J., 1948. Soil puddling. *Soil Sci. Soc. Am. Proc.*, **13**: 27–36.

Breazeale, J.F., and McGeorge, W.T., 1937. Studies on soil structure: some nitrogen transformations in puddled soils. *Ariz. Agric. Exp. Sta. Tech. Bull. No. 69*, pp. 225–252.

Briones, A.M., 1966. Nitrogen availability in five soils under different systems and its affect on growth and yield of rice. M.S. Thesis, University of the Philippines, Los Baños, 107 pp.

Buehrer, T.F., and Rose, M.S., 1943. Studies in soil structure. V. Bound water in normal and puddled soils, *Ariz. Agric. Exp. Sta. Tech. Bull, No. 100*, pp. 155–218.

Croney, D., and Coleman, J.D., 1954. Soil structure in relation to soil suction (pF). *J. Soil Sci.*, **5**: 75–84.

De Datta, S.K., and Kerim, M.S.A.A., 1974. Water and nitrogen economy of rainfed rice on puddled and non-puddled soils. *Soil Sci. Soc. Am. Proc.*, **38**: 515–518.

Gregorich, E.G., Turchenek, L.W., Carter, M.R., and Angers, D.A., 2001. *Soil and Environmental Science Dictionary.* Boca Raton, FL: CRC Press, 577 pp.

Harada, T., Hayashi, R., and Chikamoto, A., 1964. Effect of physical pretreatment of the soils on the mineralization of native organic nitrogen in paddy soils. *J. Sci. Soil Manure*, **31**: 21–24.

Kawaguchi, K., Kita, D., and Kyuma, K., 1956. A soil core sample for paddy soils and some physical properties of the soil under waterlogged conditions. *Soil Plant Food*, **3**: 22–28.

Koenigs, F.F.R., 1961. The mechanical stability of clay soils as influenced by moisture conditions and some other factors. Verslag. Landbowk. Onderzoek. 67.7 Wagnenigen: Center for Agricultural Publications and Documentation, 171 pp.

Kukal, S.S., and Aggarwal G.C., 2002. Percolation losses of water in relation to puddling intensity and depth in a sandy loam rice (*Oryza sativa*) field. *Agric. Water Manage.*, **57**: pp. 49–59

McGeorge, W.T., and Breazeale, J.F., 1938. Studies on soil structure: Effects of puddled soils on plant growth. *Ariz. Agric. Exp. Sta. Tech. Bull. No. 72,* 413–447.

Naphade, J.D., and Ghildyal, B.P., 1971. Influence of puddling and water regimes on soil characteristics, ion uptake and rice growth, *Proc. Int. Symp. Soil Fert. Eval. (New Delhi)*, **1**: 511–517.

Obermueller, A.J., and Mikklesen, D.S., 1974. Effects of water management and soil aggregation on the growth and nutrient uptake of rice. *Agron. J.*, **66**: 627–632.

Sanchez, P.A., 1968. Rice performance under puddled and granulated soil cropping systems in South-east Asia. Ph.D. Thesis, Cornell University, Ithaca, NY, 381 pp.

Sanchez, P.A., 1973. Puddling tropical rice soils. I. Growth and nutritional aspects. II. Effects of water losses. *Soil Sci.*, **115**: 149–158, 303–308.

Sanchez, P.A., 1976. Soil management in rice cultivation systems. *Properties and Management of Soils in the Tropics.* New York: Wiley, pp. 413–477.

Sharma, P.K., and De Datta, S.K., 1985. Effects of puddling on soil physical properties and processes. *Soil Physics and Rice.* Los Banos, Philippines, IRRI, pp. 217–234.

Cross-references

Aggregate Stability to Drying and Wetting
Aggregation
Dispersion
Field Water Cycle
Paddy Soils
Soil Drainage
Soil Pores
Structure
Tillage
Water Budget in Soil
Water Movement

PUGGING

The compaction and waterlogging of soil caused by the tramping of grazing animals. a process called Pugging. The animal footprints or pugs, collect standing water, the soil is bared and exposed to damage from raindrop impacts. Highly compressible soils such as Andosols are particularly prone to this damage as can be seen in the picture from the island of San Miguel, Azores (Figure P71).

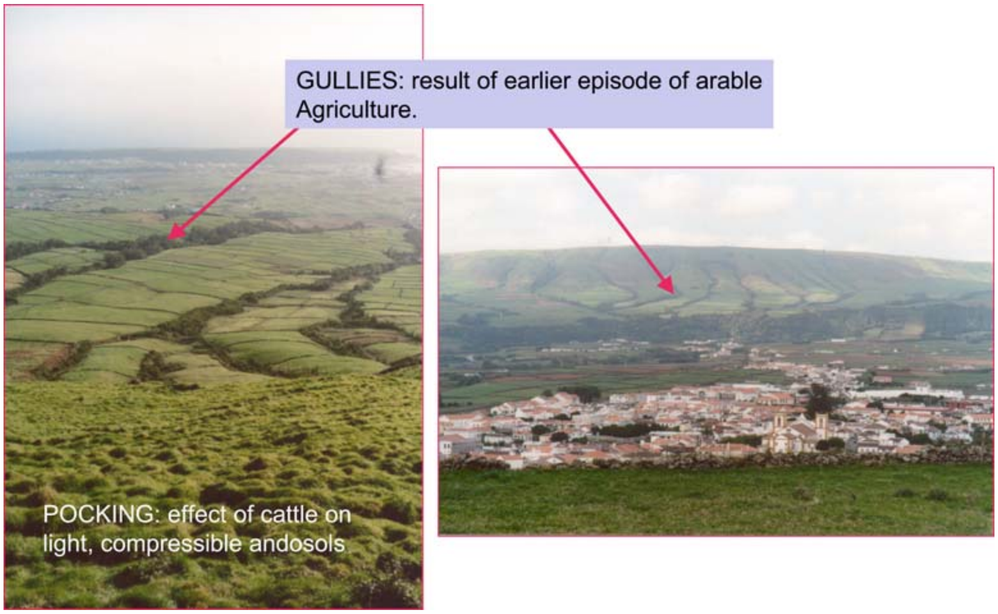


Figure P71 Effect of cattle on light, compressible Andosols at the island of San Miguel, Azores.

Q

QUALITY

Soil quality may be defined as a measure of how well a soil fulfills either its intrinsic role in the biosphere, or its role as defined by the needs of human society.

With regard to its intrinsic role, soil provides habitat on the land surface, accumulates biomass, and ensures a level of biodiversity. Photosynthesizing species in the biomass collect solar energy and become the principal source of energy for other species, either by direct consumption, or indirectly as dead organic matter in the soil, metabolized by micro-organisms, mycorrhizae and fungi. In addition the soil acts as a conduit for nutrients and is an integral part of all material cycles on the land surface. (See *Soil*, *Biogeochemical Cycles*).

For societal purposes soil quality may be defined in terms of the ability of soil to perform a number of services such as: protection of the environment, maintenance of biodiversity, disposal of the wastes we generate, production of food, provision of foundations for roads and buildings, and promotion of human health. (Details of soil quality for particular purposes can be found in specific articles: *Carbon Sequestration in Soil*, *Edaphic Constraints on Food Production*, *Health Problems and Soil*, *Irrigation*, *Plant Roots and Soil Physical Factors*, *Sludge Disposal*, *Soils*, *Non-agricultural Uses*, *Soil Engineering*, *Water Content and Retention*). Brady and Weil (2002, p 872–873) provide an excellent summary.

The specific parameters used to measure soil quality will vary with the purpose for making the assessment. In total, a large number of parameters are available for the purpose, and cover all aspects of the physics, chemistry and biology of soil (Doran et al., 1996). If the purpose is to estimate the quality of soil as an integral component of the biosphere, many properties will need to be measured. If however, the goal is utilitarian and tightly focused, the number of parameters to be measured will be correspondingly less. For example, the quality of soil in terms of drainage will normally require no more than a measure of those parameters of the soil that affect the hydrodynamics of the soil e.g., texture, porosity, bulk density, infiltration, water-holding capacity, and depth to water table (as a minimal list). Where human health is the major interest, factors that reflect nutrient, toxicant and pathogen content will need to be measured, though estimation of less tangible parameters dealing with the quality of everyday life including the aesthetics of the environment we live in, may provide operational difficulties.

Soil health is commonly used as a virtual synonym for soil quality, though Brady and Weil (2002) suggest that soil health is best considered as the quality of a soil that has undergone some form of human disturbance, use or management. However, the term soil health (as with the comparable term environmental health) carries with it a certain controversial connotation when the inherent medical metaphor is taken too literally. This aspect may be examined in light of the Gaia Hypothesis, which essentially started the ball rolling as far as questions of planetary health are concerned.

James Lovelock (1979, 1988) originated the Gaia Hypothesis, with important support from Lynn Margulis (see Margulis and Sagan, 1997). In its simplest form it considers that the earth acts as a kind of superorganism, controlled by biological feedback that maintains the earth as a comfortable, healthy abode for life, constantly adjusting the state of the planetary surface when inhospitable influences intrude. Rather than the Gaia Hypothesis it might be more accurate to speak of the Gaia Syndrome, since as Kirchner (1989) points out, the Gaia idea incorporates many hypotheses, which he labels severally as Influential, Coevolutionary, Homeostatic, Teleological and Optimizing Gaia (Kirchner, 1991). His trenchant criticism of the whole syndrome has never been fully answered by Gaia proponents. However, he accepts that Gaia, whether wrong or simply imperfect, has had the effect of provoking useful research (Kirchner, 2002).

The most notable discussion of soils in light of Lovelock's ideas is by van Breemen (1993a). He divides soil properties into "favorable" (or pro-Gaia) and "unfavorable" (or anti-Gaia). He defines a favorable property as one that "helps to increase the net primary production on a plot with a more or less uniform vegetation, of a size in the order of $10–10^3$ m^2. Favorable properties are found for example in a soil (such as a loamy textured Luvisol) with a high inherent fertility, and a structure that includes a heterogeneous system of interconnected pores.

A structure of this kind will simultaneously provide good anchoring for roots, good water-holding capacity and good aeration. By contrast, unfavorable properties would be found in soils with little rooting-depth (Regosols and Leptosols), a texture conducive to excessive drainage and droughtiness (Arenosols), heavy soils subject to waterlogging (Vertisols), and soils developed in extremely cold (Cryosols) or dry (Solonchaks, Solonetz) environments. Natural soil-forming processes lead to all of these (and many other) possibilities, and on balance it would be rash to say that the soil provides any conclusive evidence of a Gaia-directed process, leading towards a healthy soil (defined as one that is comfortable and hospitable towards life on earth).

A more reasonable conclusion, following Volk (2002), would seem to be that the weathering, soil-forming and soil-wasting processes that take place in the biosphere (indisputably with active feedback from soil organisms) produces a land surface that is a kind of dump of natural wastes, continuously recycled (see *Biogeochemical Cycling*), and collaterally useful to the maintenance of life on the planet. Life has evolved as a best fit to all possible contingencies and the fact that the biosphere has a "comfortable" look to it, can be explained perfectly well in terms of Darwin's mechanism of natural selection. As van Breemen (1993b) says: "unless Gaia can be explained in an evolutionary sense, it is impossible to accept its presence without falling back on teleology", that is that Gaia is specifically constituted to achieve the end-point of a planet in homeostasis.

Consequently, the state, quality or health of a soil is most parsimoniously explained as a consequence of the co-evolution of biotic and abiotic components of the Earth's surface, without teleological direction.

Ward Chesworth

Bibliography

Brady, N.C., and Weil, R.R., 2000. *Elements of the Nature and Properties of Soils.* Upper Saddle River, NJ: Prentice-Hall, 559 pp.

van Breemen, N., 1993a. Soils as biotic constructs favoring net primary productivity. *Geoderma*, **57**: 183–211.

van Breemen, N., 1993b. Author's epilogue. *Geoderma*, **57**: 229–230.

Doran, J.W., and Jones, A.J., 1996. *Methods for Assessing Soil Quality.* Madison, WI: Soil Science Society of America, 410 pp.

Kirchner, J.W., 1989. The Gaia Hypothesis: can it be tested? *Rev. Geophys.*, **27**: 223–235.

Kirchner, J.W., 1991. The Gaia hypotheses: are they testable? Are they useful? In Schneider, S.H., and Boston, P.J., eds., *Scientists on Gaia.* Boston: MIT Press, pp. 38–46.

Kirchner, J.W., 2002. The Gaia Hypothesis: fact, theory and wishful thinking. *Clim. Change*, **52**: 391–408.

Lovelock, J., 1979. *Gaia, A New Look at Life on Earth. Oxford: Oxford University Press*, 157 pp.

Lovelock, J., 1988. *Gaia, A New Look at Life on Earth. Oxford: Oxford University Press*, 157 pp.

Margulis, L., and Sagan, D., 1997. *Slanted Truths: Essays on Gaia, Symbiosis, and Evolution*. New York: Copernicus, 368 pp.

Volk, T., 2002. Toward a future for Gaia theory. *Clim. Change*, **52**: 423–430.

Cross-references

Biogeochemical Cycling
Carbon Sequestration in Soil
Edaphic Constraints on Food Production
Health Problems and Soil
Irrigation
Nitrogen Cycle
Phosphorus Cycle
Plant Roots and Soil Physical Factors
Potassium Cycle
Salt Leaching
Sludge Disposal
Soil
Soil Engineering
Soil Nutrients
Soil Salinity and Salinization
Soils, Non-agricultural Uses
Sulfur Transformations and Fluxes
Water Content and Retention

R

RADIOCARBON DATING

See *Geochemistry volume* in the *Encyclopedia of Earth Sciences Series*.

RADIOISOTOPES

See *Geochemistry volume* in the *Encyclopedia of Earth Sciences Series*.

RANGELAND

Land that produces primarily native forage plants suitable for grazing by livestock. Includes land with some trees, but no continuous canopy. Generally occupies the drier parts of the grassland biome, and is underlain predominantly by Kastanozems and Chernozems. Approximately 3.5 billion hectares is in permanent pasture worldwide.

REACTION

Operationally the soil reaction is the pH of a soil, used as an indication of the relative acidity or alkalinity. The following (arbitrary) designated pH ranges are used: extremely acid (<4.5), very strongly acid (4.5–5), strongly acid (5.1–5.5), moderately acid (5.6–6), weakly acid (6.1–6.5), neutral (6.6–7.3), weakly alkaline (7.4–7.8), moderately alkaline (7.9–8.4), strongly alkaline (8.5–9), very strongly alkaline (>9.1). The term soil reaction is falling out of use.

Cross-references

Acidity
Acids, Alkalis, Bases, and pH

REDOXIMORPHIC FEATURES

These comprise:

- *Reductomorphic properties* signify permanently wet conditions. They are expressed by neutral whitish/grayish or bluish and greenish '*gley colors*' in more than 95 percent of the soil matrix. Near the capillary fringe (just above the water table), the (subsoil) layer with reductomorphic properties may include up to 5 percent oxidation colors, e.g., as mottles (around air pockets) or 'root prints' (former root holes lined with iron oxide).
- *Oximorphic properties* indicate alternating reducing and oxidizing conditions, as occur near the capillary fringe and in the surface layers of soils with fluctuating groundwater depth. Oximorphic properties are expressed by reddish brown or bright yellowish brown mottles on aggregate surfaces and on walls of pores. Acid sulfate soils feature bright yellow mottles of *jarosite* $KFe_3^{+3}(SO_4)_2(OH)_6$ (at $pH < 3.5$) or *schwertmannite* $Fe_{16}^{+3}O_{16}(OH)_{12}(SO_4)_2$ (at pH 3.0–4.5).

Bibliography

FAO, 2001. See under Gleysols In: Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

Cross-references

Gleysols
Planosols
Redox Reactions and Diagrams in Soil
Stagnosols

REDOX REACTIONS AND DIAGRAMS IN SOIL

Redox reactions are those which involve a simultaneous reduction and oxidation. An example common in soil science is the oxidation of ferrous to ferric iron by the reduction of oxygen in the presence of water.

Redox reaction:

$$O_2 + 4Fe^{2+} + 4H^+ \rightleftharpoons 4Fe^{3+} + 2H_2O$$

The reduction and oxidation can also be written as separate steps, called half-reactions:

- Reduction

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

- Oxidation

$$4Fe^{2+} \rightleftharpoons 4Fe^{3+} + 4e^-$$

It is understood that neither half-reaction may exist independently of the other.

Since most redox reactions are pH dependent, Figure R1 provides a convenient way of depicting them. This is variously referred to as a redox-pH diagram, an Eh-pH diagram, a pe-pH diagram, or simply a Pourbaix diagram, after the metallurgist who devised this type of Cartesian graph for the purposes of examining corrosion (Pourbaix, 1974). Use of such diagrams in Earth science, was pioneered by Krumbein and Garrels (1952). Garrels and Christ (1965) remains a good introduction to the subject, and Brookins (1988) provides a compilation of basic diagrams useful to the geochemist.

The parameter pH as a measure of the acidity/basicity of a system is well established (see *Acids, alkalis, bases and pH*) and may be calculated or measured. The parameter pe used to evaluate the redox status of a system, may be defined analogously to pH as in Figure R1. The relationship between pe and Eh shown in Figure R1 amounts to an operational definition, which sidesteps the vagueness of the term “electron activity” see James and Bartlett (2000). As Truesdell (1968) points out, pe is simpler and more convenient to use than Eh, in the calculation of redox equilibria from basic thermodynamic data. Eh itself is defined as the difference in voltage between a platinum electrode and the standard hydrogen electrode. In practice measurements are made using a platinum electrode in combination with a saturated calomel electrode. The redox potential is ‘poised’ (resistant to change) by redox reactions in the same manner that pH is buffered by acid-base reactions. It will remain relatively stable until a reactant has been exhausted (i.e. all oxidized species have been reduced or vice versa).

Pourbaix diagrams

Berner (1970) points to a number of practical limitations related to the construction and interpretation of Eh-pH diagrams. At the most fundamental level, there is the problem of the quality of the thermodynamic data upon which the diagrams are based. In this regard, Woods and Garrels (1987) refer to “*the perils of indiscriminate selection of values from various sources*”. A major difficulty, and one which clearly has a determining influence on any ultimate conclusions to be drawn from the diagrams, lies in choosing what minerals to show on them, whether to consider metastable phases, whether to consider solid solution in condensed phases, and what to do about bacterial reductions. Furthermore, it is assumed that

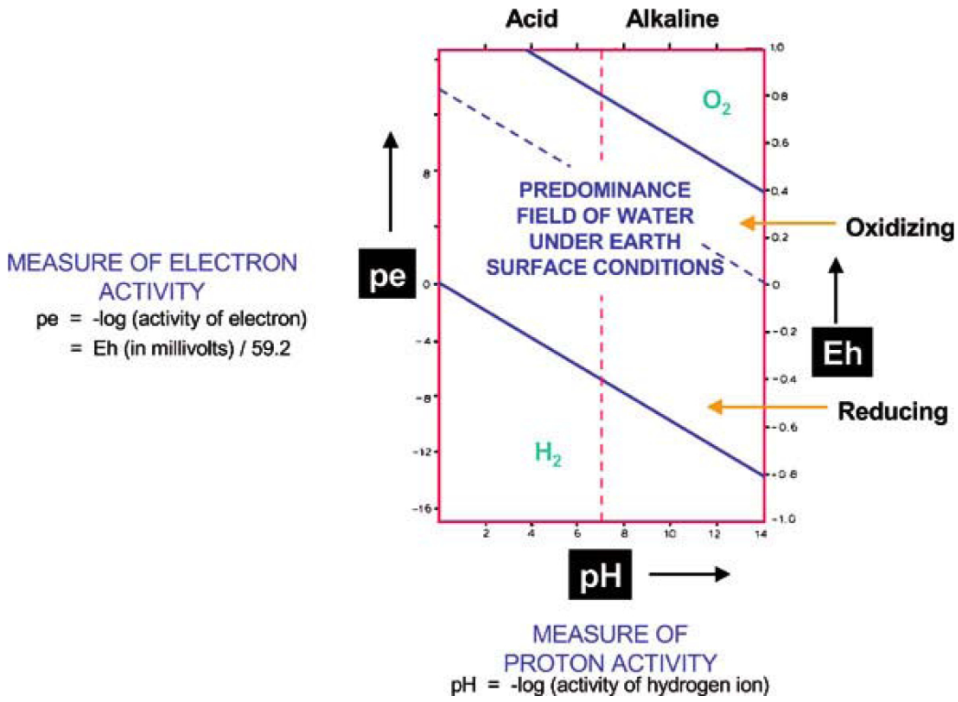


Figure R1 The Pourbaix diagram. Earth surface conditions are taken to be 25 °C and a total pressure of 100 kPa. The vertical dashed line separates acid from alkaline conditions. The dashed line with the Nernst equation slope is a contour along which the partial pressures of O_2 and H_2 are equal and separates oxidizing from reducing conditions.

equilibrium (stable or metastable) holds for a particular diagram constructed. Finally, there is the major difficulty of obtaining good measurements of Eh in the field (see Shotyk, 1988).

In spite of all this, a consensus exists that the diagrams are useful in indicating general conditions and general tendencies in a system. Even for more parochial considerations, redox-pH diagrams may prove useful provided that matters of scale, and the possibilities of local reactions are kept in mind.

Predominance fields

Figure R2 is a redox-pH diagram of the type used in the geochemical interpretation of low pressure/temperature environments. Areas called predominance fields, are labeled in terms of the minerals which would be expected to form under the Eh and pH combinations of that field, for the specific set of ionic activities chosen in calculating the appropriate mineralogical reactions for this system, and for a total pressure of 100 kPa and a standard temperature of 25 °C.

Geochemical fences

A notable contribution of Krumbein and Garrels (1952) to the usefulness of the Eh-pH approach in earth science is the concept of the geochemical fence: a relatively narrow, linear zone in redox-pH space defined by a specific chemical reaction or by a related group of reactions. Their original diagram, developed to help in the interpretation of sedimentary environments, is shown as Figure R3. Clearly it requires modification if the full scope of soil conditions are to be covered, especially below pH 7. In practical terms this amounts to changing existing geochemical fences, and adding new ones (Chesworth et al., 2006).

The modified fences are:

a. *Organic fence* (E in Figure R4). Within the upper, organic-rich part of the solum, microbially mediated breakdown of organic matter will give a range of possible Eh values for a given pH, up to the lower limit of oxidation by O_2 in soil. The latter will likely coincide with the water table in the soil system as a whole, with exclusion of oxygen to microsystems being controlled by details of micromorphology – for example by the presence of clay cutans protecting a mineral surface from oxidation. Above the water table the microbial biomass, using dead organic matter as its carbon source, will generally experience exponential growth up to the Malthusian point where free O_2 is fully utilized. Again, this will obviously coincide with the lower limit of oxidation by O_2. It should therefore be placed at the Eh-pH contour along which P_{O2} is equal to P_{H2} in the gaseous dissociation reaction of H_2O, rather than where Eh is 0, the value chosen by Garrels and Christ (1965). In theory, the upper limit would be marked by the partial pressure of oxygen in the atmosphere. In practice, the biological oxygen demand in virtually all soils, depletes oxygen to lower levels than this. The width of the organic fence shown in Figure R4 is consistent with measurements in such materials.

b. *Neutral (or Smectite) fence* (D in Figure R4). Garrels and Christ (1965) give no mineralogical justification for a neutral fence, and in the ubiquitous presence of atmospheric and respiratory CO_2 in a weathering system, it is unlikely that the ionic dissociation of water will buffer a natural system to a pH of 7. However, an average smectite (Weaver and Pollard, 1973) with so-called basic cations (Mg, Ca, Na, K)

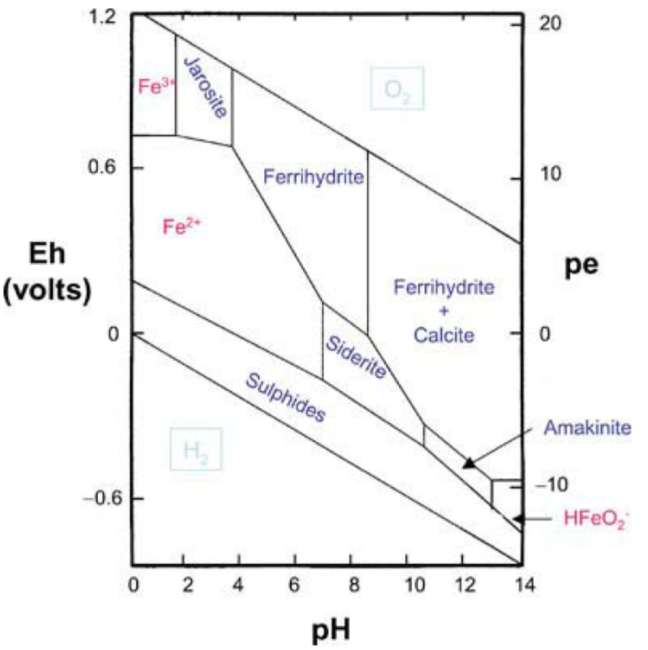


Figure R2 The system Fe–Ca–K–S–CO_2–H_2O under earth surface conditions. Activities of Fe, Ca and K are 10^{-5}. P_{CO2} is $10^{-1.5}$ (kPa approximately the partial pressure of CO_2 in the atmosphere). S activity is undefined in order to show the sulfide field at its maximum extent.

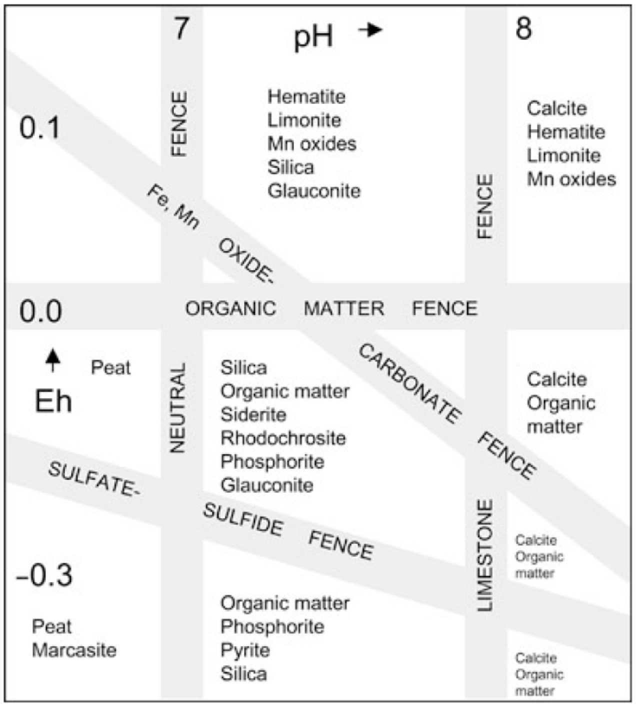


Figure R3 Earth surface environments defined in terms of Eh and pH (after Krumbein and Garrels, (1952).

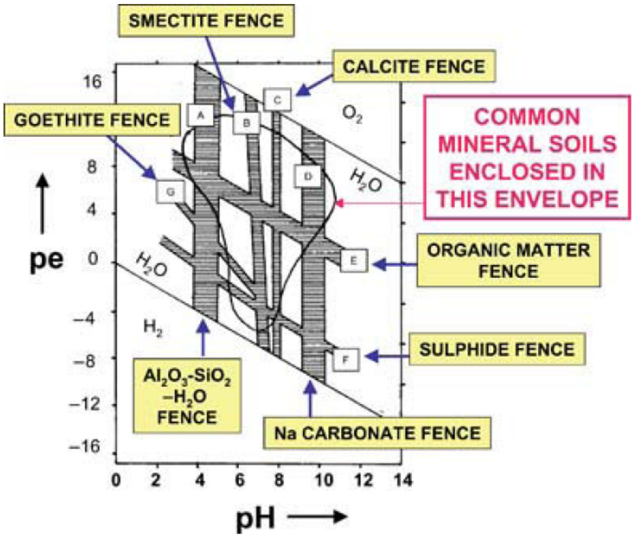


Figure R4 The pedogenic (or pedogenetic) grid, an extension of the Krumbein and Garrels (1952) diagram, modified to include tha range of Eh and pH conditions found in common soils (after Chesworth, (1992).

in exchange positions, marks a near-neutral fence according to the reaction:

$$\overset{\text{monotmorillonite}}{Mg_{0.2}Si_{3.81}Al_{1.71}Mg_{0.29}O_{10}(OH_2)} + 0.98H^+ + 0.22e^- + 0.33H_2O$$

$$\rightleftharpoons \overset{\text{kaolinite}}{0.86Al_2Si_2O_5(OH)_4} + \overset{\text{goethite}}{0.22FeOOH} + \overset{\text{quartz}}{2.1SiO_2} + 0.49Mg^{2+}$$

Because of minor substitution of Fe in the octahedral layer and the possibility of redox reactions involving that element, it will not be a vertical fence as in the Garrels and Christ (1965) diagram.

It should also be realized that this particular fence does not mark the lower pH limit of a smectite predominance field, since there exists a spectrum of smectites down to beidellite which is stable at low pH (4 or lower).

c. *Fe hydroxide fence* (G in Figure R4). Garrels and Christ (1965) based their Fe oxide fence on the solubility of Fe_2O_3. In the weathering regime Fe-hydroxy phases are overwhelmingly more important. Goethite is generally accepted as the stable hydroxide, though ferrihydrite is its probable precursor.

The new fences are:

d. *An 'aluminosilicate' fence* (A in Figure R4). This is defined by reactions in the system SiO_2–Al_2O_3–H_2O. For example by the congruent dissolution of kaolinite:

$$\overset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 6H^+ \rightleftharpoons 2Al^{3+} + \overset{\text{quartz}}{2SiO_2} + 5H_2O \quad (pH_4SiO_4 < 4.7)$$

by the incongruent dissolution of kaolinite:

$$\overset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 5H_2O \rightleftharpoons \overset{\text{gibbsite}}{2Al(OH)_3} + \overset{\text{quartz}}{2H_4SiO_4} \quad (pH_4SiO_4 < 4.7)$$

and by dissolution of gibbsite:

$$\overset{\text{gibbsite}}{Al(OH)_3} + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$$

e. *A sodium carbonate fence* (D in Figure R4). This defines the high pH extreme of the soil environment, and lies in the pH range of feldspar dissolution, if the latter were to reach a saturated equilibrium, as well as the range in which zeolites form authigenically under Earth surface conditions.

In addition, two fences on the original Krumbein and Garrels (1952) diagram are left essentially in their original form. These are

f. *The limestone fence* (C in Figure R4). Renamed the calcite fence, on the high pH side of which solid calcite persists in a soil system.
g. *The sulfate-sulfide fence* (F in Figure R4). Name simplified to sulfide fence, marking the upper limit of Eh of the field wherein sulfides, and in particular pyrite, may form in a soil.

Other geochemical fences may be useful in specific or local situations. For example in ombrotrophic bogs with low atmospheric input of particulate matter, the low pH limit could be marked by a fence defined by the dissociation of H^+ from carboxylic functional groups in the organic component of the soil system. An even lower pH fence can be defined for the interpretation of acid sulfate soils by the breakdown products of pyrite. Where neither organic matter nor pyrite are common, the system H_2O–CO_2 will be useful in defining a fence from about pH 5.7 to 5.5 depending upon the balance between atmospheric and respiratory inputs of CO_2. Under extreme reduction a CH_4 fence comes into play.

The pedogenic grid

The resulting adaptation (Figure R4) of the Krumbein and Garrels (1952) diagram is referred to as the pedogenic grid (Chesworth, 1992) and covers the broad range of conditions in common mineral soils. Certain organic soils and peatlands, and less common soils such as acid sulfate soils (see *Thionic or Sulfidic Soils*), lie outside this 'normal' range.

Parallels exist between the pedogenic grid and the pressure-temperature (PT) diagram of the petrologist. The invariant point of a PT diagram, where pressure and temperature are held constant, is similar to those regions on the grid where two fences cross. Such crossing points are called nodes by Chesworth (1992). They act as quasi-invariant points where the pH and Eh of a system is buffered and poised respectively.

A further analogy arises from the fact that the essentially univariant (or pseudo-univariant) fences of the grid delimit separate ranges of conditions with each area being characterized by its own individual assemblage of minerals. This is explicit in the diagram of Krumbein and Garrels (Figure R3). This is analogous to the interpretation of mineral facies in metamorphic petrology as a set of co-existing minerals falling within a field bounded by univariant reaction curves in PT space (Chesworth, 1975). A mineral facies approach to soil was first suggested by van der Plas and van Schylenborgh (1970).

Natural systems

Baas-Becking et al. (1960) were the first to show the spread of natural conditions in earth surface environments in an Eh-pH diagram. Generalizing from their data, Jenkins and Jones (1980), and later Chesworth (1992) produced diagrams showing the normal spread of conditions to be expected in the soil regime (see *Soil*).

Natural conditions in soils are often remarkably stable. The existence of nodes could account for this phenomenon which Bryan and Teakle (1949) called pedogenic inertia, wherein soil conditions persist in a more or less constant state in spite of changes in the larger ecosystem of which the soil is a part.

Well-drained soils

Redox potentials in well-drained soils are normally not well poised and therefore poorly reproducible because of the low concentration of soluble, chemically reactive species such as iron and manganese. Until molecular oxygen is depleted, redox potential remains in the oxic region. To obtain Eh values of <300 mV in the soil surface, the exchange of gas between the soil and the atmosphere must be restricted and there must be a high level of microbial activity. When the soil moisture tension is below 10 to 20 kPa, there is little exchange of gas between the atmosphere and the soil because the movement is controlled by the diffusion rate of the gas in water. Increases in soil temperature increase microbial activity and usually result in lower redox potentials. Even in soils that appear to be well-aerated, there are microsites; for example, the inside of aggregates, which may be under reducing conditions (see *Acid soils*, *Alkali soils*, *Calcareous soils*, *Near neutral soils*).

Poorly drained soils

During the growing season poorly drained soils are usually under reducing conditions because many of the pore spaces are filled with water, and the diffusion of dissolved oxygen through the water layers is four orders of magnitude slower than gaseous diffusion through a porous medium. Redox potential is the best measure of soil reduction processes in waterlogged soils because molecular oxygen is usually depleted within 48 hours during the growing season, and subsequent reduction reactions involve other redox couples. After molecular oxygen has been depleted, anaerobic microorganisms multiply rapidly and use oxidized forms of manganese, iron, nitrogen, sulfur, and other compounds as electron acceptors in respiration (Ponnamperuma, 1972).

Probably the best example of a poorly drained soil system used in agriculture is the paddy system used for rice production, where the fields are flooded continuously, and the plants obtain oxygen from the atmosphere and conduct it through the stems to the roots. This atmospheric oxygen diffuses out from the roots and forms an oxidizing layer which precipitates iron and manganese from the soil solution (see *Hydric Soils*, *Thionic or Sulfidic Soils*).

Effects on crop production

Redox potential can be changed in agricultural fields by tillage, water management, and incorporation of organic residues. Under irrigated conditions, an increase in flooding time will result in lower redox potential (Meek and Grass, 1975). Tillage affects redox reactions in two ways: (1) it increases soil porosity which usually increases redox potential, and (2) it incorporates residues to lower depths which may decrease redox potential (higher microbial activity) at these depths (Clay et al., 1992). The application of manure will reduce redox potential, especially under wet conditions. Redox reactions are important in agricultural soils, bringing small amounts of iron and manganese in solution (see *Micronutrients*).

Effects on the environment

Redox reactions will influence how waste disposal and crop production affect the environment. Redox potential is an important factor controlling the solubility of many metals and other species in the soil. Soluble arsenic can increase 13-fold when redox potential is reduced from 500 to –200 mV (Masscheleyn et al., 1991). In contrast when redox potential was reduced, the concentration of dissolved selenium in groundwater decreased 10-fold (White et al., 1991). Redox potential may also influence or determine the products of a reaction. For example, during denitrification the maximum amount of nitrous oxide was evolved at an Eh of 0 mV; but dinitrogen gas emissions increased at lower redox potentials (Masscheleyn et al., 1992). A well known environmental problem controlled by redox reactions is the oxidation of sulfides in soils that contain that mineral, producing soil and drainage waters of pH 3 or less (see below).

Nitrogen is an element which is of major concern in environmental pollution and is subject to many redox reactions. It can be used to illustrate the importance of redox reactions in determining how an element affects the environment. Redox reactions will affect the potential nitrate pollution resulting from application of organic wastes to soil. Denitrification is usually agriculturally undesirable because soil nitrate is not available for plant growth; but desirable from a pollution standpoint because it reduces nitrate pollution of groundwater. If the wastes contain large amounts of electron donors such as easily decomposable carbon and restricted aeration, denitrification can remove large amounts of nitrate. Glinski et al. (1992) added glucose to a soil to obtain reduction of nitrate. In contrast, electron acceptors such as nitrate can be added to anaerobic soil sites contaminated with hazardous organic compounds to encourage biological degradation of these compounds (Korom, 1992). Redox potential is useful for evaluating the potential for denitrification when the soil effluent reaches the water table (Weil et al., 1990).

Acid rock drainage

Acid rock (or mine) drainage (ARD or AMD) is formed when metallic sulfides react with water and oxygen in the weathering zone. Chemically it is the same process by which acid sulfate soils form (see *Thionic or Sulphidic soils*). Essentially the sulfide (usually pyrite) reacts to produce the ions of sulfuric acid in aqueous solution. A typical half-reaction is (Chesworth and Shelp, 2001):

$$FeS_2 + 11H_2O \rightleftharpoons Fe(OH)_3 + 2SO_4^{2-} + 19H^+ + 15e^-$$

The electrons are taken up by oxygen to give the characteristic redox reaction for weathering pyrite (Stumm and Morgan, 1996):

$$2FeS_2 + 7.5O_2 + 7H_2O \rightleftharpoons 2Fe(OH)_3 + 4SO_4^{2-} + 8H^+$$

This reaction follows the path shown in Figure R5 and leads to drainage waters with a pH of 3 or less. The usual approach to amelioration is to add lime to the drainage waters, which is

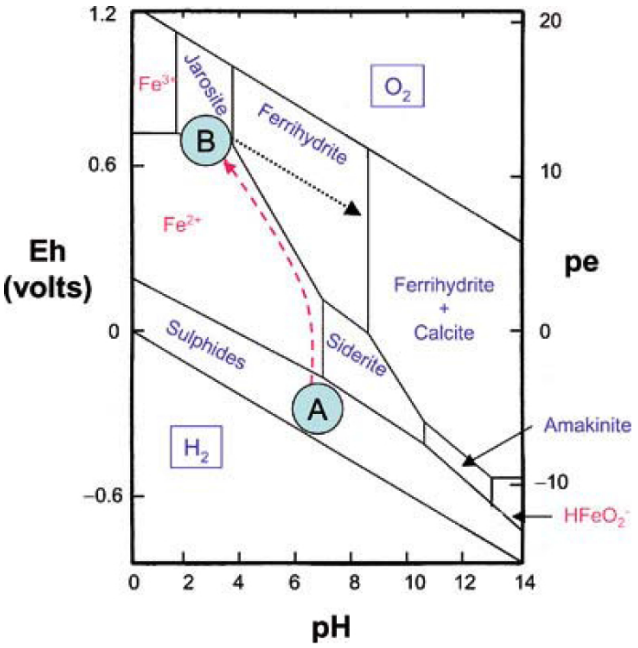


Figure R5 Formation of acid rock drainage; (A) represents connate water in equilibrium with pyrite in a water-saturated soil or sediment; (B) is the acid leachate (ARD or AMD) produced when oxygen enters the system. The path of oxidation is marked by the *dashed arrow* and leads to a state of progressive acidification because it is principally controlled by the negative slope of the ferrihydrite-Fe^{2+} boundary. The *dotted arrow* is the path taken when liming is used to ameliorate acidity. Galvanic correction of the ARD problem follows the reverse of the path indicated by the *dashed arrow*. Physical conditions as for Figure R2. The path from A to B also represents the process of acid sulfate soil formation when sulfidic materials are exposed to oxidation, for example when mangrove swamps are drained.

little more than treating the symptoms rather than the disease. Alternatives which treat the problem at source (i.e. by preventing the pyrite from breaking down) may involve the exclusion of oxygen by inundating the pyritic material with water, the exclusion of water by covering the deposit with an impermeable overlay, or by pumping electrons into the pyrite in the kind of galvanic system shown in Figure R6.

Summary

In the context of redox and related pH processes, there are five particularly significant features of soil:

1. Infiltration of atmospheric gases into the pore spaces of the vadose zone. This results in oxygen gas being the principal electron acceptor in the upper part of the profile, and the predominance of oxidized mineral phases amongst the weathered materials. Below the water table, free oxygen will be generally absent, though it may be present in solution close to the water table, or as a result of the addition of oxygenated water from an upwelling groundwater source.
2. The ubiquitous presence of water, even in soils of the arid zones of the world. Within the weathering column there will be a water table at some depth, above which is the vadose zone, and below which is the saturated zone. In the saturated zone water fills all pore spaces and excludes oxygen. Gleying phenomena occur in such situations.

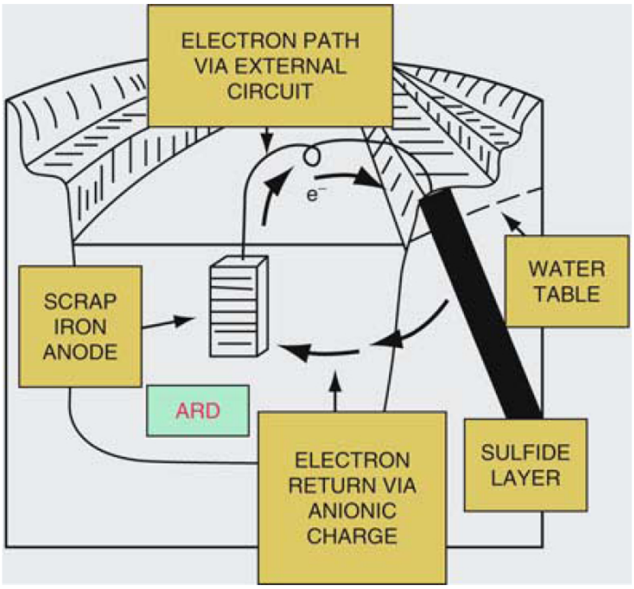


Figure R6 Galvanic system tested in the South Pit of the Sherman Iron Mine, District of Temagami, Ontario, Canada (Shelp et al., 1995). Weathering of the sulfide produces *ARD* in the pit at pH 3. The *ARD* and its groundwater extension provides an electrolyte (analogous to battery acid) which allows the setting up of a galvanic cell as shown. This pumps electrons into the sulfide which is thereby stabilized and further production of acid is prevented. The technique is a form of cathode protection.

3. Organic activity, especially in upper horizons. The aerobic metabolization of dead organic matter by microbial organisms in near surface horizons of a soil is the principal process by which oxygen is consumed. It is the process responsible for the overall redox state of the solum, though local and microscopic reactions produce great variability at a fine scale.
4. The occurrence of inorganic minerals and associated amorphous compounds. These are predominantly aluminosilicate in nature, but with local dominance of other minerals, most notably calcium carbonate. Minerals containing elements such as Fe, Mn, Cr and Mo, capable of existing in two or more oxidation states may affect redox locally. Sulfides when present, especially the commonest (pyrite FeS), will be the main determinants of redox-pH conditions if exposed to an oxidizing environment.
5. The importance of the ferrous-ferric relationship. Amongst elements that occur as cations in the approximately close packed oxygen-framework of crustal materials, iron ranks third after silicon and aluminum. Consequently Fe^{2+}/Fe^{3+} will normally be the dominant inorganic redox couple in soils and weathering systems generally.

Burl D. Meek and Ward Chesworth

Bibliography

Baas-Becking, L.G.M., Kaplan, I.R., and Moore, O., 1960. Limits of the natural environment in terms of pH and oxidation potentials. *J. Geol.*, **68**: 243–284.

Berner, R.A., 1970. Behaviour of iron during weathering, sedimentation and diagenesis. In Wedepohl, K.H., ed., *Handbook of Geochemistry,* Section 26G. Berlin: Springer, pp. 1–8.

Brookins, D.G., 1988. *Eh-pH Diagrams for Geochemistry.* Berlin: Springer, 176 pp.

Bryan, W.H., and Teakle, L.G.H., 1949. Pedogenic inertia: a concept in soil science. *Nature*, **164**: 969.

Chesworth, W., 1975. The system SiO_2–AlOOH–Fe_2O_3–H_2O and the kaolinitic stage of the goethite facies. *Clays Clay Miner.*, **23**: 389–392.

Chesworth, W., Martinez Cortizas, A., and Garcia-Rodeja, E., 2006. The redox-pH approach to the geochemistry of the Earth's land surface, with application to peatlands. Chapter 8. In Martini, I.P., Martinez Cortizas, A., and Chesworth, W., (Eds.) *Peatlands*: *Evolution and Records of Environmental and Climatic Changes*. New York: Elsevier, pp. 175–195.

Chesworth, W., 1992. Weathering systems. In Martini, I.P., and Chesworth, W., eds., *Weathering, Soils and Paleosols.* New York: Elsevier, pp. 19–40.

Chesworth, W., and Shelp, G., 2001. Galvanic control of oxygen fugacity as a treatment of problems associated with leachates from mine wastes. *ARCSACC Proc.*, *01*, pp. 240–244.

Garrels, R.M., and Christ, C., 1965. *Solutions, Minerals and Equilibria.* New York: Harper and Row, 450 pp.

James, B.R., and Bartlett, R.J., 2000. Redox phenomena. In Sumner, M. E. Editor-in-Chief: *Handbook of Soil Science*. Boca Raton, Fl: CRC Press. pp. B169–B194.

Jenkins, D.A., and Jones, R.G.W., 1980. Trace elements in rocks, soils, plants and animals. In Davies, B.E., ed., *Applied Soil Trace Elements.* New York: Wiley, pp. 1–20.

Krumbein, W.C., and Garrels, R.M., 1952. Origin and classification of chemical elements in terms of pH and oxidation-reduction potentials. *J. Geol.*, **60**: 1–33.

Pourbaix, M., 1974. *Atlas of electrochemical equilibria in aqueous solutions.* Nat. Assoc. Corrosion Eng., Houston, 644 pp.

Shelp, G., Chesworth, W., and Spiers, G., 1995. The amelioration of acid mine drainage by an in situ electrochemical method Pt. 1. Applied Geochem. vol.10, 705–713.

Shotyk, W., 1988. Review of the inorganic geochemistry of peats and peatland waters. *Earth Sci. Rev.*, **25**: 95–176.

Truesdell, A.H., 1968. The advantage of using pe rather than Eh in redox equilibrium calculations. *J. Geol. Educ.*, **16**: 17–20.

van der Plas, L., and van Schylenborgh, J., 1970. Petrochemical calculation applied to soils with special reference to soil formation. *Geoderma*, **4**: 357–385.

Weaver, C.E., and Pollard, L.D., 1973. *The Chemistry of Clay Minerals.* New York: Elsevier, 213 pp.

Woods, T.L., and Garrels, R.M., 1987. *Thermodynamic Values at Low Temperature for Natural Inorganic Materials.* New York: Oxford University Press, 266 pp.

Cross-references

Acid Soils
Acids, Alkalis, Bases and pH
Alkaline Soils
Calcareous Soils
Hydric Soils
Iron Oxides
Micronutrients
Near-neutral Soils
Soil
Thionic or Sulfidic Soils

REGOLITH

The blanket of unconsolidated rock-material of whatever origin, residual or transported, that mantles solid rock. Includes any rudimentary soil present. Term invented by Merrill, 1897, p. 299.

Bibliography

Merrill, G.P., 1897. *A treatise on Rocks, Rock-weathering and Soils.* London, Macmillan. 411 pp.

REGOSOLS

Regosols are young, mineral soils with a minimal ochric surface horizon, developed on deep, well-drained, medium-textured, parent materials.

Connotation. Soils in the weathered shell of the Earth; from Gr. *rhegos*, blanket.

Synonyms. In other systems of classification soils at the incipient stage of formation represented by the WRB group Regosols, are classed as 'entisols' (USA), 'skeletal soils' (Australia), 'Rohböden' (Germany), and 'sols peu évolués régosoliques d'érosion' or even 'sols minéraux bruts d'apport éolien ou volcanique' (France).

Definition. Regosols are operationally defined as very weakly developed mineral soils in unconsolidated materials with only an ochric surface horizon. They are not shallow enough to be leptosols, sandy enough to be arenosols, and lack the fluvic properties that would allow them to be classed as fluvisols. In effect, Regosols are considered to be a "*taxonomic rest group*" (FAO, 2001), defined negatively as all soils that could not be accommodated in any of the other Reference Soil Groups.

Parent material. Unconsolidated, finely grained weathering material.

Environment. They occur extensively in eroding lands, particularly in the drier climatic zones and in mountain regions.

Distribution. Figure R7 shows the global distribution of the approximately 260 million ha of the Regosols. Regosolic areas are not generally very extensive. Notable occurrences are in dry climatic regions in the USA, North Africa, the Near East and Australia. The dry tropics account for about 50 million ha, with 36 million ha in mountainous regions. Regosols are found associated with a wide range of other Reference Soil Groups, especially other young or poorly evolved soils. Many grade into other soil types for example cryosols in cold regions, andosols, leptosols or umbrisols in mountain regions, calcisols or gypsisols in arid regions, arenosols and podzols in sandy deposits, or cambisols.

Characteristics. As a taxonomic rest group, Regosols are too varied to permit extensive generalization about their characteristics. The authors of FAO (2001) make the following points.

- Parent material and climate dominate the morphology of Regosols. The content of weatherable minerals varies from low to extremely high (little transformation).
- In cool climates, the surface horizon contains poorly decomposed organic matter whereas (ochric) surface horizons tend to be thin, low in organic matter and generally weakly expressed in hot, dry climates.
- Regosols in dry regions have generally a higher base status than Regosols in more humid (mountain) regions.
- Low coherence of the matrix material makes most Regosols in sloping areas prone to erosion.
- Low water holding capacity and high permeability to water make most Regosols sensitive to drought.

Many Regosols in colluvial material are prone to slaking in particular those in loess. This makes them sensitive to erosion in wet periods. Many Regosols form a hard surface crust early in the dry season; the crust hinders emergence of seedlings and infiltration of rain and irrigation water in the dry season.

Origin. The limited pedogenetic evolution of Regosols is indicated by the presence of a thin, organic-poor, ochric horizon, its color determined by the composition of the mineral

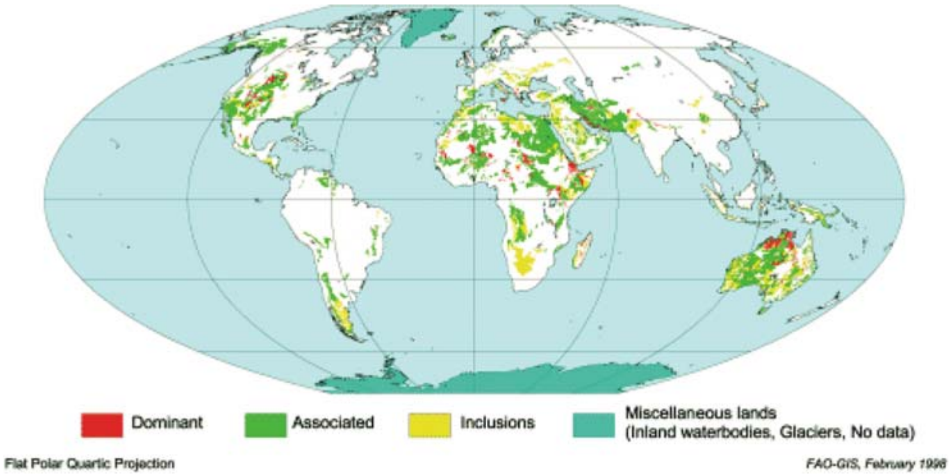


Figure R7 Global distribution of Regosols.

fraction. Reasons for the poor development depend on the environment of formation. For example, they occur in arid desertic regions where chemical weathering is inhibited by lack of water. Mountain zones are another typical environment for these soils. Here, erosion continually removes developing soils on upper slopes and leads to the accumulation of colluvium lower down. In both topographic positions the soil is inevitably kept at an early stage of genesis. In climates where evaporation exceeds precipitation for most of the year, minerals such as calcite and/or gypsum may form in the solum, but not in amounts to qualify as a calcic or gypsic horizon. Finally, disposal of wastes from urban, mining and industrial sources, sediment from dredging operations and other human activities are sources of new weatherable materials. Such deposits are too young for any significant soil development, and are included in the Reference Soil Group of the Regosols.

Use. Land use and management vary widely. Some Regosols are used for capital-intensive irrigated farming but the most common land use is low volume grazing. The low structural coherence of Regosols means that in areas where erosive activity is strong, as on mountain slopes, forestry is the best use for these soils.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science*, 2nd ed. Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils

RELIEF

The changes in elevation over a landscape. Relief is considered to be one of the five principal factors of soil formation and a catena of soils that varies solely (or essentially so) as a function of relief, is called a toposequence.

Cross-reference

Factors of Soil Formation

RENDZINA

A fertile soil with a friable, brown to black surface horizon, underlain by a lighter colored horizon containing calcite, formed directly on soft calcareous rocks such as chalk soil. Typically under grass or open woodland in regions of humid to semi-arid climate. Rendzinas are Leptosols formed on calcareous rocks.

Cross-references

Calcareous Soils
Classification of Soils: FAO
Leptosols

RESIDENCE TIME

The period of time a particular element or other substance spends in a system, including the soil. It is a function of the amount of the substance in a defined volume of soil (the reservoir) divided by the net rate of change measured in terms of rate of efflux minus rate of influx. It may vary between a matter of minutes to hours for non-capillary water in the vadose zone to an order of 10^6 to 10^7 years for elements such as Fe, Al, Ti and Zr, in well-oxidized soils on stable land surfaces of the tropics.

RESIDUA SYSTEM OF WEATHERING

The compositional system SiO_2–Al_2O_3–Fe_2O_3–H_2O, so called because it contains within it, the common end points (or residua) of prolonged weathering, such as Ferralsols, laterites, bauxites, and all soil horizons such as the albic and oxic horizons made up predominantly of some combination of quartz, 1:1 sheet silicates, simple aluminosilcate amorphous (or short range order) phases, and Fe and Al hydroxides.

Cross-reference

Geology and Soils

RESIDUAL SOIL

A soil formed in place on a parent material gradational into the rock from which it is derived. In other words it has not been transported and therefore still has a genetic relationship with the geological material it rests upon. Where residual soils overlie ore deposits, vestigial traces of the ores may be detected by studying the mineralogy or chemistry of the soil, even where the latter is highly weathered. Hence the usefulness of residual soils in geochemical prospecting (Hawkes and Webb, 1962, Chapter 9).

Bibliography

Hawkes, H.E., and Webb, J.S., 1962. *Geochemistry in Mineral Exploration*. New York: Harper and Row. 415 pp.

Cross-references

Regolith
Saprolite

REVERSE WEATHERING

A geochemical process whereby the chemical composition of a soil or other weathering system acquires an influx of elements such as Ca, Mg, Na and K that are normally lost during weathering. In effect, reverse weathering results in a chemical trend away from compositions within the system SiO_2-Al_2O_3-Fe_2O_3-H_2O, the residua system of weathering. Reverse weathering was first hypothesized by Garrels (1965), as a process that probably occurred in the oceanic environment.

Bibliography

Garrels, R.M., 1965. Silica: Role in the Buffering of Natural Waters. Science: **148**: 69.

Cross-references

Residua System of Weathering
Weathering Systems in Soil Science

REVISED UNIVERSAL SOIL LOSS EQUATION (RUSLE)

RUSLE states that:

$$A = R.K \cdot LS.C.P$$

A form that is identical to the original Universal Soil Loss Equation. In RUSLE A is the average annual soil loss. Originally this was expressed in tons per acre per year. Now Mg ha^{-1} yr^{-1} is more appropriate.

- R = rainfall/runoff erosivity
- K = soil erodibility
- LS = hillslope length and steepness
- C = cover-management
- P = support practice

R represents the erosivity expressed in terms of rainfall and runoff at a particular location. The value of R increases with the amount and intensity of rainfall.

K represents the inherent erodibility of the surface cover under standard experimental conditions. It is estimated as a function of particle-size distribution, organic matter content, structure, and permeability of the soil or surface material for the specific locality of interest.

C represents the effects of surface covers and roughness, soil biomass, and soil-disturbing activities on rates of soil loss at a specified locality. As surface cover and soil biomass increase, C decreases, lower values indicating increased protection of the soil from rain splash and runoff.

LS combines the factors that express the effect of topography on rates of soil loss at a particular site. Specifically these are the length and steepness of the slope. The value of LS increases with hillslope length and steepness. The assumption is that runoff accumulates and accelerates downslope. Although this can be assumed to be valid for a landscape experiencing overland flow, it may not be valid for densely vegetated terrain, forests for example.

P expresses the effects of supporting conservation practices on soil loss at a specific site – contour plowing, grassed waterways, terracing and so on. Its value increases with the effectiveness of the practice employed in reducing runoff volume and velocity and in encouraging the deposition of sediment on the surface of the hillslope.

Bibliography

Renard, K.G., Foster, G.R., Weesies, G.A., Porter, J.P., 1991. RUSLE. Revised universal soil loss equation. *J. Soil Water Conserv.,* **46**: 30–33.

Cross-reference

Water Erosion

RHIZOSPHERE

The *rhizosphere* comprises the small zones immediately surrounding plant roots in the soil, in which the kinds, numbers and activities of microorganisms differ from that in the bulk soil (Gregorich et al., 2001). Included are the microorganisms and the organic and inorganic materials released by the roots themselves. The rhizosphere is thus a poorly defined zone around any root, commonly extending out no more than 1 or 2 mm but occasionally as far as 20 mm. The name was originally proposed in 1904 by Hiltner for the volume of soil near legume roots in which the growth of heterotrophic bacteria might be stimulated by the nitrogen released from nodules (Neal et al., 1970). The meaning has since been expanded to cover roots of all plants.

The root surface and adhering soil particles are called the *rhizoplane*. It is rather distinct as compared to the rhizosphere. It is where microorganisms invade and modify the viscous mucilaginous coatings on the epidermal surfaces of roots.

The microbial population of the rhizosphere differs both quantitatively and qualitatively from that outside these small zones and may vary with plant species, root zone and soil type (Marschner et al., 2001). Soil sampling, followed by standard biochemical and microscopic techniques and plate counts are used in the study of the microorganisms and various substances present in the rhizosphere (van Elsas and Smalla, 1997). Latterly, DNA extraction and molecular fingerprinting have made possible the study of the structure of bacterial community in considerable detail (Gelsomino et al., 1999). The numbers of viable organisms in the rhizosphere (R) are greater than those in the remainder of the soil (S). The *R:S ratio* for bacteria commonly ranges from 5 to 20 but may exceed 100. Ratios of 10 to 20 are common for fungi, based on estimates from numbers of fungal spores rather than active mycelia. Ratios for actinomycetes are lower than for bacteria, whereas reports on numbers of algae and protozoa are conflicting and therefore uncertain. The R:S ratio for free-living nematodes may be as high as 70. For the various organisms, the R:S ratios differ widely with differences in environmental conditions and in experimental techniques.

Qualitative effects are comparable to the quantitative ones. Within the rhizosphere, there is a selective stimulation of Gram-negative bacteria with fast growth rates and a reduction in the spore-forming *Bacillus* spp. and the grampositive cocci. Fungi become more abundant near the older parts of roots where specialized forms such as *Fusarium oxysporum, Penicillium* spp. and *Trichoderma viride* predominate. The detection of more responsive groups of microorganisms may therefore be more useful in defining the extent of the rhizosphere than total counts.

Substances within the rhizosphere also have evident nutritional effects on microorganisms. Bacteria that use amino acids directly are stimulated whereas those with more complex nutritional requirements are not. Selective stimulation of organisms with specific physiological activities also occurs. Examples include ammonifiers, denitrifiers, non-symbiotic nitrogen fixers and aerobic cellulose-decomposing microorganisms (Sylvia et al., 2005).

The basis of the rhizosphere phenomenon is apparently biochemical and nutritional. Rovira and McDougall (1967) list as excreted compounds: 10 sugars, 21 amino acids, 10 vitamins, 11 organic acids, 4 nucleotides, 16 fungal stimulators or attractors, 3 fungal inhibitors, 4 eelworm hatching factors, 2 eelworm attractors, and 11 miscellaneous compounds including enzymes. The possibility of inducing a rhizosphere population favorable to agricultural or horticultural crops has led to the development of several lines of research. Seed and root inoculation have been used and in 1970 Neal et al., were the first to show that chromosome substitution from wheat resistant to root-rot to wheat susceptible to the disease produced wheat cultivars with markedly different rhizosphere populations presumed antagonistic to the root-rot organism. This potential for manipulating the chemistry, organisms and structure of the rhizosphere chemistry by the genetic modification of a crop is still largely untapped, but according to Richards et al. (2007) "is likely to be very important in systems with minimum soil disturbance that are prone to interactions with soil organisms constraining wheat growth."

Michael Herlihy

Bibliography

Gelsomino, A., Keijzer-Wolters, A.C., Cacco, G., and van Elsas, J.D., 1999. Assessment of bacterial community structure in soil by polymerase chain reaction and denaturing gradient gel electrophoresis. *J. Microbiol Meth.*, **38**: 1–15.

Gregorich, E.G., Turchenek, L.W., Carter, M.R., and Angers, D.A., 2001. *Soil and Environmental Science Dictionary.* Boca Raton, FL: CRC Press, 577 pp.

Macura, J., 1967. Physiological studies of rhizosphere bacteria. In Gray, T.R.G., and Parkinson, D., eds., *The Ecology of Soil Bacteria.* Liverpool: University Press, pp. 379–395.

Marschner, P., Yang, C.-H., Lieberei, R., and Crowley, D.E., 2001. Soil and plant specific effects on bacterial community composition in the rhizosphere. *Soil Biol. Biochem.*, **33**: 1437–1445.

Neal, J.L., Jr., Atkinson, T.G., and Larson, R.I., 1970. Changes in the rhizosphere microflora of spring wheat induced by disomic substitution of a chromosome. *Can. J. Microbiol.*, **16**: 153–158.

Richards, R.A., Watt, M., and Rebetzke, G.J., 2007. Physiological traits and cereal germplasm for sustainable agricultural systems. *Euphytica*, **154**: 409–425.

Rovira, A.D., and McDougall, B.M., 1967. Microbiological and biochemical aspects of the rhizosphere. In McLaren, A.D., and Peterson, G.H., eds., *Soil Biochemistry,* Vol. 1. New York: Marcel Dekker, pp. 417–463.

Sylvia, D.M., Fuhrmann, J.J., Hartel, P.G., and Zuberer, D.A., 2005. *Principles and Applications of Soil Microbiology.* 2nd edn. Upper Saddle River, NJ: Pearson Prentice-Hall, 640 pp.

van Elsas, J.D., and Smalla, K., 1997. Methods for sampling soil microbes. In: Hurst, C.J., Knudsen, G.R., McInerney, M.J., Stetzenbach, L.D., and Walter, M.V., Ed., *Manual of Environmental Microbiology.* Washington, DC: ASM Press, pp. 383–390.

RIA

A Gallego or Portugese word for a drowned coastal inlet found particularly in northwestern Spain and the southwestern coast of Ireland, differing from a fiord by showing no evidence of glaciation. In Spain the Rias Altas along the Biscay coast are distinguished from the Rias Bajas on the Atlantic south of Santiago de Compostela. The dominant soil types here, and also along rias in California, Australia, New Zealand and elswhere, are Fluvisols. In some cases they are sulfidic.

RIDGE

A long, narrow strip of rising ground of any earth-material and any origin. Also used in agriculture to denote the elongated mound of soil turned up by a plow in the process of cutting a furrow. Parallel ridges and furrows, running along contour lines are a simple and effective means of minimizing soil erosion on farmland.

ROCKLAND

An area of sparse soil with a substantial proportion (usually >25%) of exposed rock outcrop. Figure R8 shows rockland in the Canadian Shield near Sudbury, northern Ontario.

ROLLING

Describes a landform that is gently undulating with a wave-like relief. No particular process of origin is implied. Soils on rolling topography tend to show much local variation in texture. The pattern of variation follows the rhythm of the undulations, since fine particles tend to wash down from highs into hollows. Consequently the lower soils are enriched in the clay-fraction at the expense of adjacent soils upslope. Compare with soils in hummocky terrain in the article *Ice Erosion*.

Cross-reference

Landscape and Soils

ROTATION

A method of managing the fertility of soil by changing the crops on a given piece of ground, in a particular sequence over a succession of seasons. One of the most famous is the Norfolk Rotation devised in the eighteenth century, and based on a four season sequence such as Winter Grains (Wheat and Rye) → Clover → Summer Grains (Oats and Barley) → Turnips. Arguably, the rotations developed in 18th and early 19th century Europe brought farming as close as it has ever been to sustainability (Hawkes, 1991). The seasonal sequence turnips-barley-clover-wheat wheat, turnips, oats, and fallow.

Figure R8 Rockland in the Canadian Shield near Sudbury, northern Ontario. This is an anthropic landscape produced by excessive soil erosion, following the dying-off of the boreal forest as a result of atmospheric contamination from copper and nickel smelting.

Bibliography

Hawkes, J.H., 1991. *A Land*. Boston: Beacon Press. 248 pp.

RUBIFACTION OR RUBEFACTION

The reddening of soil or rock caused by the release of iron during weathering, its oxidation to the ferric state, and its precipitation as a hydroxy phase (commonly ferrihydrite, at least initially). The process is typical of the tropics and adjacent parts of the sub-tropics (Pedro, 1968).

Bibliography

Pedro, G., 1968. Distribution des principaux types d'altération chimiques a la surface du Globe – présentation d'une esquisse géographique. *Rev. Géol. Phys. Géol. Dyn.*, **10**: 457–470.

RUNOFF

The water that drains directly from the surface of land after a precipitation event, without soaking into the soil. It is a major factor in the erosion of soil, and in the contamination of waterways with agricultural chemicals.

Cross-references

Water Budget in Soil
Water Erosion

S

SABKHA

An Arabic term meaning ‘morning’, applied to coastal flats that are occasionally inundated, and where evaporation leads to the formation of salt deposits at the surface. The characteristic soil is a Solonchak, with hygroscopic salts such as $CaCl_2$ or $MgCl_2$, and NaCl (which is less hygroscopic than the other two). During the night as temperature declines towards the dew point, the salts pick up water from the atmosphere and the soil surface becomes dark and muddy during the early morning. Evaporation during the day allows the salts to recrystallize to form a loose crust of crystals (or, where Na_2SO_4 is present, a fluffy, puffed layer).

The Spanish term salina is also applied to salt deposits on coastal flats, but also to salt deposits in depressions inland.

Bibliography

Hans-Jörg, B., Hans-Jörg, and Böer, B., 2002. *Sabkha Ecosystems*. Berlin Heidelberg New York: Springer-Verlag, 368 pp.

Cross-reference

Solonchaks

SALINE

Impregnated with salt or salts. The process by which a soil becomes so impregnated is called salinization, the essential step being the evaporation of salty water. Salinity is the quantity of salt in water or soil. It may be estimated in terms of electrical conductivity (see Figure S1).

SALT AFFECTED SOILS

See *Alkaline Soils*.

SALT LEACHING

Salt-affected soils are wide-spread in occurrence in the arid and semi-arid regions of the world (Keren, 2000). In arid regions washing down of salts already present in the soil, or those released through weathering, is only a local phenomenon and salt may not be transported very far because of limited rainfall. Due to high evapotranspiration rates in arid climates, soluble salts often tend to concentrate in the root zone of crops thereby rendering the soils less suitable for crop production. The problem of excess salts in the rhizosphere is accentuated when soils of the arid and semi-arid regions are brought under irrigation. This is particularly true when quality of ground water is poor and not used conjunctively. Under such situations, the water table begins to rise. Once the water table rises to within 1 to 2 m from soil surface, appreciable quantities of ground

Figure S1 Saline soil in the Nile delta, Egypt. Salinization in the delta region has two sources. One comes from the evaporation of irrigation water, as seen in the photograph. A second arises by sea-water incursion. Photo by John Fitzsimons.

water move upward into the root zone and are lost by evaporation, leaving the dissolved salts in the root zone. Ground water, as well as irrigation water, thus contributes to soil salinization. Consequently, survival of irrigated agriculture in arid and the semi-arid regions in perpetuity would depend on reducing soil salinity to acceptable levels by leaching and alleviating waterlogging caused by irrigation and preventing subsequent salinization.

Leaching is by far the most effective means of removing salts from the root zone of soils. Information on the amount of leaching required for salinity control can be obtained from the established simple empirical relationship (Jury et al., 1979):

$$\frac{C}{C_0}\frac{\Delta w}{\Delta s\,\Theta} = \frac{C}{C_0}PV = 0.8 \tag{1}$$

where C is the salt concentration in the soil after leaching, with a Δw depth of leaching water, applied to a depth of soil Δs, and Θ equals the volumetric moisture content. C_0 represents initial concentration of salts in the soil. Pore volume, PV, equals $(\Delta w/\Delta s\Theta)$. Water requirement for percent salt removal can be read from generalized leaching curves computed on the basis of field leaching tests conducted on texturally different soils (Hoffman, 1980). It may be pointed out that leaching of soils salinized by solutions with notable amounts of sulfate ions generally needs more water. Equation (1) suggests that salt leaching increases as the soil water content during leaching decreases (Nielsen et al., 1966). This is because unsaturated moisture flow allows the salts present in the non-conducting pores to diffuse.

Dieleman (1963) had earlier proposed a simple leaching equation, which describes reasonably well the leaching of salts from any given soil depth:

$$\frac{\Delta_{\mathrm{dw}}}{\Delta s} = \frac{\Theta}{f}\frac{\ln(\mathrm{EC_e} - \mathrm{EC_{eq}})}{\mathrm{EC_0} - \mathrm{EC_{eq}}} \tag{2}$$

The term $\mathrm{EC_{eq}}$ represents the EC of the surface 5 cm soil after exhaustive leaching with a given quality of irrigation water under existing drainage conditions. The terms $\mathrm{EC_0}$ and Δ_{dw} represent initial electrical conductivity of the soil and the depth of drainage water, respectively. Leaching efficiency factor (f) generally varies from 0.6 to 0.7 for sandy soils. It decreases sharply with fineness of texture, and also when $\Delta_{\mathrm{dw}}/\Delta s$ ratio exceeds 0.5 for sandy loam and 0.75 for the clay loam to clay soils. Poor drainage conditions affect the leaching and redistribution of salts under one-dimensional flow. However in two-dimensional leaching, salts directly move into tiles from above and near the drains, but are removed little midway between the drains. Thus in order to leach uniformly and more efficiently, initiate leaching midway between the drains.

Leaching methods

Leaching of saline soils can be accomplished in several ways by ponding of water on the soil surface either continuously or intermittently, using surface or any other irrigation method including sprinklers. Different irrigation methods vary as to their application and leaching efficiency.

Continuous ponding

In continuous ponding, water is impounded on the surface using a surface irrigation method. The method has all the merits and limitations that are inherent to flood irrigation. For effective salt leaching under continuous ponding, it is necessary to facilitate uniform application of water and its infiltration. This requires leveling and bunding of land when the fields are dry. If there are any hard subsoil layers, the soils might need to be plowed deep or chiseled. Continuous ponding although reduces the leaching efficiency of water, leaching requires less time because salt displacement takes place at near saturation. Use of saline water ($\mathrm{EC_{iw}} < \mathrm{EC_e}$) for initial leaching, reduces the requirement for good quality water. Leaching is usually considered adequate with a given quality water if the observed average root-zone salinity, $\mathrm{EC_e}$ is less than the maximum permissible salinity limit, $\mathrm{EC_t}$ with no yield reduction. Adoption of continuous ponding during a crop season may cause soil aeration problems for growing crops and may also lead to rise in water table and increase the drainage volumes for disposal. Adopting furrow irrigation can reduce aeration and crusting problems due to continuous ponding. Furrow irrigation is well adapted to row crops and lands that are too poorly drained for flooding. In furrow irrigated soils soluble salts tend to accumulate in the raised beds wetted by subbing water from the furrows. This tendency is greatest in single-row, round topped beds. In double-row beds, most of the salts are carried into the center of the bed leaving the shoulders relatively free of salts. If for the given bed-furrow conditions there is a tendency for the salts to accumulate, leaching can be enhanced by reducing the depth of furrows and increasing the irrigation depth. In areas with high water table, alternate row irrigation reduces salt accumulation. In this method every other row is flooded to remove salts into the unirrigated area. A similar redistribution of soluble salts can be effected in alternate border leaching method in orchards (Miyamoto, 1988) or with bed-furrow method in forestry (Tomar and Gupta, 1986).

Intermittent ponding

Intermittent ponding method allows the rise in water table following ponding to subside before next application and would therefore appear appropriate in areas having no provision of tile drains etc. Intermittent ponding of water has been reported to increase the efficiency of salt leaching (Nielsen et al., 1966; Talsma, 1967). However, the method works well only in low evaporative demand conditions because the gains of increased leaching efficiency will be lost by high evaporative losses of water (Minhas and Khosla, 1986). Intermittent ponding is particularly useful when practiced with mulch under low drainage rates and high water table conditions.

Rainwater leaching

In areas where good quality water is not available in plentiful, leaching with rainwater is the usual practice. Salt leaching during monsoon season can be accomplished through adoption of appropriate moisture conservation practices and improvement in the permeability of soils. In a properly leveled and bunded field, leaching with rainwater is accomplished uniformly. Creation of a soil mulch by plow in the rain free period reduces unproductive losses of water. Although the number of rainfall events, their depth, intensity and duration may vary but the salt removal from texturally different soils followed the general functions (Minhas and Gupta, 1991):

- Finer textured soils (clay loam and silty clay loam):

$$\frac{\mathrm{EC_a}}{\mathrm{EC_b}} = 0.1916\frac{\Delta s}{\Delta rw} - 0.0962$$

- Medium textured soils (sandy loam and loam):

$$\frac{EC_a}{EC_b} = 0.1919\frac{\Delta s}{\Delta rw} - 0.0017$$

- Coarse textured loamy sands:

$$\frac{EC_a}{EC_b} = 0.1577\frac{\Delta s}{\Delta rw} + 0.0368$$

where subscripts ‘a’ and ‘b’ refer to soil salinity after and before the monsoon season. Depth of rainwater is represented by Δrw. High $\Delta s/\Delta rw$ ratio for finer textured soils was primarily due to run off losses of rain water. Indian experience has demonstrated that 300 mm of precipitation received in the monsoon season, leached most of the salts from the surface – 400 mm of loamy sand and about 80% of the salts from the medium textured soils. Salt leaching efficiency of rainwater can be significantly improved if antecedent moisture content of the soils is scrupulously increased by saline irrigation just before the onset of the monsoons.

Sprinkler method

Sprinkler irrigation method has the advantage that water can be applied to unprepared fields on a flat or undulating terrain. It is compatible with coarser textured soils as it reduces the deep percolation of water in conveyance and actual field application. Leaching with sprinklers can reduce drainage volume and seepage problems. Nielsen et al. (1966) reported high leaching efficiency through sprinkling. However, under conditions of high evaporative demands and on strong windy days its efficiency is seriously affected respectively due to losses and uneven distribution of applied water.

Surface flushing

Reeve et al. (1955) have reported that passing of water over the surface by sheet flow is ineffective for flushing of soluble salts accumulated near the surface of the soil. However, when the soluble salts are of alkaline nature it would appear desirable to flush them out rather than leach into the soil profile. The surface flushing and disposal of flushed water in natural drains has proved quite useful for growing crops in alkali soils of the Indo-Gangetic plains.

Leaching requirement

To maintain salinity in the root zone below a desired level, excess of salts must be leached out. The fraction of infiltrated irrigation water that must be leached through the root zone to maintain soil salinity at some predetermined level is called as the leaching requirement (*LR*) of the soil under given land use condition. The term leaching requirement is interchangeably used with the leaching fraction (*LF*) and is expressed as:

$$LF - \frac{D_{iw} - D_{ET}}{D_{iw}}$$

where D_{iw} refers to the amount of water applied to meet both evapotranspiration (D_{ET}) need of crop plants and the leaching fraction (*LF*). Under steady state conditions leaching requirement can be calculated as:

$$LR = \frac{D_{dw}}{D_{iw}} = \frac{EC_{iw}}{EC_{dw}} = \frac{EC_{iw}}{EC_{e'}} \tag{3}$$

Leaching requirement is related to EC_{iw} and to root zone salinity $EC_{e'}$, through the expression (Rhoades, 1984):

$$LR = \frac{EC_{iw}}{5(EC_{e'})} - EC_{iw}$$

where $EC_{e'}$ is the salinity of the saturation extract of the soil at 10 percent yield reduction.

The strategy for leaching a short season crop wherein salinity decreases with soil depth is different from that under steady state. In perennial crops under steady state conditions, leaching may be done either with every irrigation or periodically (Shalhevet, 1984). However, short season crops should be irrigated normally up to a time when salts become excessive and then leaching carried at a later growth stage of crop (Minhas and Gupta, 1991).

Raj K. Gupta and I. P. Abrol

Bibliography

Dieleman, P.J., ed., 1963. *Reclamation of Salt Affected Soils in Iraq: Soil Hydrological and Agricultural Studies.* Wageningen, The Netherlands: H. Veenman & Zonen, 175 pp.

Gupta, R.K., and Abrol, L.P., 1990. Salt-affected soils: their reclamation and management for crop production. *Adv. Soil Sci.* **11**: 224–288.

Hoffman, G.J., 1980. Guidelines for reclamation of salt-affected soils. Proc. 2nd Inter-American Conference on Salinity and Water Management Technology, Juarez, Mexico, 11–12 Dec. 1980, pp. 49–64.

Jury, W.A., Jarrell, W.M., and Devill, D., 1979. Reclamation of saline-sodic soils by leaching. *Soil Sci. Soc. Am. J.*, **43**: 1100–1106. Errata 1987, *Soil Sci. Soc. Am.J.*, **51**: 1092.

Keren, R., 2000. Salinity. In: Sumner, M.E., ed., *Handbook of Soil Science*, Boca Raton, FL: CRC Press, G3–G25.

Minhas, P.S., and Gupta, R.K., 1991. *Irrigation water quality: Assessment and Management.* New Delhi: Indian Council of Agricultural Research, 73 pp.

Minhas, P.S., and Khosla, B.K., 1986. Solute displacement in a silt loam soil as affected by method of water application under different evaporation rates. *Agric. Water Manage.*, **12**: 64–74.

Miyamoto, S., 1988. *Reclamation of Salt Affected Orchards. Proc.* Texas Pecan Conf. College Station, Texas, pp. 25–37.

Nielsen, D.R., Biggar, J.W., and Luthin, J.N., 1966. Desalinization of soil under controlled unsaturated flow conditions. *Sixth Congr. Int. Comm. Irrig. Drainage, New Delhi*, **19**: 15–19.

Reeve, R.C., Pillsbury, A.F., and Wilcox, L.V., 1955. Reclamation of a saline and high bron soil in the Coachella Valley of California. *Hilgardia*, **24**(4): 69–91.

Rhoades, G.D., 1984. Reclamation and management of salt-affected soils after drainage. In: Proceedings of 1st Annual Western Provincial Conference on Rationalization of Water and Soil Research and Management. Lethbridge, Alberta, pp. 123–187.

Shalhevet, J., 1984. Management of Irrigation with brackish water. In Shainberg, and Shalhevet, J., eds., *Soil Salinity Under Irrigation Processes and Management*, Berlin: Springer, pp. 298–318.

Talsma, T., 1967. Leaching of tile drained saline soils. *Aust. J. Soil Res.*, **5**: 37–46.

Tomer, O.S., and Gupta, R.K., 1986. Salt redistribution and tree planting methods. Annual Report. Karnal, India: Central Soil Salinity Research Inst.

SAND

A material consisting of particles between 0.05 and 2 mm diameter, representing comminuted grains obtained by the breakdown of rocks. Also the textural fraction of a soil made of such particles. Most sands are quartzose, with feldspar in younger, less weathered sands. Much less common, and essentially ephemeral, are sands composed of easily weathered minerals, the olivine beach sands of Hawaii for example. Amongst WRB soil groups Arenosols is the main one for sandy textured soils. Sandy soils are also common as Regosols, Leptosols and Fluvisols.

Soils with a sandy texture present several problems to the farmer. They generally have a poor water holding capacity and consequent rapid drainage makes them 'droughty'. They are also prone to wind erosion, especially where a cover of protective vegetation is sparse or absent. Inherent fertility is usually low, and applied fertilizer is readily leached.

Cross-reference

Arenosols

SANDUR, SANDR

The gravelly or sandy deposits laid down as glacial outwash, winnowed of finer material by eolian removal originally named for examples in Iceland.

Cross-reference

Ice Erosion

SAPROLITE

Either (*a*) any thoroughly decomposed rock formed in place and grading downwards into solid rock, or (*b*) the same definition with the rider that the decomposed rock retains the macrostructural elements of the unaltered rock (foliation, bedding planes, microfolds and so on. The original meaning is (*a*).

SAPROLITE, REGOLITH AND SOIL

Most of the Earth's land surface (about 95%), at least in the middle and lower latitudes, is covered by unconsolidated deposits of one sort or another (Hunt, 1986). In the higher latitudes, glacial erosion has removed some of the surface cover, exposing bare rock surfaces that account for about 5% of the land area. In the low-lying tropical and peritropical regions, most of the land surface is covered by soils and thick accumulations of detritus, largely derived from weathering mantles. Researchers who have been directed to prepare maps of bedrock geology on parts of weathered cratons, shields, and stable platforms appreciate the difficulties associated with mapping in strongly weathered terranes. Similar problems occur in other regions where there are extensive covers of sand, volcanic ash, loess, alluvium, colluvium, wash deposits, vegetal accumulations, and soil. These kinds of surficial covers also pose serious problems for economic geologists who must attempt to elucidate bedrock structure and composition at depth. By applying indirect field techniques that involve geochemical sampling of cover deposits and geophysical survey it is often possible to interpret the nature of bedrock under many meters of masking cover. Whether attempting to discern the bedrock geology below a surficial mantle or preparing maps of surficial geology, it becomes necessary for the field geologist to distinguish effectively the major kinds of surface deposits – viz. saprolite, regolith, and soil. The well-trained field geologist thus employs the principles and practices of surficial geology and pedology.

Regolith

The terms *saprolite* and *regolith* are used to designate a range of unconsolidated deposits that occur at the surface of the Earth (see Table S1). *Regolith* is the more general term of the two. It applies to the layer or mantle of fragmental and unconsolidated rock material, whether residual or transported and of highly variable character, that nearly everywhere forms the surface of the land and overlies or covers the bedrock (Anand and Butt, 1988). This rock debris includes all kinds of materials such as volcanic ash, glacial drift, alluvium, colluvium, loess and other aeolian deposits, organic accumulations, and soil (Table S1). The term was originated by Merrill (1897) and is derived from the Greek *rhegos*, blanket, combined with the suffix *lithos*, stone. The term *regolith*, sometimes spelled *rhegolith*, is frequently interchanged with *mantle rock* (also spelled *mantlerock*), *rock mantle*, and *overburden*, although the terms are not all synonymous. The term *overburden* is mainly applied to designate all sorts of barren rock materials, either loose or consolidated, that overlie mineral deposits or other materials that are being studied at depth. Overburden might include *caprock*, which is a consolidated material. Sedimentologists apply *overburden* in a similar context as *regolith* in reference to the upper part of a sedimentary deposit that compresses and consolidates the material below. This other usage applies mainly to the loose soil, silt, sand, gravel, or other unconsolidated material that overlies bedrock, whether transported or formed in place.

According to the original definition as proposed by Merrill (1897), *regolith* embraced the following transported and in situ types (with additional comments made here):

a. *Sedentary* or *in situ regolith:* (*i*) Residual deposits – lag gravels, loams, residual sands and clays, grits, red clays, laterite, bauxite (Table S1). These deposits therefore include *saprolite*. (*ii*) cumulative ("cumulose") deposits – peaty, organic soils and other organic-rich accumulations (gytja, dy, etc.). The term *muck*, as employed by Merrill, refers to highly decomposed organic material in which the plant parts are not recognizable. Muck contains more mineral matter and is usually darker in color than peat. In some regions outside the United States (e.g., Great Britain), the term *muck* commonly refers to agricultural farmyard manure; this definition is quite different from the one employed by Merrill.
b. *Transported regolith:* (*i*) Colluvial deposits – scree, talus and cliff debris, avalanche, mud-slide, rockslide, and landslide debris; *grezes litees* (bedded, partly cemented talus debris and soil); appreciably displaced solifluction material (at the foot of slopes), (*ii*) Alluvial deposits – modern alluvium (but not ancient alluvium, which constitutes distinct stratigraphic formations), including fluvioglacial deposits such as outwash sands (sandur) and piedmont gravels, (*iii*) Aeolian deposits such as sand dunes, parna (clay dunes), and loess. (*iv*) Glacial deposits – morainal material, till or boulder clay (drift), drumlins, kames, eskers, etc. (Table S1).

Table S1 Categories of surficial materials

Saprolitic residuum	
Micaceous residuum	Without much quartz; clay, mostly kaolinite
Residuum with quartz	Mica content equal to clay
Red clay	Massive clay that is generally kaolinitic
Cherty red clay	Incorporates chert from parent rock
Residuum on Triassic formations	Shallow saprolite, reddish color
Sandy residuum	Weathered sandstone formations
Clay residuum	Swells when wet; derived from montmorillonitic shales
Loam	Texture ranges from sand to clay; contains nonswelling kaolinitic clays
Gravels	Intensively weathered upper Tertiary and Quaternary gravels; saprolite generally less than 10 m thick
Phosphatic clays	Poorly sorted clay and phosphate pebbles; 3–18 m thick; major source of phosphate fertilizer
Sandy, silty residuum	Includes some loess; generally less than 3 m thick
Thin Residuum	
Silt on limestone	Includes some loess blankets
Sandy ground	Mostly poorly consolidated sandstone formations
Shaley or sandy ground	On mixed sandstone and shale formations; where shaley, contains swelling clays
Sandy gypsiferous ground	Contains sinks, local dunes
Clayey ground	Mostly on weathered Permian or Triassic red beds
Organic deposits	
Marshes, swamps	Includes peat deposits; may be locally thicker than 3 m
Sandy coastal ground	May include organic layers over a shallow water table
Transported deposits	
Colluvial deposits	
Sandy, stony colluvium	Derived mostly from sandstone and shale
Stoney colluvium on limestone	Contains admixed silt, loess
Stony colluvium on metamorphic rocks	Contains moderate amounts of silt and clay
Colluvium on volcanic rocks	Includes wide range of textural grades
Bouldery colluvium	Includes sandy colluvium on granitic rocks
Clayey and loamy colluvium	On poorly consolidated rocks
Shore deposits	
Bayhead and bayside sandbars	Usually separated by rocky headlands
Sandy shores	Siliceous and calcareous sands
Sea islands	Irregularly shaped sandy islands
Coral	Includes patch reefs, knolls; sandy deposits from corals, coral-lines, shellfish fragments
Backshore deposits	Coastal organic-rich swamp, marshland deposits less than 8 m above sea level; have shallow groundwater tables
Glacial deposits	
Pre-Wisconsin drift	Older glacial deposits mostly covered by loess and younger glacial materials
Terminal moraines	Mark equatorial boundaries of glacial drift and poleward limits of most residuum
End moraines	Hummocky ridges of poorly sorted weathered gravel, sand
Till, ground moraine	Poorly sorted bouldery, sandy deposits; generally less than 8 m thick
Ice-laid deposits	Mostly sand and silt forming smooth plains, sometimes with pitted ground
Deposits of mountain glaciers	Gravel and sand in U-shaped valleys; generally less than 8 m thick
Fluvioglacial deposits	Gravel, sand, silt, and clay deposited by glacial streams; commonly more than 18 m thick in some valleys
Stream deposits	
Floodplain, alluvium gravel terrace	Well-bedded lenticular gravel, sand, and silt; fills may be up to 35 m thick
Fan gravels	Commonly exceed 350 m in thickness; rest on pediments; some have desert pavements
Fan sands	Lie between gravels upslope and silty beds of floodplains or playas in valleys; some extensively reworked into sand dunes
Ancient stream deposits	Broad fans of sand and gravel; generally less than 35 m thick
Lake deposits	
Lacustrine sands, clays	From lakes formed by damming of rivers by continental ice sheets; overdeepening of river valleys by ice scour; infilling of closed basins
Aeolian deposits	
Sand sheets	Includes sand mounds and dunes; most have a basal layer of weathered, partly cemented, and stabilized older sand
Loess	Silty blanket deposits that frequently overlie Wisconsin and older glacial deposits or outwash

Source: Modified from Hunt, C.E. (1984). Surficial Geology. *National Atlas of the United States of America* (Map No. NAC-P-0204-75M-0). Washington, D.C.: U.S. Geological Survey.

Merrill (1897) emphasizes that the upper part of the regolith incorporates the *soil* of pedologists. It specifically includes that part of the unconsolidated mantle that supports plant life. The lower boundary of soil where it may merge into deep saprolite is ill defined, and the distinction between the two different kinds of deposits remains blurry. The lower limit of soil is usually taken as the depth to which biological activity extends. This concept of *pedochemical weathering* thus essentially embraces biochemical activity that takes place in the soil solum, the A and B horizons (Buol et al., 2003).

Geochemical weathering takes place below the soil solum in the C horizon and lower zones of weathering. Other terms are commonly applied to regolith. The term *head* is widely used in England and France for *regolith*, but as employed in these localities, it denotes both transported saprolite and solifluction debris. German workers apply the term *grus* to both rock-rotted debris and mechanical weathering detritus such as products of exfoliation, frost disintegration, and salt weathering. Another term of Germanic origin that is sometimes used, *geest* (favored by McGee, 1891, p. 279), specifically refers to the gravelly or gritty varieties of regolith.

Saprolite

The term *saprolite*, which is based on the Greek *sapros*, "rotten," was proposed by Becker (1895) in reference to rock that was rotted in situ, i.e., rock that was chemically altered, but remaining coherent and not texturally disintegrated. The term *saprolith*, as sometimes used to designate sapropelic rocks, asphaltites, and related petroleum (Pettijohn, 1957, p. 489), as well as the spelling *sathrolith* of Sederholm (1931), should be avoided. *Saprolite*, as defined in the *Glossary of Geology* (Jackson and Bates, 1997), is a soft, earthy, typically clay-rich, thoroughly decomposed rock, formed in place by chemical weathering of igneous, sedimentary, and metamorphic rocks. Because saprolites are characterized by preservation of structures that were present in the unweathered rock, it is often possible to designate structured saprolites as "granitic saprolite," "basaltic saprolite," "doleritic saprolite," etc. when its origin can be clearly identified. Saprolites are commonly some shade of red or brown but may be white or gray. Although such colors are not always diagnostic of parent rocks, they do give some indication of the environments of formation. The zone of fluctuating groundwater typically produces a mottled zone that is characteristic of alternating oxidizing and reducing conditions. Saprolitic zones occurring below the water table in a zone of permanent saturation are commonly pale colored, such as the pallid zones (lithomarge) of laterite deep-weathering profiles. In the tropics and peritropics, the thickness of saprolite can be quite remarkable: it frequently exceeds 100 m and may reach 200 m or more. Greater depths of weathering have been reported, but these may be related to shear zones where bedrock has been affected by hydrothermal alteration. This thick weathering mantle, together with derivative products from the reworking of the soft surface layers and also the formation of duricrusts, has frustrated geologists because they cannot easily map or gain access to the unaltered bedrock.

Saprolites assume a variety of morphologies that result from different influences of parent rock, drainage conditions, site (topographic position), and age. Profiles resulting from the deep chemical weathering of basic rocks such as dolerites and basalts on well-drained sites tend to be reddish in color with moderate morphological differentiation. Those saprolites developed in ultramafic rocks show rather more differentiation. Smith (1977) describes a typical unmineralized laterite profile in ultramafic rocks in Western Australia as being comprised by a surface ferruginous (plinthite) zone that is immediately underlain by mottled clays. Below the mottled clays and lower in the profile occurs a silicified saprolite zone from 30 to 90 m. The saprolitic clays show the morphology of the original rock-forming minerals with a slow gradation to oxidized rock at the base of the profile. A groundwater table is believed to have fluctuated about the boundary of the ferruginous zone and mottled clay zone, based on observations of laterites presently forming in the tropics (Van Schuylenborgh, 1969). The classical laterite deep-weathering profile formed over metamorphic terrains displays a different but distinctive sequence of horizons with depth. Morphological zonation of laterite profiles developed from granitoid rocks, for example, is commonly described in terms of an upper ferruginous zone (the ironstone crust being a cuirasse or carapace, depending on the degree of induration), an underlying mottled zone (*Flecken* zone of German workers), and a still lower bleached or pallid zone (*bleich* zone of Walther, 1915), referred to as lithomarge by Tardy (1992), that grades into a soft rotten layer that retains essential rock structure (*Zersatz* zone) before merging with the weathering front (Mabbutt, 1961). All three major zones (mottled, pallid, and Zersatz zones) may show degrees of silicification (Finkl, 1984).

Economic value of saprolites

The *nickeliferous laterites*, also commonly referred to as *laterite nickel deposits*, are associated with ultramafic rocks. The ultramafic terrains, greenstone belts, in which they occur on tropical cratons, are easily distinguished from the surrounding reddish-colored, lateritized granitic terrains by their lighter yellowish-gray color. Although these surface colors are subtle, the trained observer with a keen eye will find them to be fairly reliable indicators of bedrock types. Lateritic nickel deposits such as those in New Caledonia are most commonly worked in open cuts. Ore grade saprolitic materials are dug out by large shovels and then moved to refineries by truck, earth hauler, or overland conveyor belt. The alumina-rich saprolite is *bauxite*, the principal ore of aluminum. These deposits, resulting from intense deep chemical weathering, show similar characteristics to nickel-rich laterites and are also mined from open pits and broad excavations. Bauxite (a hydrous aluminum oxide) is mined by these methods in the Darling Ranges of Western Australia, now a world leader in the extraction of this residual material. Other producers of bauxite include Surinam, the United States, the USSR, and southern Europe. The largest deposits of bauxitic saprolite in the United States occur in Arkansas. Some of the deposits were formed as saprolite on nepheline syenite, an igneous rock rich in aluminum (Gordon et al., 1958). Gemstones (e.g., emeralds and rubies in Burma and Ceylon, diamonds in Africa) are often worked in old saprolites because they are not weathered and the enclosing weathered (soft) rock can be easily worked. Tin (in the form of cassiterite) is similarly contained in the granite saprolites of Malaya, Indonesia, and Australia.

Soils

The term *soil* is derived from the Latin *solum*, which at one time had the same general meaning as the modern term. According to *Webster* (Woolf, 1974) soil is "*the upper layer of the Earth that may be dug or plowed and in which plants grow.*" This definition is nearly as old as the word. Some geologists for a long time have considered soil to be an unconsolidated heterogeneous aggregate of disintegrated rock material that contains some organic matter (usually less than 5% by composition) near the ground surface (e.g., Geike, 1958). Many field geologists still find this definition adequate for most purposes as they rarely attempt to identify specific kinds of soils. There are four main technical perceptions of soil that may be conveniently referred to as the edaphic, geographic, pedologic, and engineering concepts (Finkl, 1979). Edaphologists view soil as the natural medium for the growth of land plants, whereas the geographic concept of soil relates to the study of the areal distribution of soils (Butler, 1958). The pedologic concept embraces the study of soils as independent natural bodies, each with a distinct morphology resulting from the integrated effect of climate and living matter, acting on parent materials, as conditioned by relief, over periods of time (Soil Survey Staff, 1951). Thus, according to this view soil is the unconsolidated mineral matter on the surface of the Earth that has been subjected to the influence of genetic and environmental factors – in short, a product of low-grade epidiagenesis. From the engineer's point of view, soil is a material with which and upon which one builds structures. It includes any unconsolidated material found between the ground surface and bedrock. Thus, soil in the engineer's view includes all regolith materials – unconsolidated accumulations of rock fragments and organic matter that is intermixed – or the entire vertical section down to consolidated rock (Peck et al., 1974).

When it becomes necessary to identify particular occurrences of distinct kinds of soils, the legend to the international *Soil Map of the World* (FAO/UNESCO, 1961, 1974, 1990; Nachtergaele et al., 2000) is commonly referred to. The geographical application of modern soil classification systems has been summarized, on a worldwide basis (e.g., Finkl, 1982; Nachtergade et al., 2000; Buol et al., 2003). The main categories of soil units listed in the legend to the *Soil Map of the World* are summarized in Table S2. These modern terms, or others required by national soil surveys, should be used whenever practical. No matter what system of soil classification is used in a particular geographic area, it is useful to be cognizant of the international system of soil classification.

Field relations of regolithic materials

Efforts to better understand the field relations of regolithic materials, the temporal and spatial interactions of weathering profiles (soils), sediments, and residuum, focus on basic tenets of stratigraphical geology and soil (Daniels and Hammer, 1992). The principles of soil stratigraphy, perhaps less familiar than the basic laws of geologic chronology, have been summarized by Butler (1959), Ruhe (1969), Morrison (1967), Follmer (1978), and Finkl (1980, 1984, 1994), Finkl and Churchward (1976), among others. Generalized examples of field relations among surficial materials are drawn here, for illustrative purposes, from the deeply weathered tropical cratons and from mid-latitude glacial landscapes.

The deeply weathered shield landscapes contain evidence of widespread stripping (erosion) of regoliths. The degree of stripping produces a wide range of distinct landscapes that characterize so much of Africa, Australia, Brazil, southern India, tropical South America, and even parts of Western Europe. The process and resulting surface form, detailed for parts of the peritropical African (Thomas, 1974; Twidale and Campbell, 2005) and Australian cratons (Finkl, 1979, 1994), are based on the concept of etchplains where there are "double planation surfaces" as explained by Büdel (1982). The vertical succession of master horizons, including caps of ferruginous duricrust, in laterite profiles provides a measure of the degree of truncation. Regions with lateritic mantles that remain nearly intact, the oldest and most stable parts of the cratons, commonly display sandy ground surfaces that are underlain by ferricrete and a complete laterite profile (i.e., one that exhibits master mottled and pallid horizons) (Smith, 1977). A moderate degree of stripping exposes the mottled zone, imparting a reddish-brown color to the contemporary soilscape. More extensive erosion that strips away the upper parts of the laterite profile typically exposes pallid zone materials (Finkl and Churchward, 1973; Smith, 1977; Finkl, 1979; Cornelius et al., 2001). These strongly eroded landscapes are characterized by light-colored soils derived from the pale white to gray-colored kaolinitic clays of the lower laterite profile. Nearly complete removal of the deep weathering mantle exposes the irregular contour of the weathering front and leaves corestones behind on the ground surface. Inselberg landscapes are believed to form in this manner, by the stripping of weathered materials and subsequent exposure (exhumation) of bedrock highs, a process sometimes referred to as etchplanation (Thomas, 1974; Twidale and Campbell, 2005).

Recognition of deeply weathered landscapes and especially their stripped counterparts is essential to competent interpretations of extant field conditions. The occurrence of different kinds of regoliths will determine the field methods that can be used to best advantage. Accurate identification of stripped surfaces and the nature of surficial materials, especially those derived from weathering mantles, provide a rational basis for the selection of sample media in geochemical surveys. The same rationale applies to geophysical surveys where thick regoliths and saline groundwaters can affect survey results.

Although completely different from the tropical and peritropical shield landscapes with their thick weathering mantles, other ectropical landscapes with extensive regoliths pose similar challenges to the field geologist, e.g., the glacial out-wash and loess plains of northern latitudes. These glacial and periglacial landscapes with complex regoliths exhibit many different kinds, often a bewildering range, of surficial materials that frequently contain intercalated weathering zones (soils).

Typical relations between soil mantles may be identified in two simple cases by what Butler (1959) calls overplaced and underplaced contacts. An overplaced contact is where two soil mantles are locally separated by intervening deposits (Figure S2). Horizons of the younger soil mantle (Figure S2, A) are replaced from the bottom upward by those of the older (lower), more strongly developed soil mantle (Figure S2, B). An underplaced contact is where an erosion surface intervenes between the development of two soil mantles (Figure S3). Where the older soil mantle (Figure S3, B) is truncated, its horizons are replaced from the top downward by those of the younger, weaklier developed soil mantle (Figure S3, A). These basic field relations are complicated by the intensity (duration) of weathering phases and erosional-depositional cycles. Overplaced contacts can be identified only where the younger soil mantle (cf. Figure S2) is weaklier developed than the older; otherwise, the discontinuity is masked by pedogenic overprinting (Finkl, 1980). As shown in Figure S7, the more strongly developed soil mantle (Figure S7, B) exists in both buried (covered by overburden) and relict (exposed at the ground surface) states.

Other basic field relations are depicted in Figures S4 through S12. Figure S4 shows a single erosion-weathering cycle where deposition was immediately followed by soil development. The deposit formed during an unstable phase, and the weathering profile developed during a stable interval. Figure S5 shows two cycles where an early instability deposit is overlain by a weathering profile that was also subsequently weathered. Thus, there was deposition, then stability (weathering), a second instability involving erosion and deposition of materials similar to the underlying deposit, and then a second phase of weathering. Figure S6 records deposition followed by a different type of deposition, then there was a stable phase of soil development. In this case, there was no stable phase of sufficient duration for weathering to take place between depositions. An alternative field relation is presented in Figure S7, which shows two different depositions, each followed by weathering during stable geomorphic conditions.

Relationships between erosion surfaces and weathering profiles, as described by Morrison (1967) and based on the

Table S2 Soil map units listed in the legend to the FAO/UNESCO *Soil Map of the World*

- Fluvisols (water-deposited soils with little alteration)
  - Dystric
  - Eutric
  - Calcaric
  - Thionic
- Regosols (thin soil over unconsolidated material)
  - Dystric
  - Eutric
  - Calcaric
  - Gelic
- Arenosols (soils formed from sand)
  - Ferralic
  - Luvic
  - Cambic
  - Albic
- Gleysols (mottled or reduced horizons due to wetness)
  - Mollic
  - Dystric
  - Eutric
  - Gelic
  - Humic
  - Calcaric
  - Plinthic
- Rendzinas (shallow soil over limestone)
- Rankers (thin soil over siliceous material)
- Andosols (volcanic ash with dark surfaces)
  - Ochric
  - Mollic
  - Humic
  - Vitric
- Vertisols (self-mulching, inverting soils, rich in montmorillonitic (smectite clay))
  - Pellic
  - Chromic
- Yermosols (desert soils)
  - Haplic
  - Calcic
  - Gypsic
  - Luvic
  - Takyric
- Xerosols (dry soils of semiarid regions)
  - Haplic
  - Calcic
  - Gypsic
  - Luvic
- Solonetz (high sodium content)
  - Orthic
  - Mollic
  - Gleyic
- Planosols (abrupt A-B horizon contact)
  - Eutric
  - Dystric
  - Mollic
  - Gelic
  - Humic
  - Solodic
- Kastanozems (chestnut surface color, steppe vegetation)
  - Haplic
  - Calcic
  - Luvic
- Chernozems (black surface, high humus under prairie vegetation)
  - Haplic
  - Calcic
  - Luvic
  - Glossic
- Phaeozems (dark surface, more leached than Kastanozem or Chernozem)
  - Haplic
  - Calcaric
  - Luvic
  - Gleyic

Table S2 (Continued)

- Greyzems (dark surface, bleached A2, and textural B)
  - Orthic
  - Gleyic
- Cambisols (light color, structure, or consistence change due to weathering)
  - Gelic
  - Eutric
  - Gleyic
  - Dystric
  - Ferralic
  - Calcic
  - Vertic
  - Humic
  - Chromic
- Luvisols (medium to high base status soils with argillic horizons)
  - Orthic
  - Chromic
  - Calcic
  - Vertic
  - Ferric
  - Albic
  - Plinthic
  - Gleyic
- Solonchaks (soluble salt accumulation)
  - Orthic
  - Mollic
  - Takyric
  - Gleyic
- Podzoluvisols (leached horizons tonguing into argillic B horizons)
  - Eutric
  - Dystric
  - Gleyic
- Podzols (light-colored alluvial horizon and subsoil accumulation of iron, aluminum, and humus)
  - Humic
  - Ochric
  - Placic
  - Gleyic
  - Ferric
  - Leptic
- Acrisols (highly weathered soils with argillic horizons)
  - Orthic
  - Ferric
  - Humic
  - Plinthic
  - Gleyic
- Nitrosols (low CEC clay in argillic horizons)
  - Dystric
  - Eutric
  - Humic
- Ferralsols (sesquioxide-rich clay)
  - Orthic
  - Rhodic
  - Humic
  - Acric
  - Plinthic
  - Xanthic
- Histosols
  - Dystric
  - Eutric
  - Gelic
- Lithosols (shallow soils over hard rock)
- Arenosols (sandy soils)
  - Ferralic
  - Luvic
  - Cambic
  - Albic

Source: Compiled from FAO/UNESCO Staff (1964, 1974, 1990); Buol et al. (1980).

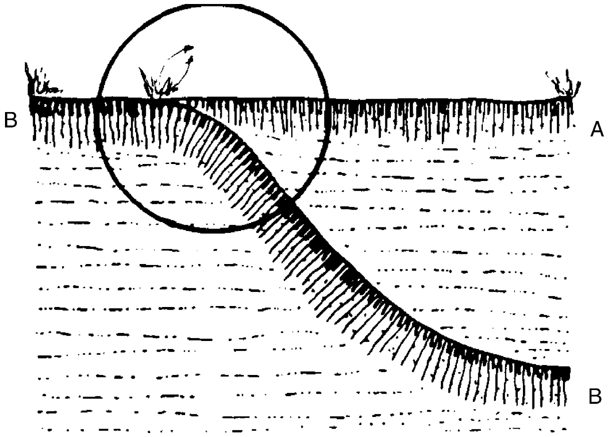


Figure S2 An overplaced contact between two soil mantles (*circle*). An intervening deposit similar to the original deposition separates the younger, more weakly developed mantle (*A*) from a fossil soil (*B*), which occurs at the ground surface and in buried situations.

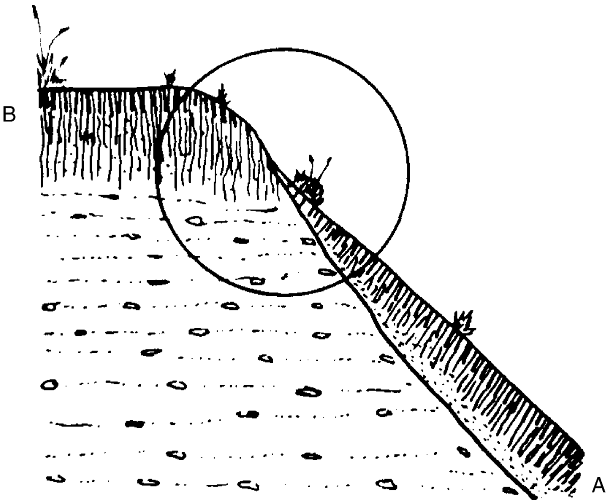


Figure S3 An underplaced contact (*circle*) where a younger, more weakly developed soil mantle (*A*) replaces an older truncated soil (*B*) downprofile from the eroded surface.

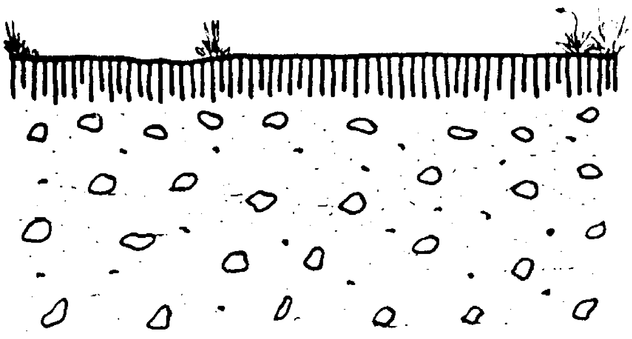


Figure S4 A single soil mantle formed in a single deposit of homogeneous parent materials.

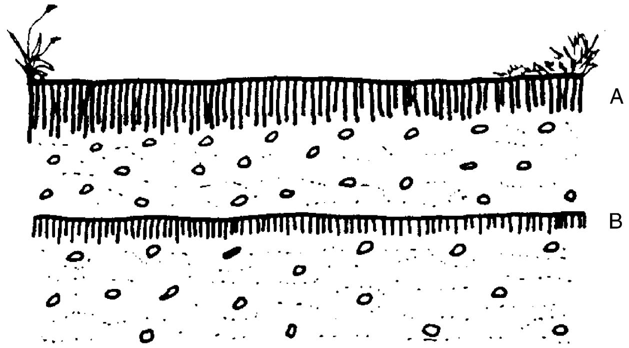


Figure S5 Two cycles of instability (erosion-deposition), each followed by a stable interval (soil development). The buried, weakly developed soil mantle (*B*) is overlain by a deposit similar to the original deposition. The second deposit was strongly weathered to form a surface soil mantle (*A*).

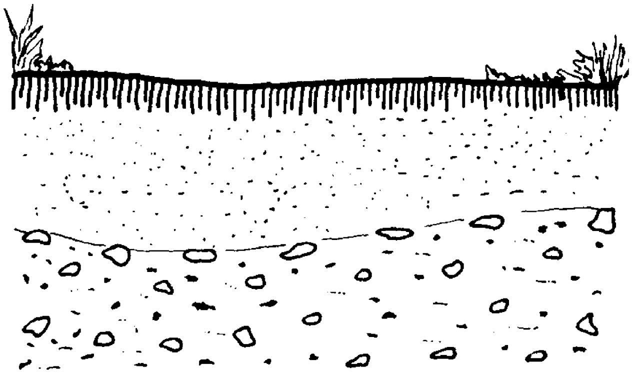


Figure S6 Two depositional sequences separated by an erosional unconformity, followed by stability (weak phase of soil development). No stable phase occurred between depositions.

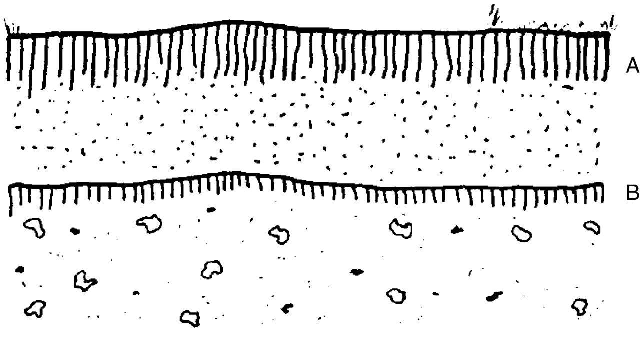


Figure S7 Two different depositions, each followed by a stable phase of weathering. The older buried soil mantle (*B*) is more weakly developed than the weathered ground surface (*A*). Unweathered parent materials separate the second deposit from the buried soil.

K-cycle concept (erosion/deposition/weathering models) of Butler (1959), are graphically summarized in Figures S8 through S12. Figure S8, for example, shows a deposit and its weathering mantle truncated by a subsequent unstable phase to produce a sequence of deposition, stability, then erosion. Figure S9, in contrast, shows erosion intervening between the depositional and stability phases, giving a sequence of deposition-erosion-stability. In Figure S10, there are two successive phases of differing deposition, with erosion synchronous with the second deposition or intervening between the depositional phases, followed by weathering. The surface-weathering mantle here transgresses the lithological discontinuity and the geomorphological unconformity. The sequence of events is thus deposition, then erosion followed by a second deposition, with subsequent weathering taking place across the contact.

Still other possibilities include situations where there is deposition, then erosion, followed by strong weathering and then a second deposition followed by a weak phase of weathering (Figure S11). In this case, the second, weaker, phase of weathering does not mask the effects of the previous stronger phase of weathering. The strongly weathered profile occurs as a surface soil and as a buried soil associated with a paleogeomorphic surface. The contact between strongly and weakly developed weathering profiles coincides with the lithogeomorphic discontinuity at the ground surface. Figure S12 depicts an alternative to the previous sequence whereby the older weathering mantle is weakly developed and the younger one is more strongly developed. Consequently, there is no pedologic-geomorphic discontinuity evident at the ground surface. The triple discontinuity, however, is marked at depth by breaks in lithology (parent materials), soil development, and subaerial erosion surfaces. Pedogenic overprinting by younger weathering mantles may also mask the relict occurrence of older weakly

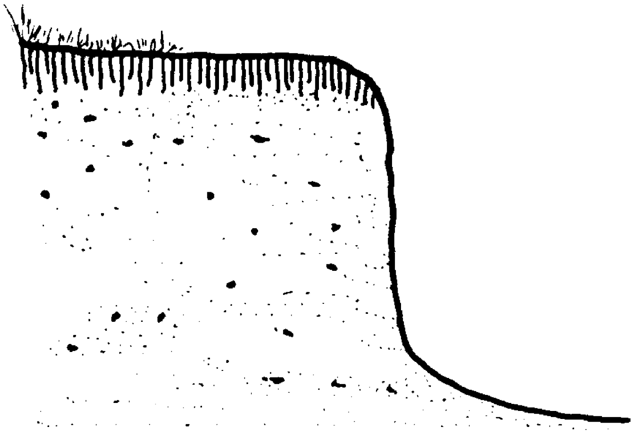


Figure S8 A simple soil developed in a single deposit, both subsequently truncated by an unstable erosive phase giving a deposition-weathering-erosion sequence.

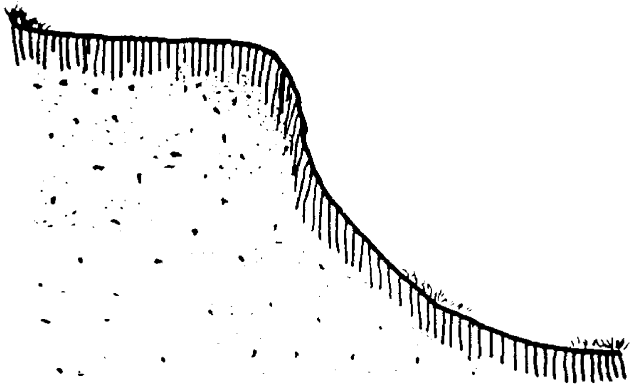


Figure S9 Intervention of erosion between deposition and weathering, truncation of deposit prior to soil development, to produce a deposition-erosion-weathering sequence.

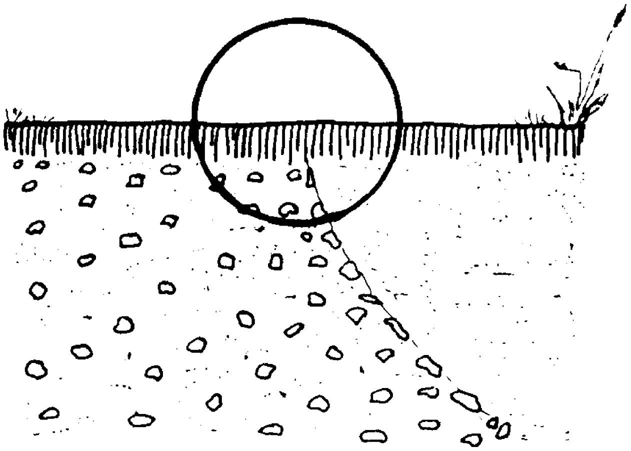


Figure S10 Two separate depositions followed by weathering across the contact (*circle*) to produce a sequence of deposition-erosion-second deposition-weathering.

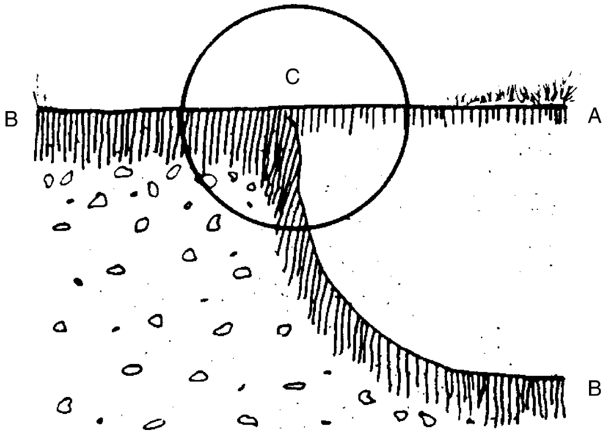


Figure S11 Two separate depositions, each followed by stable weathering intervals. The triple discontinuity (*circle*) is marked by a lithological contact, a paleogeomorphic unconformity, and pedogenic masking of a younger weak phase of weathering (*A*) by an older, strongly developed relict soil mantle (*B*). Surface expression of the discontinuities is placed by the soil boundary (*C*).

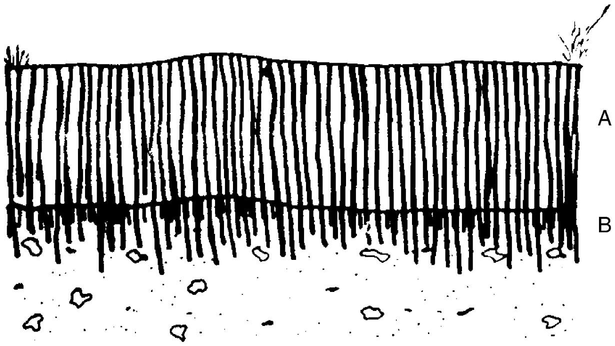


Figure S12 Two different depositions, each followed by stability (soil development). The intensely developed surface soil mantle (*A*) partly masks the paleogeomorphic unconformity, lithological discontinuity, and weakly developed soil mantle (*B*) by pedogenic overprinting.

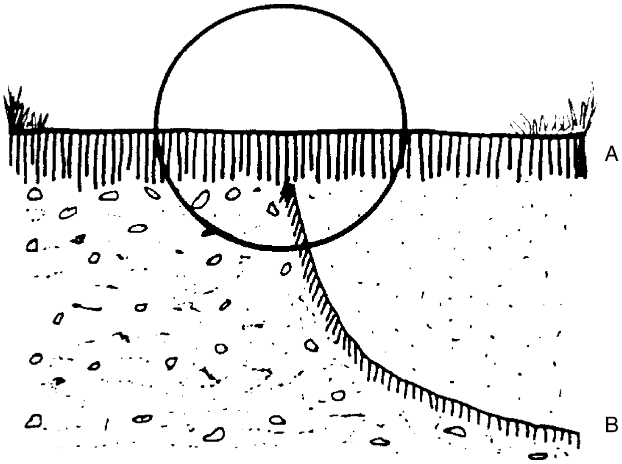


Figure S13 Two different depositions, each weathered. The triple discontinuity (*circle*) lacks surface expression due to pedogenic overprinting by younger strong weathering. The older, weakly developed soil mantle (*B*) is replaced downward by a younger phase of strong weathering (*A*).

developed profiles (Figure S13). The sequence may be summarized in terms of deposition, erosion, and weak weathering followed by a second deposition and strong weathering in both deposits.

Charles W. Finkl

Bibliography

Anand, R.R., and Butt, C.R.M., 1988. *The Terminology and Classification of the Deeply Weathered Regolith.* Perth, Western Australia: CSIRO, Division of Exploration Geoscience.

Becker, G. F., 1895. Reconnaissance of the gold fields of the southern Appalachians, *U.S. Geoogical Survey, 16th Annual Report*, Part III, pp. 251–331.

Budel, J., 1982. *Climatic Geomorphology.* (trans. Fischer L., and Busche, D.). Princeton, NJ: Princeton University Press, 443 pp.

Buol, S.W., Southard, R.J., Graham, R.C., and McDaniel, P.A., 2003. *Soil Genesis and Classification.* Ames: Iowa State Press, 494 pp.

Butler, B.E., 1958. The diversity of concepts about soils. *J. Aust. Inst. Agric. Sci.*, **24**: 14–20.

Butler, B.E., 1959. Periodic phenomena in landscapes as a basis for soil studies. *CSIRO (Australia) Soil Publication No. 14.*

Cornelius, M., Smith, R.E., and Cox, A.J., 2001. Laterite geochemistry for regional exploration surveys – a review, and sampling strategies. *Geochem.: Explor. Environ. Anal.*, **1**: 211–220.

Daniels, R.B., and Hammer, R.D., 1992. *Soil Geomorphology.* New York: Wiley, 236 pp.

FAO/UNESCO, 1961. *Soil Map of the World; Legend.* Paris: UNESCO, 59 pp.

FAO/UNESCO, 1974. *Soil Map of the World; Legend*, Vol. 1. Rome, Italy: FAO, 59 pp.

Finkl, C.W., 1979a. Soil. In: Fairbridge, R.W., and Finkl, C.W., eds., *The Encyclopedia of Soil Science, Part I: Physics, Chemistry, Biology, Fertility, and Technology.* Stroudsburg, PA: Dowden, Hutchinson & Ross, pp. 433–435.

Finkl, C.W., 1979b. Stripped (etched) land surfaces in southern Western Australia. *Aust. Geogr. Stud.*, **17**(1): 33–52.

Finkl, C.W., 1980. Stratigraphic principles and practices as related to soil mantles. *Catena*, **7**(2/3): 169–194.

Finkl, C.W., 1982. The geography of soil classification. *Quaestiones Geographicae*, **8**: 55–59.

Finkl, C.W., 1984. Chronology of weathered materials and soil age determination in pedostratigraphic sequences. *Chem. Geol.*, **44**: 311–335.

Finkl, C.W., 1994. New interpretations of chemical alterites on paleosurfaces. In Menon, J., ed., *Trends in Chemical Geology.* Trivandrum, India: CSIR, pp. 187–198.

Finkl, C.W., and Churchward, H.M., 1976. Soil stratigraphy in a deeply weathered shield landscape in south-western Australia. *Aust. J. Soil Sci.*, **14**(2): 109–112.

Follmer, L., 1978. The Sangamon soil in its type area – a review. In Mahaney, W. C., ed., *Quaternary Soils.* Norwich, England: Geo Abstracts, pp. 125–166.

Geike, J., Campbell, R., and Craig, R.M., eds., 1958. *Structural and Field Geology.* Edinburgh: Oliver and Boyd, 397 pp.

Gordon, M., Tracey, J.I, and Ellis, M.W., 1958. Geology of the Arkansas bauxite region. *U.S. Geological Survey Professional Paper 299*, 268 pp.

Hunt, C.E., 1986. *Surficial Deposits of the United States.* New York: Van Nostrand Reinhold.

Jackson, J.A., and Bates, R.L., 1997. *Glossary of Geology.* Falls Church, VA: American Geological Institute, 769 pp.

Mabbutt, J.A., 1961. A stripped land surface in Western Australia. *Trans. Inst. Br. Geogr.*, **29**: 101–114.

McGee, W.J., 1891. The Pleistocene history of northeastern Iowa. U.S. Geological Survey, 11th Annual Report. (for 1889–1890), Part I, pp. 189–577.

Merrill, G. P., 1897. *A Treatise on Rocks, Rock-Weathering and Soils.* New York: Macmillan, 411 pp.

Morrison, R. B., 1967. Principles of Quaternary soil stratigraphy. In Morrison, R.B., and Wright, H.E., eds., *Quaternary Soils* (Proc. VII INQUA Conference). Vol. 9, pp. 1–69.

Nachtergade, F.O., Spaargaren, O., and Deckers, J.A., 2000. New developments in soil classification: world reference base for soil resources. *Geoderma*, **96**: 345–357.

Peck, R.B., Hanson, W.E., and Thornburn, T.H., 1974. *Foundation Engineering.* New York: Wiley, 514 pp.

Pettijohn, F.J., 1957. *Sedimentary Rocks.* New York: Harper, 781 pp.

Ruhe, R.V., 1969. Principles for dating pedogenic events in the quaternary. *Soil Sci.*, **107**(6): 398–402.

Sederholm, J.J., 1931. On the sub-Bothnian unconformity and on Archaean rocks formed by secular weathering, *Finland Comm. Geol. Bull.*, **95**: 1–81.

Smith, B.H., 1977. Some aspects of the use of geochemistry in the search for nickel sulphides in lateritic terrain in Western Australia. *J. Geochem. Res.*, **5**(2): 259–281.

Soil Survey Staff, 1951. *Soil Survey Manual.* U.S. Department of Agriculture Handbook No. 18, 503 pp.

Tardy, Y., 1992. Diversity of terminology of lateritic profiles. (Chapter 15). In: Martini, I.P., and Chesworth, W., eds., *Weathering, Soils & Paleosols*, Amsterdam: Elsevier, pp. 379–405.

Thomas, M. F., 1974. Tropical Geomorphology. New York: Wiley, 332 pp.

Twidale, C.R., and Campbell, E.M., 2005. *Australian Landforms: Understanding a Low, Flat, Arid and Old Landscape.* Duval Distribution Centre. New South Wales: Rosenberg, 336 pp.

Van Schuylenborgh, J., 1969. Weathering and soil-forming processes in the tropics. In *Soils and Tropical Weathering,* Vol. 11, Natural Resources Research. Paris: UNESCO.
Walther, J., 1915. Laterit in West Australien. *Deutsche Geologische Gesellschaft Zeitschrift*, **67B**: 113–140.

SATURATION

The state of a soil or a solution of being completely charged with a substance. Used especially with respect to a soil being saturated with water, in which case the pore space of the soil is completely filled with water. A solution, including a soil solution, is saturated with a salt (or other substance) when it has reached the state where the salt may precipitate under the prevailing ambient conditions. Minerals precipitate from soil solution in order of increasing solubility, the common sequence in soils of arid climates being calcite → gypsum → Na salts.

Cross-reference

Alkaline Soils

SAVANNA

Grassland of the tropics and subtropics in regions with distinct wet and dry seasons. Scattered drought-resistant trees such as the acacia and baobab of East Africa, are common. In South America, the *cerrado* of Brazil is the most extensive savanna. The soils are highly weathered and commonly kaolinitic e.g., Lixisols and Nitisols.

Bibliography

Whitehead, D.C., 2000. *Nutrient Elements in Grassland: Soil-Plant-Animal Relationships*. Wallingford: CABI, 369 pp.

Cross-references

Biomes and their Soils
Phosphorus Cycle

SCALPING

To strip off (the turf or upper soil), used especially in forestry to prepare land for the planting of trees.

SCARIFY

To break up or loosen (ground) and expose lower horizons, aerate soil and prepare the soil for seeding. A simple agricultural scarifier is a share equiped with tines or teeth to engage the ground and rip the surface when pulled over it by a tractor.

SCRUB

Small trees or shrubs, or the tract of land (also called scrubland) overgrown by them. Characteristic of desert and Mediterranean biomes, and of temperate heathlands, some of which are anthopogenic.

Cross-reference

Biomes and their Soils

SECONDARY MINERAL

A mineral formed from a pre-existing primary mineral by metamorphism or by weathering, such as a clay mineral. The process of formation of a secondary mineral in a soil or weathering environment generally, is called neoformation.

Cross-reference

Clay Mineral Formation

SEDIMENTARY

The family of rocks that begin as sediments deposited at the Earth's surface as the products of weathering. As sediments are buried and subjected to pressures and temperatures higher than surface values, they undergo diagenesis involving compaction (with or without a certain amount of crystallization) and cementation, to become solid rock (a process known as lithification). As the pressures and temperatures increase with depth, sedimentary processes grade into metamorphic ones. Soil may be an ephemeral product of the early (weathering) stage of the process. In fact, the prolific writer Anon, has described soil as sediment on its way to the sea.

SEEPAGE

The slow movement of water into or out of the ground under the action of gravity.

Cross-references

Flow Theory
Water Movement

SELF-MULCHING

Shrink and swell cycles in smectite-rich soils such as Vertisols, break the surface soil into coherent aggregations, granules or crumbs to form a mulch. This tends to fall into shrinkage cracks and upon re-wetting, part of the space that the soil requires for its increased volume is occupied by mulch material.

Cross-reference

Vertisols

SEMI-ARID

A climate or region with an annual precipitation between 25 and 50 cm. Chernozems and Kastanozems are characteristic of the high end of the precipitation range, and Calcisols and alkaline soils of the low end.

Cross-references

Alkaline Soils
Calcareous Soils
Calcisols
Chernozems
Solonetz

SERIES

See *Classification of Soils: soil taxonomy*.

SESQUAN

See *Cutan*.

SESQUIOXIDE

A superannuated term for the oxides and hydroxides of trivalent metals, particularly Fe and Al. Still commonly used in the earth sciences.

SHEAR

A type of strain consisting in a movement of layers or sheets of a body along their line of contact and resulting in a mutual displacement of the layers. In soils with a high proportion of smectite in the clay fraction, swelling as the clay takes up water generates a pressure in the soil mass that may exceed the shear strength of the mass. This pressure acts in all directions and is relieved by movement along shear planes at angles between 20 or 30 degrees of the horizontal. Clay becomes smeared along the moving surfaces and peds assume a kind of superficial polish or slickness, grooved in the direction of movement. These smoothed surfaces are called slickensides.

Cross-references

Micromorphology
Microstructure, Engineering Aspects

SHIELD

See *Basement*.

SHRINKAGE

A reduction in the size or volume of a substance or material due to contraction. Loss of water is the most common cause in soils and similar materials (muds for example which will normally show shrinkage cracks). Smectite-rich soils are prone to cycles of swelling and shrinking as the clay alternately loses water or takes it up in response to a succession of droughty and wet periods. A form of self-mulching takes place in the surface horizons of soils such as Vertisols, affected by this process.

SILICATES

See *Soil Mineralogy*.

SILT

Particulate mineral materials in soil, commonly of quartz, with or without feldspar, with a size falling between 0.002 and 0.05 mm in diameter. Loess is a predominantly silty sediment that has become the parent material of agriculturally important soils of the temperate grasslands, and to a lesser degree of the temperate forests. It occurs as a yellowish-gray deposit in a Eurasian belt stretching from north-central Europe to eastern China, as well as in the grasslands of North American prairies and the South American pampas. Loess is generally calcite-bearing, with the calcite acting commonly, as a weak cement. It is formed from material transported by wind reworking glacial and fluvio-glacial materials exposed to erosion at the end of the Pleistocene glaciations. Much of the area of loess and loessial soils is now in arid and semi-arid zones of the Earth, and requires intensive irrigation when exploited for the purposes of arable farming. See Ice Erosion.

SIMULATION OF SOIL SYSTEMS

See *Computer Modeling*.

SKELETAN

See *Cutan*.

SKELETON GRAINS

Mineral grains within the soil matrix that have been inherited from parent material. The particles are larger than clay size and commonly visible to the naked eye.

Cross-reference

Micromorphology

SLICKENSIDES

See *Shear*.

SLOPE CLASSES

A classification of slopes in terms of their steepness. For example see Table S3.

Table S3 Classification of slopes

Class	Slope (%)	Terminology
1	0–0.5	Level
2	>0.5–2	Nearly level
3	>2–5	Very gentle slopes
4	>5–10	Gentle slopes
5	>10–15	Moderate slopes
6	>15–30	Strong slopes
7	>30–45	Very strong slopes
8	>45–70	Extreme slopes
9	>70–100	Steep slopes
10		Very steep slopes

SLUDGE

The mud or ooze-like mixture of solids suspended in water that occurs naturally along waterways and at the bottom of water bodies, or that is produced as a waste as a result of human activities. Large amounts of sludge are produced in the treatment of urban sewage and it is an accepted practice in some jurisdictions to dispose of it by spreading it on land. Opponents of the practice point to problems for human health, agricultural productivity, and the environment, arising from this practice, especially in those cases where the sludge contains industrial wastes.

SLUDGE DISPOSAL

Definition and problem

Sludge is the precipitated solid matter produced during water and wastewater treatment. The quantities of sludge resulting from water treatment are less than those from wastewater treatment, and disposal of water-treatment-plant sludge is not a major problem.

The disposal of sludge from wastewater-treatment plants is the most difficult and costly task of sanitary district staffs. Although sludge contains solids, the problem of its disposal does not only involve them, but also the water that is in close association with the waste solids. The major part of the cost of sludge treatment and disposal is directly related to the tons of water associated with each ton of solids (Dean and Smith, 1973).

The traditional means of sludge handling and disposal are (1) ocean disposal through barging or pipeline transport, (2) dewatering and drying with disposal in a landfill, (3) incineration, and (4) lagooning. Ocean disposal in the United States has been banned. New York was the last city to give up ocean disposal; it ended on 30 June 1992. Deep ocean injection is still being investigated experimentally in the United States.

The traditional means of disposal only displace the wastes and do not get rid of them. Dried sludge can sometimes be sold or given away as a fertilizer, but drying is expensive. Because ocean disposal is no longer allowed in the United States, coastal cities are pelletizing some of their sludge through a heat-drying process.

Land application of wet sludge is another method of disposal that is economical and beneficial, because nutrients, organic material, and water are returned to the land. The U.S. Environmental Protection Agency encourages recycling of sewage sludge to land, since rules for sludge management were promulgated in the United States in November 1992, when the Administrator of the U.S. Environmental Protection Agency signed a notice for publication in the *Federal Register* that describes disposal standards for sewage sludge. The regulation was published in the *Federal Register* on 19 February 1993. Documentation for the regulation, called 40 CFR (Code of Federal Regulations) Part 503, was published in 1992 (U.S. Environmental Protection Agency, 1992). After the 1993 regulations were published, the word "biosolids" was suggested by the U.S. EPA as a replacement for the term "sewage sludge," because it felt that the word reflected more accurately the beneficial characteristics inherent in sewage sludge.

The value of human and animal wastes has been recognized for a long time. "Night soil" has been used as a crop fertilizer and soil conditioner for centuries in the Orient (King, 1911). The extensive and successful sewage farms in Berlin and Paris were begun around 1850. Sludge has been applied to the land for many years in the United States. Most sludge, however, has been spread in the dried form. About 60 percent of the sewage sludge generated in the United States (dried or wet) is land applied (National Research Council, 2002). In the United Kingdom, where agricultural use of sewage sludge is of high priority, nearly 50% is utilized on land, compared with 30% in other countries of the European Economic Community (Karapanagiotis et al., 1991). The Netherlands, however, limits application of wastes to agricultural land. Several books published since 1979 document the agricultural use of sludge (Loehr et al., 1979a,b; Page et al., 1983; Berglund et al., 1984; Fuller and Warrick, 1985; Page et al., 1987; Dirkzwager and L'Hermite, 1989; L'Hermite, 1991; Gregg and Currie, 1992; Girovich, 1996; Epstein, 2002; National Research Council, 2002).

Terminology

Sludge is classified as (1) untreated (raw) and (2) treated. Primary sludge results from the first major treatment in a sewage-treatment works. This treatment consists of sedimentation. Most suspended matter is removed, but colloidal and dissolved matter is not. In secondary treatment, which follows primary treatment, microorganisms are used to treat the sludge. Activated sludge is obtained in secondary treatment by settling flocculated bacterial cells feeding on soluble and suspended organic material in raw or settled sewage. Primary and activated sludges are treated to obtain a stabilized sludge in which organic matter has been decomposed into a stable material. During digestion, the usual method of sludge stabilization, anaerobic or aerobic microorganisms convert organic matter in sludge into less putrefiable matter. Anaerobic digestion is more common than aerobic digestion. Sludges also can be stabilized by pasteurization, chlorination, lime treatment, or irradiation. Chemicals such as alum or iron salts can be added at any stage of treatment including treatment of the final effluent in a tertiary process (Dean and Smith, 1973).

Characteristics of sludge

Digested sludge contains 3–5% solids as finely divided and dispersed particles. It looks like crude oil and can be easily transferred by pipes. Table S4 lists the nutrient and trace element content of anaerobically digested sludge (Keeney et al., 1975; Page, 1974), plus the highest concentration of an element allowed in sludge applied to land in the United States, according to the 40 CFR Part 503 regulation (Bastian, 1997).

Soil physical changes after sludge application

Once the sludge is applied to land, the most obvious physical change that takes place is the formation of a crust of sludge. The crust develops because the solids content causes liquid sewage sludge to infiltrate slowly into soils. The rate of *infiltration* (*q.v.*) of sludge liquid depends on the initial soil moisture content and solids content of the sludge. The higher the soil moisture and sludge solids content, the lower is the infiltration rate. Initially, after a sludge application, the *hydraulic conductivity* (*q.v.*) of sand (or infiltration rate of sludge into sand) is greater than that of silt loam soils. After a few days of successive applications, the infiltration rate is about the same regardless of soil type. Therefore, the infiltration rate is eventually determined by the sludge cake and not by the soil surface. If successive sludge applications are made so that the sludge cake is not allowed to dry, infiltration rates decrease to low levels; but if the sludge cake is allowed to dry, the initial infiltration capacity is largely, if not entirely, recovered. If the sludge is plowed in, infiltration capacity is often maintained. Wet sludge applied to pasture or turf initially settles quickly into the soil.

Application of sludge increases soil *aggregation* (*q.v.*). Aggregation is influenced by microorganisms decomposing organic matter in sludge. Rapidly oxidizable organic matter can produce a desirable soil structure. Continual additions of organic matter are necessary to maintain good structure. If no further organic matter is added, the residual organic matter decomposes slowly.

Because addition of liquid digested sludge to land often has favorable effects on the physical characteristics of the soil, it has been used as a soil conditioner. In clay soil, sludge alleviates undesirable structure by changing the spacing of *soil pores* (*q.v.*). In sandy soil, it increases ion exchange sites for nutrient retention, improves soil aggregation, acts as a binder to hold sand from blowing away, and reduces erosion.

Table S4 Concentration of elements in sludge

Element	Range	Median	Proposed maximum suggested by EPA
	% of solids		
Total-N (moist)[a]	3.4–9.5	. . .[b]	. . .
Total-N (dried)	2.4–3.1	. . .	. . .
NH_4-N (moist)	0.8–4.1	. . .	. . .
NH_4-N (dried)	0.02–0.26	. . .	. . .
Organic C	25.7–38.5	. . .	. . .
P	2.7–6.1	. . .	. . .
K	1.2–1.9	. . .	. . .
Ca	4.2–18.0	. . .	. . .
Mg	0.8–1.2	. . .	. . .
Na	0.6–2.2	. . .	. . .
Al	0.36–1.2	. . .	. . .
Fe	0.8–7.8	. . .	. . .
	mg/kg		
Ag	5–150	20	. . .
As	1–18	7.5	100
B	6–1 000	50	. . .
Ba	150–4 000	1 500	. . .
Cd	1–1 500	12	18
Co	2–260	12	. . .
Cr	20–40 615	380	2 000
Cu	52–11 700	700	1 200
Hg	0.1–56	3.0	15
Mn	60–3 860	400	. . .
Mo	2–1 000	5	35
Ni	10–5 300	52	500
Pb	15–26 000	480	300
Sn	40–700	120	. . .
Sr	52–7 810	. . .	. . .
V	20–400	60	. . .
Zn	72–49 000	2 200	2 700

Data from Chaney, 1990; Keeney et al., 1975; Page, 1974.

[a] Elements other than N are expressed on a dry weight basis.

[b] Data not available.

Soil chemical changes after sludge application

Nitrogen

Much of the nitrogen in sludge is in the ammonium-nitrogen form, which is derived from part of the organic nitrogen in raw sludge during digestion (Table S4). Some ammonia is fixed by organic matter and clays and, thus, is protected from biological attack. However, significant volatilization losses of ammonia do occur from surface-applied sludge. Often about 50% of ammonium-nitrogen is lost within a week after spreading liquid sludge.

Mineralization, the conversion of organic nitrogen to inorganic nitrogen as a result of microbial decomposition, proceeds at various rates depending on climate, soil, and type of organic matter. About 5–50% of the organic nitrogen in anaerobically digested sewage sludge can be mineralized to nitrate- plus nitrite-nitrogen in four months. Aerobically treated sewage sludges have higher mineralization rates than anaerobically treated sludges (Serna and Pomares, 1992).

Even though the ammonium-nitrogen in sludge nitrifies readily in soils, some denitrification (see *Nitrogen cycle*) occurs.

Denitrification is the transformation of nitrate- or nitrite-nitrogen to gaseous nitrogen. If free oxygen is absent or deficient and other conditions, including a supply of carbon, are favorable for biological activity, denitrification takes place. Some sludge nitrogen also is immobilized in the soil organic matter or remains as refractory organic nitrogen. Therefore, a variable amount of sludge-applied nitrogen is available for crop uptake or for leaching to the groundwater.

Under proper soil conditions (appropriate aeration and temperature), ammonium-nitrogen in anaerobically digested sludge is converted rapidly into mobile nitrate-nitrogen. The annual loading rate of sludge on land is limited by the amount of soluble nitrogen in the sludge-treated soil plus nitrogen from mineralization. If the applied nitrogen in the sludge greatly exceeds gaseous losses or plant uptake, concentrations of nitrogen in groundwater may be excessive. Excess nitrogen is converted to nitrates that percolate down and contaminate the groundwater (Dean and Smith, 1973). Also eutrophication results when surface water is enriched with nitrogen after runoff. Because high nitrate concentrations in drinking water are toxic to humans and livestock, application of large amounts of digested sludge on land can cause nitrate problems. About 5–8 cm of sludge will satisfy the nitrogen needs of nonleguminous crops without producing excessive nitrates in percolated water. But, if higher loading rates are used, the nitrogen content of sludge should be reduced, for example, by flooding to induce denitrification, which will result in gaseous loss of nitrogen (see previous paragraph). Leachates can also be collected for nitrogen removal, but this is not often done under normal field conditions.

Phosphorus

Many sewage-treatment plants remove phosphates from wastewater by concentrating them in the sludge as an insoluble residue. Phosphates in sludge, except for a small fraction bound in organic compounds, are present as calcium, iron, aluminum, or magnesium phosphate, depending on the process used. Calcium and magnesium phosphates are reasonably available to plants in neutral soils, whereas the phosphate in iron and alum (aluminum sulfate) precipitates is relatively unavailable. These precipitates can persist in the soil for long periods and slowly liberate phosphorus to plants. Recycling of sludge to the soil is the only economical way to conserve phosphates wasted in sewage (Kirkham, 1982). Application of sewage sludge builds up phosphorus reserves in degraded soils (Brossard et al., 1991).

In most soils, phosphorus is retained by adsorption and conversion to sparingly soluble precipitates. Therefore, phosphorus levels in drainage water from sludge-treated soils are usually less than 1 μg ml^{-1}. With high sludge-loading rates, movement of phosphorus to the groundwater may occur. However, surface-water pollution with phosphorus is a more serious problem because phosphorus-loaded surface soils can be eroded if soil conservation practices are not followed.

Potassium

Sludge is low in potassium compared to its nitrogen and phosphorus contents. Therefore, potassium may be in short supply for good crop growth. Inorganic potassium fertilizers sometimes are added to sludge-treated land.

Organic material

Anaerobically digested sludge typically contains from 20 to 30% organic carbon (Boyd and Sommers, 1990). Thus, when applied to land, it increases soil organic matter (humus) content. In Illinois, anaerobically digested sludge was applied each year during seven years on a silt loam soil. A total of 417 t ha^{-1} was applied during the seven years. The sludge increased the soil's organic carbon content from 1.2 to 3.4% in the surface 15 cm (Hinesly et al., 1977). During the seven years of annual applications, 55% of the organic C added as a constituent of sludge was lost by volatilization, probably mainly as carbon dioxide. Karapanagiotis et al. (1991) found that 23 to 26% of total organic matter degraded after five months in soil treated with varying amounts of sewage sludge.

Trace elements

Sewage sludge contains an abundance of trace elements necessary for plant growth (boron, copper, iron, manganese, molybdenum, and zinc) as well as others considered to be nonessential (e.g., cadmium, chromium, mercury, lead). The trace elements in sludge are sometimes called the heavy metals, because most of them (boron being the major expection) have a density greater than 5.0 (Page, 1974). Industrialized sludges, of course, can contain high concentrations of trace elements. Source control with limits on discharges of toxic trace elements is practiced by cities that use their sludge for agricultural purposes. But even the tightest source control is unlikely to reduce the trace-element content much below the median value (Dean and Smith, 1973). This is because household products contain trace elements. The trace elements likely to cause toxicities to plants in soils treated with large amounts (for example, 400 t ha^{-1}) of domestic sludge for a number of years (15 yr) are cadmium, copper, zinc, boron, and possibly nickel (Page, 1974). In industrialized sludges, in addition to the elements listed, concentrations of arsenic, barium, cobalt, chromium, manganese, lead, and vanadium may be sufficiently high to reduce crop yields when applied in large amounts. Plants can grow normally and yet contain concentrations of selenium, cadmium, molybdenum, and possibly lead that are toxic to man and animals.

Cadmium is the element of most concern in sludge, because it poses the greatest threat to human health (Sommers and Barbarick, 1986). Food obtained from plants grown on sludge-treated soil might contain concentrations of cadmium toxic to man and animals. Cadmium is used in electroplating, pigments, chemicals, batteries, alloys, photographic supplies, fungicides, as well as other products (Page, 1974). Even though industrial sources of cadmium in sludge can be controlled, domestic sources cannot. For example, cigarette ends flushed down toilets raises the cadmium concentration in sludge, because tobacco has a high concentration of cadmium (Juste and Mench, 1992).

Long-term studies suggest that cadmium is a problem in sludge-treated soils (Juste and Mench, 1992). Nine years after a one-time sludge addition to a fine sandy loam, Bell et al. (1991) found that the cadmium was more extractable (up to 60%) than zinc, manganese, and iron (less than 4%), which indicated a greater potential mobility for cadmium than for the other metals. Dowdy et al. (1991) reported that after 14 years of large additions of sludge (765 t ha^{-1} total added), sludge-born cadmium moved out of the tillage zone into the subsoil. At the 83–100 cm depth, the concentration of extractable cadmium in the soil was 2.5 times higher in the sludge-treated plots than in control plots. Kirkham (1975) showed that, at the 30–61 cm depth, a silt-loam soil spread with moderate amounts of sludge (28 t ha^{-1} yr^{-1}) for 35 years had 46 times more total cadmium than a control soil, and leaves of corn plants growing on that soil had concentrations of cadmium higher than normal. More studies are needed on sites that have received sludge for many years to evaluate the mobility and bioavailability of cadmium.

Because tissues from different crop species and varieties vary widely in their concentrations of trace elements, the selection of crops provides a way to control the entrance of undesirable amounts of trace elements into food chains (Chaney, 1990). In addition, synergistic and antagonistic interactions occur between elements in sludge and soil that affect the absorption of elements by plant roots. For example, high phosphorus levels in soil often inhibit uptake of trace elements. Therefore, it is possible to decrease uptake of one element by supplying another element to the soil.

After application to soil, trace elements tend to remain in the plow layer with the sludge residue, although cadmium appears to be an exception, based on the studies cited above. Trace elements are often associated with the organic-rich sludge fractions. Oxides of iron and manganese absorb trace elements and limit their movement (Bell et al., 1991). Citric acid, present in sewage sludge (e.g., from washing fluids), forms complexes with metals, which may play a part in migration of metals away from disposal sites (Francis et al., 1992). Chelating agents such as organic acids produced in the rhizosphere by root exudation or by microbial activity also affect the mobility of heavy metals in soils and their transfer to plants. In addition, microbes can absorb heavy metals and prevent their transfer to plants (Munier-Lamy et al., 1991). But microbes are short-lived, and when they die the metals will again be available for uptake by plants. The distance that the elements leach is determined by the oxidation-reduction potential and pH of the system. Practices that promote good soil aeration, such as drainage and structure development, lead to decreasing solubilities of trace elements. Also, soils with high cation exchange capacities are desirable for sludge disposal, because they have a great ability to hold and immobilize trace elements. Because of the nitrification reaction and the microbial production of carbon dioxide, sewage sludge usually lowers the pH of soils; thus, liming is recommended at sludge-disposal sites, but only when the soil pH is acidic (i.e., <pH 6). Liming also controls the uptake of trace elements of concern in sludge (cadmium, nickel, and zinc). Trace elements can form inert and insoluble compounds with clays and organic compounds. Therefore, they may be less available to plants than total concentrations of these elements in the soil indicate. Trace elements tend to move little with percolating water and remain at the site of application, unless they are transported away on eroded sediments.

Trace synthetic organic compounds

Synthetic organic compounds, like polychlorinated biphenyls (PCBs), in sludge applied to soil appear to pose a minimal risk to human health because plant uptake is small (Boyle, 1990; Wild and Jones, 1992). They have a low solubility and leach slowly into water as it moves through sludge and soil. Losses of PCBs into groundwater are less than 0.1% per year (Henry and Harrison, 1991), but even that amount is not insignificant for a highly toxic substance. The presence of commonly used pesticides in groundwater beneath agricultural areas indicates that additional studies are needed to evaluate their fate in sludge-amended soils (Sommers and Barbarick, 1986).

Alkylphenol ethoxylates are used as surfactants in a wide variety of household products, including detergents, paints, pesticides, and personal care products. They degrade to more toxic and estrogenic alkylphenols during the wastewater treatment process. Alkylphenols are more hydrophobic than their parent compounds and, therefore, tend to accumulate in sewage sludge. Of all the alkylphenolic compounds, nonylphenol and its ethoxylates have generated the most environmental health concerns because they are the most abundant. Low levels of nonylphenol (8.3–85.6 μg l^{-1}) have been shown to cause endocrine-disrupting effects in rainbow trout. There have been no field studies showing that sewage sludge containing high levels of alkylphenols and their ethoxylates cause deleterious effects to health or the environment when applied to agricultural lands (Erickson, 2002).

Pathogens

No incidence of disease transmission has been traced to the use of digested sludge on land. Most intestinal pathogenic bacteria are either destroyed or their populations greatly reduced by anaerobic digestion of sludge. The fate of viruses during anaerobic digestion is less certain. A 14 day anaerobic digestion period appears to destroy most viruses (Hinesly et al., 1974). Indigenous thiobacilli in sludge have been used to reduce populations of pathogenic microorganisms (Blais et al., 1992).

After sludge is applied on soil, the viability of pathogenic organisms varies, ranging from a few hours to several months. Sunlight disinfects sludge spread on the surface of the soil. Spore-forming bacteria can remain viable for years in soil, and some microorganisms survive almost indefinitely; however, the death of many pathogenic organisms occurs rapidly. Bacteria and viruses seldom move more than 30 m. This movement would most likely be vertical through macropore flow. Like many of the potential chemical pollutants, lateral movement of pathogenic organisms that survive digestion occurs only if soil erodes at the sludge disposal site. Under these conditions, surface water pollution is a problem.

Contamination of groundwater with pathogens happens, if undisinfected sludge is placed on shallow soils underlain by porous material or on soil that cracks when dry. Cracks and continuous channels that bypass the main soil mass can be more important than physical and chemical characteristics of soil that control movement of pathogens. Groundwater contamination is not a serious hazard in unfissured soil (Sommers and Barbarick, 1986). The National Research Council (2002) recommends a survey of pathogen occurrence in raw and treated sewage sludge. The survey should include careful examination of management practices to ensure that land application of sludge protects public health.

Soil organisms

One result of sludge disposal on land is an increase in earthworms. Trace elements also can accumulate in earthworms that live in polluted soils, thereby entering the food chain, when birds eat the worms. Earthworms added to soil, where they normally do not live, will not survive, even if sludge is added to the soil as a source of organic material. Sludge also increases numbers of nematodes (Weiss and Larink, 1991), but rhizobial populations are decreased (Madariaga and Angle, 1992). Mycorrhizal fungi have been suppressed in sludge-treated soil, perhaps by toxic levels of the ammonium ion (Lambert and Weidensaul, 1991).

Field application

Sludge can be applied on the surface of the soil or under the surface by injection into the soil. Surface application of liquid sludge is done by spraying, by ridge and furrow irrigation, or by tank truck or farm wagon. Portable spray irrigation systems using a single large-nozzle gun (2–5 cm orifice) are used. Sludge accumulating on plant leaves during spray irrigation can reduce photosynthetic rates. Ridge and furrow irrigation requires preparation of the land before spreading, and only level land can be used. It is suitable for row crops during the growing season. Tank trucks and farm tank wagons are most commonly used to apply sludge, especially in smaller communities. After surface application, sludge usually is plowed into the soil. Subsurface injection of liquid sludge has a number of advantages over surface application: (1) odors and insects are not a problem; (2) nitrogen is not wasted because ammonia volatilization and runoff are minimized; (3) water in the sludge is conserved for plant uptake rather than evaporated (important in semi-arid regions); (4) and public acceptance is better.

Modeling

Models (mathematical descriptions of the transport of organic or inorganic chemicals added to the soil) are becoming increasingly important (Jury and Ghodrati, 1989). They help to determine the effect of waste loadings, to identify proper application rates, to predict the environmental impact of waste management alternatives, and to determine the food-chain risk associated with these alternatives (Loehr, 1986; Haith et al., 1992). However, predictions obtained from models have not always agreed with actual observation (Granato et al., 1991).

M. B. Kirkham

Bibliography

Bastian, R.K., 1997. Biosolids management in the United States. *Water Environ. Technol.*, **9**(5): 45–50.

Bell, P.F., James, B.R., and Chaney, R.L., 1991. Heavy metal extractability in long-term sewage sludge and metal salt-amended soils. *J. Environ. Qual.*, **20**: 481–486.

Berglund, S., Davis, R.D., and L'Hermite, P., eds., 1984. *Utilisation of Sewage Sludge on Land: Rates of Application and Long-Term Effects of Metals.* Dordrecht: D. Reidel, 229 pp.

Blais, J.F., Tyagi, R.D., Auclair, J.C., and Lavoie, M.C., 1992. Indicator bacteria reduction in sewage sludge by a metal bioleaching process. *Water Res.*, **26**: 487–495.

Boyd, S.A., and Sommers, L.E., 1990. Humic and fulvic acid fractions from sewage sludges and sludge-amended soils. In MacCarthy, P., Clapp, C.E., Malcolm, R.L., and Bloom, P.R., eds., *Humic Substances in Soil and Crop Sciences: Selected Readings.* Madison, WI: American Society of Agronomy and Soil Science Society of America, pp. 203–220.

Boyle, M., 1990. Biodegradation of land-applied sludge. *J. Environ. Qual.*, **19**: 640–644.

Brossard, M., Mench, M., Clairon, M., and Laurent, J.Y., 1991. Effect of sewage sludge on short-term evolution of phosphorus forms in an oxisol. *Agronomie*, **11**: 699–706.

Chaney, R.L., 1990. Public health and sludge utilization. *BioCycle*, **31**(10): 68–73.

Dean, R.B., and Smith, J.E., Jr., 1973. The properties of sludges. In *Recycling Municipal Sludges and Effluents on Land.* Joint Conf. Proc. (Champaign, Illinois). Washington, D.C.: National Association of State Universities and Land-Grant Colleges, pp. 39–47.

Dirkzwager, A.H., and L'Hermite, P., eds., 1989. *Sewage Sludge Treatment and Use: New Developments, Technological Aspects and Environmental Effects.* London: Elsevier, p. 536.

Dowdy, R.H., Latterell, J.J., Hinesly, T.D., Grossman, R.B., and Sullivan, D.L., 1991. Trace metal movement in an Aeric Ochraqualf following 14 years of annual sludge applications. *J. Environ. Qual.*, **20**: 119–123.

Epstein, E., 2002. *Land Application of Sewage Sludge and Biosolids.* Boca Raton, Fl: Lewis Publishers, 192 pp.

Erickson, B.E., 2002. Aklyphenols in sewage sludge applied to land. *Environ. Sci. Technol.*, **36**: 10A–11A.

Francis, A.J., Dodge, C.J., and Gillow, J.B., 1992. Biodegradation of metal citrate complexes and implications for toxic-metal mobility. *Nature*, **356**: 140–142.

Fuller, W.H., and Warrick, A.W., 1985. *Soils in Waste Treatment and Utilization. Vol. I: Land Treatment.* Boca Raton, FL: CRC Press. 268 pp.

Girovich, M.J., ed., 1996. *Biosolids Treatment and Management.* Processes for Beneficial Use. New York: Marcel Dekker, 453 pp.

Granato, T.C., Richardson, G.R., Pietz, R.I., and Lue-Hing, C., 1991. Prediction of phytotoxicity and uptake of metals by models in proposed USEPA 40 CFR Part 503 sludge regulations:comparison with field data for corn and wheat. *Water Air Soil Pollut.*, **57&58**: 891–902.

Gregg, P.E.H., and Currie, L.D., eds., 1992. The use of wastes and byproducts as fertilizers and soil amendments for pastures and crops. *Proceedings of the Workshop*, Massey University, Palmerston North, New Zealand. Occasional Rep. No. 6. Palmerston North, New Zealand: Fertilizer and Lime Research Centre, p. 340.

Haith, D.A., Reynolds, J.E., Landre, P.T., and Richard, T.L., 1992. Sludge loading rates for forest land. *J. Environ. Eng.*, **118**: 196–208.

Henry, C.L., and Harrison, R.B., eds., 1991. *Literature Reviews on Environmental Effects of Sludge Management.* Seattle, Washington: University of Washington, College of Forest Resources, 238 pp.

Hinesly, T.D., Braids, O.C., Dick, R.I., Jones, R.L., and Molina, J.-A.E., 1974. Agricultural benefits and environmental changes resulting from the use of digested sludge on field crops, EPA/530/SW-30d.l. Washington, DC: Environmental Protection Agency, 375 pp.

Hinesly, T.D., Jones, R.L., Ziegler, E.L., and Tyler, J.J., 1977. Effects of annual and accumulative applications of sewage sludge on assimilation of zinc and cadmium by corn (*Zea mays* L.). *Environ. Sci. Technol.*, **11**: 182–188.

Jury, W.A., and Ghodrati, M., 1989. Overview of organic chemical environmental fate and transport modeling approaches. In Sawhney, B.L., and Brown, K.W., eds., *Reactions and Movement of Organic Chemicals in Soils.* Madison, WI: Soil Science Society of America and American Society of Agronomy, pp. 271–304.

Juste, C., and Mench, M., 1992. Long-term application of sewage sludge and its effects on metal uptake by crops. In Adriano, D.C., ed., *Biogeochemistry of Trace Metals.* Boca Raton, FL: Lewis Publishers, pp. 159–193.

Karapanagiotis, N.K., Sterritt, R.M., and Lester, J.N., 1991. Heavy metal complexation in sludge-amended soil. The role of organic matter in metal retention. *Environ. Technol.*, **12**: 1107–1116.

Keeney, D.R., Lee, K.W., and Walsh, L.M., 1975. Guidelines for the application of wastewater sludge to agricultural land in Wisconsin. Tech. Bull. 88. Madison, WI: Department of Natural Resources. 36 pp.

King, F.H., 1911. *Farmers of Forty Centuries or Permanent Agriculture in China, Korea and Japan.* Emmaus, PA: Rodale Press, pp. 441.

Kirkham, M.B., 1975. Trace elements in corn grown on long-term sludge disposal site. *Environ. Sci. Technol.*, **9**: 765–768.

Kirkham, M.B., 1982. Agricultural use of phosphorus in sewage sludge. *Adv. Agron.*, **35**: 129–163.

Lambert, D.H., and Weidensaul, T.C., 1991. Element uptake by mycorrhizal soybean from sewage-sludge-treated soil. *Soil Sci. Soc. Am. J.*, **55**: 393–398.

L'Hermite, P., ed., 1991. *Treatment and Use of Sewage Sludge and Liquid Agricultural Wastes.* London: Elsevier, 560 pp.

Loehr, R.C., Jewell, W.J., Novak, J.D., Clarkson, W.W., and Friedman, G.S., 1979a. *Land Application of Wastes*, Vol. I. New York: Van Nostrand Reinhold, 308 pp.

Loehr, R.C., Jewell, W.J., Novak, J.D., Clarkson, W.W., and Friedman, G.S., 1979b. *Land Application of Wastes.* Vol. II. New York: Van Nostrand Reinhold. 431 pp.

Loehr, R.C., 1986. The role of soil science in the utilization, treatment, and disposal of waste. In Runge, E.C.A., Chair, ed. comm., *Utilization, Treatment, and Disposal of Waste on Land.* Madison, WI: Soil Science Society of America, pp. 305–318.

Madariaga, G.M., and Angle, J.S., 1992. Sludge-borne salt effects on survival of *Bradyrhizobium japonicum*. *J. Environ. Qual.*, **21**: 276–280.

Munier-Lamy, C., Adrian, P., and Berthelin, J., 1991. Fate of organo-heavy metal complexes of sludges from domestic wastes in soils: a simplified modelization. *Toxicol. Environ. Chem.*, **31&32**: 527–538.

National Research Council, 2002. *Biosolids Applied to Land. Advancing Standards and Practices.* Washington, D.C.: The National Academies Press, 345 pp.

Page, A.L., 1974. *Fate and Effects of Trace Elements in Sewage Sludge when Applied to Agricultural Lands*, EPA-670/2-74-005. Cincinnati, OH: Environmental Protection Agency, 98 pp.

Page, A.L., Gleason, T.L., III, Smith, J.E., Jr., Iskandar, I.K., and Sommers, L.E., eds., 1983. *Utilization of Municipal Wastewater and Sludge on Land.* Proceedings of the 1983 Workshop, Riverside, CA: University of California, 480 pp.

Page, A.L., Logan, T.J., and Ryan, J.A., eds., 1987. *Land Application of Sludge. Food Chain Implications.* Chelsea, MI: Lewis Publishers, 168 pp.

Serna, M.D., and Pomares, F., 1992. Indexes of assessing N availability in sewage sludges. *Plant Soil*, **139**: 15–21.

Sommers, L.E., and Barbarick, K.A., 1986. Constraints to land application of sewage sludge. In Runge, E.C.A., Chair, ed. comm., *Utilization, Treatment, and Disposal of Waste on Land.* Madison, WI: Soil Science Society of America, pp. 193–216.

United States Environmental Protection Agency, 1992. *Technical Support Document for Land Application of Sewage Sludge*. Vol. I (Revised). Office of Water. Washington, DC: U.S. Environmental Protection Agency. 821 pp. Available from the National Technical Information Service, Springfield, Virginia 22161. Order document no. PB93-110575.

Weiss, B., and Larink, O., 1991. Influence of sewage sludge and heavy metals on nematodes in an arable soil. *Biol. Fertil. Soils*, **12**: 5–9.

Wild, S.R., and Jones, K.C., 1992. Polynuclear aromatic hydrocarbon uptake by carrots grown in sludge-amended soil. *J. Environ. Qual.*, **21**: 217–225.

Cross-references

Aggregation
Conductivity, Hydraulic
Infiltration
Nitrogen Cycle
Pollution
Soil Pores
Trace Elements

S-MATRIX

See *Micromorphology*.

SOD

A mat of soil and vegetation, usually grass covered, at the surface of the land, or a piece of the same cut from the surface.

SODICITY

The amount of exchangeable sodium in a soil. An excessive amount of sodium in soil causes clays to disperse and swell, which has adverse effects on drainage and aeration. Sodium toxicity to the biomass is a further problem.

Two indices are used to indicate the sodicity of soil: Exchangeable Sodium Percentage (ESP), and Sodium Adsorption Ratio (SAR).

Cross-reference

Soil Salinity and Salinization

SOIL

Soil is a generally loose, porous mixture of materials the porosity of which is the result of aggregation of organic and/or inorganic soil particles which forms an ephemeral cover on most of the Earth's land surface. It originates in response to ambient physical, chemical and biological conditions acting on organic residues, geological materials and anthropogeomorphic products (unconsolidated mineral or organic materials produced by human activity; FAO 1998), and is prone to erosional transport by wind, water, ice or organisms. Its significant components are (*a*) crystalline and amorphous, solid, inorganic phases, particularly aluminosilicates, iron hydroxides, and carbonates (*b*) organic materials both living and dead, of which the microbial biomass is of fundamental importance (*c*) an aqueous solution of inorganic and organic complexes, molecules and ions, commonly sufficiently dilute that H_2O has a thermodynamic activity of or close to 1, and (*d*) a gaseous phase containing the usual components of the Earth's atmosphere, their proportions modified by the chemical and biochemical reactions attendant upon mineral-water interactions, respiration and organic decay.

Soil is subject to continuous dynamic change, a prerequisite agent of which is water. The gravitational movement of water within soil effects the downward transport of solid particles and dissolved species whereas the solar energy concentrates constituents at the surface, either indirectly through plants, or directly, with the upward transport of water under evaporitic conditions. This produces over a relatively short period (order of 10^2 to 10^3 years), a vertical differentiation that appears megascopically as a series of horizons more or less parallel to the land surface. The simplest, complete profile is comprised of three major horizons A, B, and C. A and B together make up the solum, and C is the parent material modified by weathering and/or disaggregation. An organic horizon (O or H, depending on whether water-undersaturated or saturated, respectively) may be recognized, where organic matter is dominant. Certain horizons that are useful in discriminating one soil from another are called diagnostic horizons, a concept first introduced by the U.S. Department of Agriculture in the system of soil classification, which became Soil Taxonomy. It has since been adopted in other modern classifications.

Figure S14 displays a common sequence of horizons on a basaltic soil from central France. It also shows the relationship of soil to the underlying geological materials in the simplest case where the soil is residual (that is, formed in place). Where the parent material has no direct genetic connection with its immediate geological substratum, the soil is said to be developed from allocthonous materials deposited on top of the geologic substrate. In the latter case, the deposited materials can either be sediments (of alluvial, colluvial or eolic origin), volcanic products (ashes, lava, etc.), materials that have already gone through pedogenesis (cumulic soils), or anthropogeomorphic materials (sludges, mine spoils, urban fill, dredgings, etc.). Figure S15 is a generalized representation of the type of system illustrated in Figure S14.

Dokuchaev was the first to suggest a "factorial" approach to soil formation. He considered that soil was formed by the combined effects of the following factors: living and dead organisms, parent rock, climate and relief (Strzemski, 1975). Outside the Russian sphere, Jenny's (1961) version of this

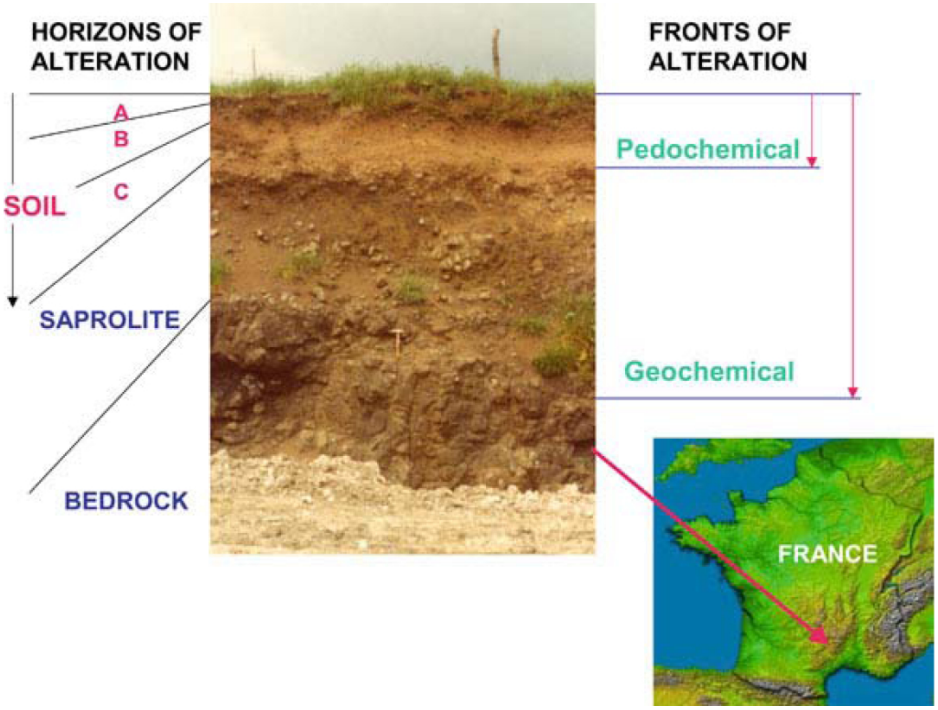
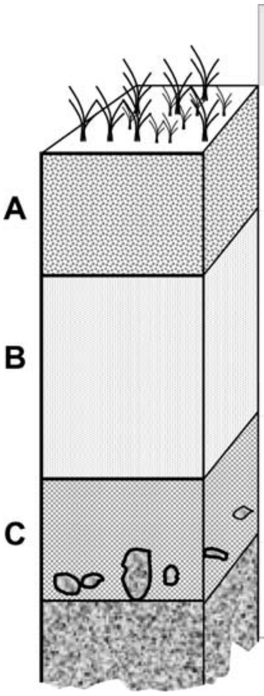


Figure S14 A common sequence of horizons on a basaltic soil from Belbex, central France. It also shows the relationship of soil to the underlying geological materials in the simplest case where the soil is residual (that is, formed in place). The distinction between pedochemical and geochemical weathering fronts is after Jackson and Sherman (1953).



ORGANICS	UNSTABLE MINERALS	RELICT MINERALS	NEW PHASES	REACTIONS
Rich in organic matter (OM), living and dead	Virtually everything	Quartz with minor amounts of accessories (zircon, rutile etc.,)	Organo-mineral complexes	Acid-base reactions. H^+ from organic sources
OM relatively unimportant	Primary silicates and carbonates	Relict quartz and alkali feldspar.	Amorphous and short-range order phases. 2:1, 1:1 clays, Fe, Al hydroxides. Depends on vigor of leaching	Acid-base, Ion Exchange. Organics important as H^+ source near top, H_2O-CO_2 near bottom
Parent material, OM relatively unimportant	Primary silicates	Relict quartz, feldspar. Ferromagnesians less common except micas.	As above, with possibility of secondary calcite	Acid-base with H_2O-CO_2 providing H+
Geological substratum, OM negligible			All original minerals in place	

Figure S15 An abstract representation of the type of system (a basaltic soil) illustrated in Figure S14.

approach has had the most influence. Figure S16 is an attempt to display weathering factors within the framework of interactions between the major geochemical reservoirs responsible for soil formation – lithosphere, atmosphere, hydrosphere, and biosphere. Figure S16 emphasizes interaction and feedback, unlike Jenny's approach, which considers the factors as independent variables. See *Factors of Soil Formation*.

Formation of soil

Two major processes are involved in the production of soil: weathering and pedogenesis. Weathering is the process by which materials of the Earth's surface change in response to prevailing conditions. Since prevailing conditions themselves change on timescales ranging from the instantaneous to the geological, dynamic change in the soil never stops. Weathering is a wasting process, that leads essentially to an increase in entropy and a continuous decrease in free energy within the weathering system.

By contrast pedogenesis is a building process by which the anisotropic complexity of the soil is built up from more or less isotropic parent materials through additions, losses, translocations and transformations of their components (Simonson, 1959). It is the sum total of the physical, chemical and biological processes that are needed to elaborate the structures and the new components found in soil at all levels, but most obviously at the level of the horizonated profile. As a constructive process it leads to a decrease in the entropy of the system, with a consequent increase in the entropy of the surroundings of the system. All pedogenic processes tend to decrease the free energy of the system.

Evolutionary trends

Evolution of the weathering mantle for most aluminosilicate or carbonate dominated parent materials, follows the three general chemical trends shown in Figure S17. The presence of less common minerals in the weathering regime may produce trends and conditions that lie outside the envelope of normal conditions shown in the diagram.

The acid trend

This is the common evolutionary pathway in soils. It is found in regions of humid climate on materials with a relatively unimpeded drainage. Acid-base reactions replace so-called basic cations in mineral structures and on exchange sites, with H^+. A generic reaction may be represented in the following way:

$$\text{primary minerals} + (H^+\ \text{ions})_{aq} = (Ca^{2+}, Mg^{2+}, Na^+, K^+, \ldots)_{aq} \pm \text{secondary minerals}$$

In essence, this is a titration of the parent material (e.g., a quenched igneous rock) against acids derivable ultimately from volcanic sources from the biomass, or from anthropogenic sources (e.g., acid rain). It results in the land surface being "*inevitably over-titrated, acting as a sink for protons*" (Edmond et al., 1979). Where acid attack is most aggressive, no secondary minerals are produced and the reaction is said to be

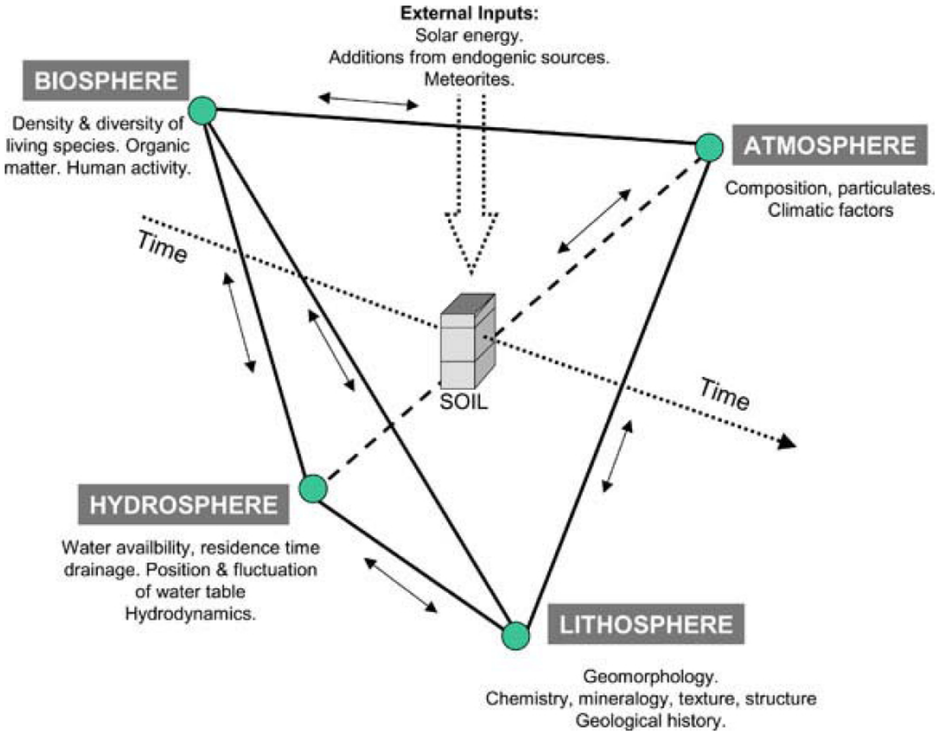


Figure S16 An attempt to display weathering factors within the framework of interactions between the major geochemical reservoirs responsible for soil formation – lithosphere, atmosphere, hydrosphere, and biosphere.

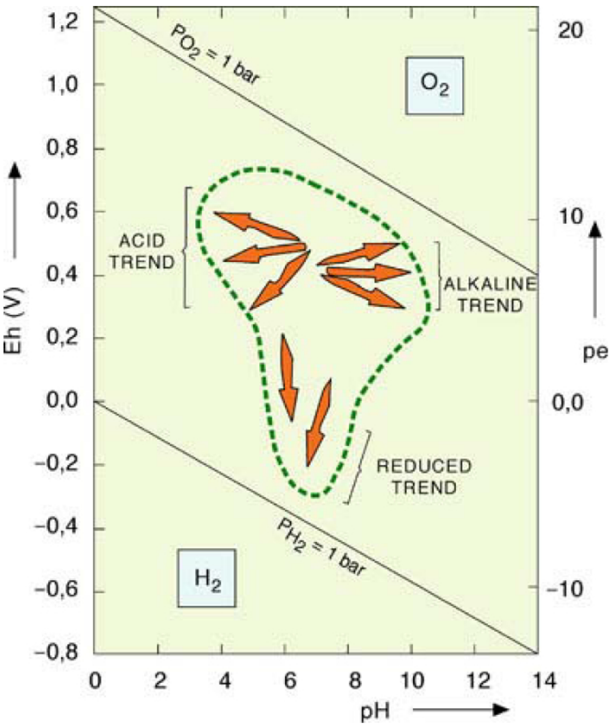


Figure S17 The three general chemical trends in terms of redox and pH variables. The dashed envelope is the approximate extent of redox-pH conditions in mineral soils.

congruent. Secondary minerals (clay minerals, hydroxides) and amorphous phases are formed under a less aggressive regime, and the reaction is labeled incongruent. The secondary minerals themselves are open to attack and given enough time, will tend to evolve from 2 : 1 sheet silicates (bisiallitisation) through 1 : 1 sheet silicates (monosiallitisation, to simple hydroxides (ferrallitisation and allitisation). The cations that are gradually released are flushed from the system as a consequence of the effect of gravity on the movement of the aqueous phase. The four component system SiO_2–Al_2O_3–Fe_2O_3–H_2O is the locus of soils produced over the long term by this winnowing process, for example in the humid tropics, and can therefore be considered as a *residua system of weathering*. In humid temperate regions the winnowing process is encouraged by the presence of organic acids and complexants. The resulting combination of hydrolysis and complexation is termed acido-complexolysis by Pedro and Sieffermann (1979). Podzols are the characteristic products.

Where pyrite occurs in the soil parent material, or where it is exposed by drainage of wetlands, an extreme acidity (equal to or less than pH 3) will be produced leading to the genesis of Thionic Luvisols (acid sulfate soils).

The alkaline trend

The alkaline trend occurs where there is a net annual water deficit that is in arid and semi-arid climatic zones. Hydrolysis still takes place, but scarcity of water means scarcity of hydrogen ions, so that under-titration is typical. Capillary rise and evaporation of soil water are the distinctive features, with evaporation leading to electrolyte-rich solutions and ultimately to the precipitation of new mineral phases. The most characteristic electrolytes are Na^+, Mg^{2+}, Ca^{2+}, HCO_3^-, CO_3^{2-}, SO_4^{2-}, $H_3SiO_4^-$, and Cl^-, and the most common precipitated phases are salts (carbonates, sulfates, and chlorides) with 2:1 neoformed clay minerals, secondary silica and even zeolites (Spiers et al., 1984) forming. The salts precipitate in order of increasing solubility product, with each precipitating salt acting as a chemical barrier separating pairs of evolutionary trends (Eugster and Hardy, 1970; and see *Alkaline Soils*). In soil science this kind of alkalinization is called solonization (Buol et al., 2003) and may lead to the accumulation of toxic amounts of less common elements, such as B and Se. If there is a wet season in the climatic zones where alkalinization takes place, de-alkalinization will result as electrolytes are partially flushed from the system.

The reduced trend

The main characteristic in this pedogenesis is an excess of water leading to saturation in all, or a major part of the profile. The result is the exclusion of atmospheric oxygen and the stabilization of reduced forms over oxidized forms of solid phases and ions. In some instances, anoxic conditions can be created in the water-unsaturated zone, when the O_2 demand by aerobic organisms in the soil is greater than supply. A notable contrast with the previous evolutionary trends relates to the behavior of Fe^{II}/Fe^{III} the commonest inorganic redox couple in mineral soils. In acid and alkaline pedogeneses the ferric state prevails and since Fe^{III} has only a low solubility in all but hyperacid situations, solids such as goethite, ferrihydrite or hematite are found in soils. In reduced systems iron is much more soluble in the ferrous form and will tend to be flushed from the soil, except when the appropriate anions are present due to precipitation of siderite, pyrite, vivianite, and so on, or when more oxidizing conditions are found nearby, and they precipitate as Fe^{III} oxyhydroxides. Alternating oxidation-reduction conditions occur, especially close to the water table, owing to fluctuations in level. Manganese may be mobilized in a similar fashion, as manganous rather than manganic ions. All these processes lead to the appearance of redoximorphic features, with a grayish, slightly bleached appearance in the reduced matrix (when the soil is said to be gleyed) and a reddish/yellowish brown color in the oxidized soil matrix. Concretions and indurated layers (or pans) can form in the latter. Under favourable drainage and topographic conditions (together with an acid pH and high concentration of Fe^{II} relative to other exchangeable cations) ferrolysis occurs as a distinctive pedogenic process (Brinkman, 1970). The sequence is as follows: when anoxic conditions occur, reduction takes place first, and Fe^{II} replaces Ca^{2+} and K^+ on exchange sites. This is followed by oxidation, attendant for example on a lowering of the water table. Hydrolysis then replaces Fe^{II} with H^+ and an acid clay forms, which is unstable and evolves to an Al-clay with degradation of the internal structure, with Fe (and Mn) hydroxides as accompanying solid phases. The latter produce mottles, concretions and extensive indurated layers (hardpan).

Under more reduced conditions, SO_4^{2-} is reduced to sulfide, by means of sulfate-reducing bacteria, and acid volatile sulfides, framboidal pyrite, and other Fe^{II} sulfides are formed. This is a common process in mangrove forests, salt marshes and other areas close to the coast, where “sulfidic soils” are formed. Saturation with respect to water, also promotes the preservation of organic matter and therefore the production of the peat deposits characteristic of bogs and mires.

Summary diagram

Individual articles within the Encyclopedia treat soils in more detail according to the groupings shown in the summary diagram (Figure S18).

Biospheric role

Soil is an integral part of the biosphere, the outer zone of the solid earth in which the manifestations of life are found. The biosphere is more or less coincident with the zone in which the low temperature, low pressure processes of the supergene cycle take place. Soil is the most active part of this zone on land, and plays a crucial role in the workings of the biosphere. It has at least four important biospheric functions:

1. It provides habitat for organisms.
2. It acts as a short-term reservoir and reaction vessel for water.
3. It accumulates, stores and redistributes solar energy.
4. It accumulates, stores and redistributes nutrient elements.

The soil constitutes an environmental restriction or choke point within the biosphere through which materials and energy are squeezed. The concept can be illustrated as an hourglass, (Chesworth, 2006) representing the biosphere, with all major biogeochemical cycles passing through the neck where the soil resides (Figure S19).

This paradigm emphasizes the fact that soil constitutes a particularly vulnerable part of the biosphere. Any disruption may potentially affect large areas of the planetary surface by virtue of the interconnectedness that the major cycles impart.

Questions of sustainability

Soil forms slowly and by comparison tends to erode rapidly, especially where used in agriculture. Estimates have been made that in the USA agricultural soil erodes 12 times faster on average than it forms. In other words ultimately soil is not currently a sustainable resource in the human economy.

Disruption and damage by human activity began with the Paleolithic use of fire to clear large regions starting as much as 50 000 years ago. It has become an increasing threat since the Neolithic invention of agriculture, some 10 000 years ago. This made possible the subsequent invention of civilization and led to further damage to the soil as a result of urbanization and industrialization. Currently, we have damaged to a greater or a lesser degree about 60 percent of the soils of the world.

Recognition of the vulnerability of soil is at least as old as written history, yet it was not until the first half of the twentieth century that preventative or remedial action at a governmental level was proposed. The European Union has recently elaborated the Thematic Strategy for Soil Protection (EC, 2006). The threats to soil functions identified are erosion, loss of organic matter, contamination, soil sealing, compaction, loss of biodiversity, salinization, and landslides. These are mainly the result of pollution, unsustainable use and climate change. The soil functions identified are (a) food and biomass production (b) storage, filtration and transformation of nutrients and

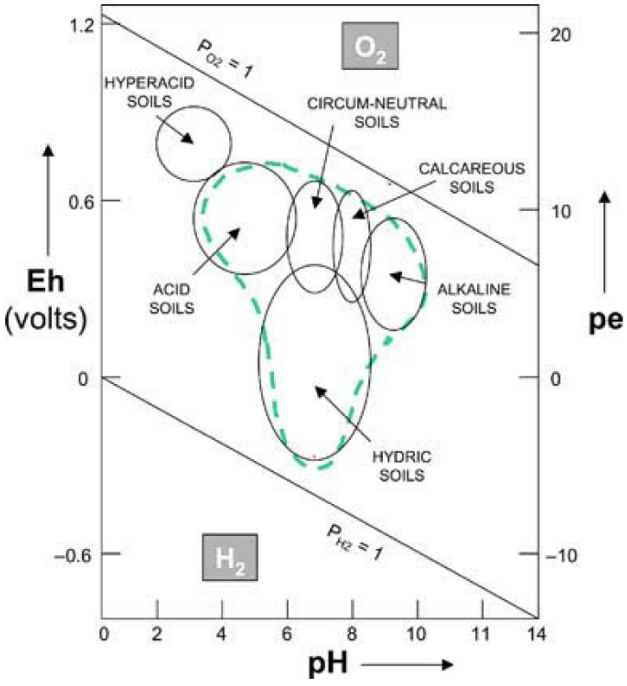


Figure S18 A summary grouping of soils on the basis of redox and pH variables. See individual articles for details of the soils in each group. Hyperacid Soils are treated in the article *Thionic or Sulfidic Soils*.

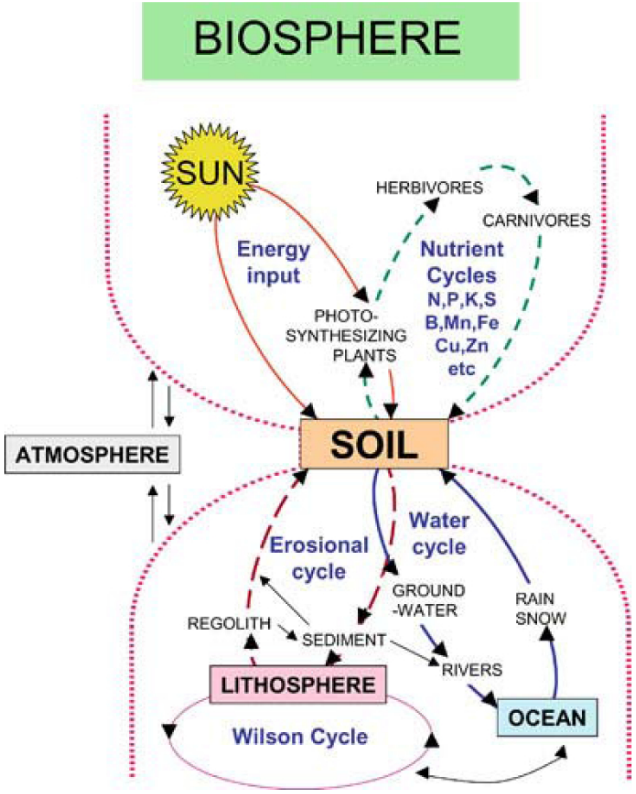


Figure S19 Hourglass paradigm: a schematic view of the biosphere that emphasizes soil as a vulnerable zone of constriction through which energy and materials pass between different compartments of the biosphere. Within the soil energy and materials are also exchanged between nested compartments in a similar way.

water, (c) habitat and gene pool, (d) platform for most human activities, (e) sources of raw materials, (f) carbon pool, and (g) storage of geological and archeological heritage. Soil protection is now a recognized imperative worldwide, though exigencies of population pressure and of economics over the short term mean that the recognition is more common in an abstract sense than in practice.

Marta Camps Arbestain, Felipe Macías, and Ward Chesworth

Bibliography

Brinkman, R., 1970. Ferrolysis, a hydromorphic, soi-forming process. *Geoderma*, **3**: 199–206.

Buol, S.W., Southard, R.J., Graham, R.C., and McDaniel, P.A., 2003. *Soil Genesis and Classification.* 5th edn. Ames, IA: Iowa State Press, 494 pp.

Chesworth, W., Martinez Cortizas, A., and Garcia Rodeja, E., 2006. The redex-pH approach to the geochemistry of the earth's land surface, with application to peatlands. Chapter 8 in peatlands edited by Martini, I.P., Martinez Cortizas, A., and Chesworth, W. pp. 175–195.

Edmond, J., Corliss, J.B., and Gordon, L.I., 1979. Ridge crest hydrothermal metamorphism in the Galapagos center and reverse weathering. Washington DC: American Geophysical Union, *Maurice Ewing Series*, **2**: 383–390.

EC. 2006. COM 2006/231, 2006. Communication from the Commussion to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions. Thematic Strategy for Soil Protection. Commission of the European Communities. Brussels, 22.9.2006, 12 pp.

Eugster, H.P., and Hardy, L.A., 1970. Saline lakes. In Lerman A., ed., *Lakes: Chemistry, Geology, Physics.* New York: Springer. 363 pp.

FAO, 1998. World Reference Base for Soil Resources. World Soil Resources Rep. No. 84. FAO, Rome. 88 pp.

Jackson, M.L., and Sherman, G.D., 1953. Chemical weathering of minerals in soils. *Adv. Agron.,* **5**: 219–318.

Jenny, H., 1961. Derivation of state factor equations of soils and ecosystems. *Soil Sci. Soc. Am. Proc.*, **25**: 385–388.

Pedro, G., and Sieffermann, G., 1979. Weathering of rocks and formation of soils. *Earth Sci.*, **16**: 39–55.

Simonson, R.W., 1959. Outline of a generalized theory of soil genesis. *Soil Sci. Soc. Am. Proc.*, **23**: 152–156.

Spiers, G.A., Pawluck, S., and Dudas, M.J., 1984. Authigenic mineral formation by solodization. *Can. J. Soil Sci.*, **64**: 515–532.

Strzemski, M., 1975. *Ideas Underlying Soil Systematics.* Washington, DC: U.S. Dept. of Commerce. 542 pp.

Cross-references

Acid Soils
Alkaline Soils
Calcareous Soils
Hydric Soils
Near Neutral Soils
Thionic or Sulfidic Soils

SOIL BIOLOGY

Soil biology is the study of living organisms and life processes in terrestrial ecosystems. The complexity and variability of soils makes scientific study extremely difficult. For soil biologists, these problems are often magnified by the inherent variability of biological systems and the fact that biological processes occur at the level of the microsite, which is a localized point of heterogeneity generally beyond the resolution of current analytical techniques (Figure S20). Detailed knowledge of soil biology is essential to better understand the heterogeneity, complexity and stability of soil ecosystems.

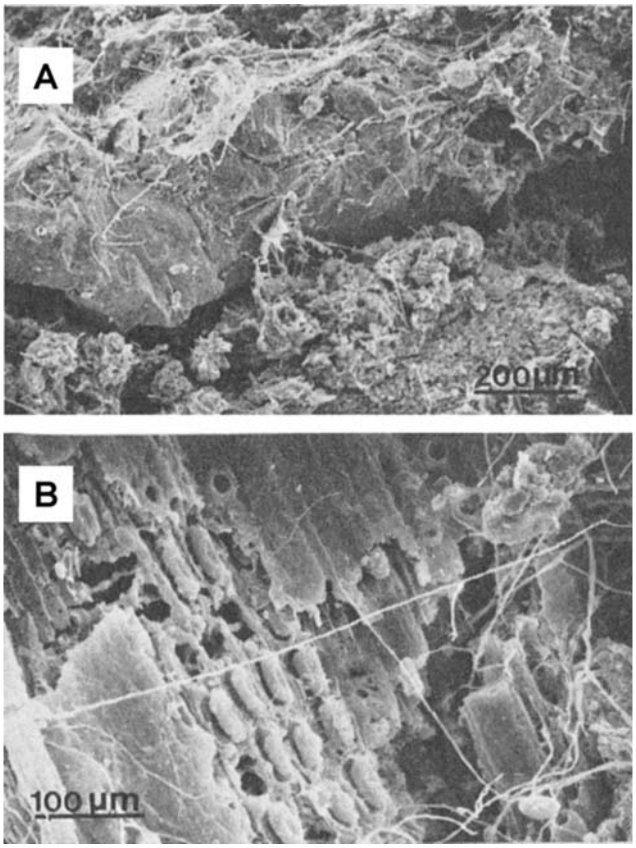


Figure S20 Examples of microsites; (a) fungal and actinomycete colonization of a microsite (from Gupta and Germida, 1988); (b) fungal hyphae on the surface of a partially humified plant leaf (from Cho and Mermut, 1992).

The purpose of this entry is not to cover all aspects of soil biology, but rather to provide a brief introduction to soil organisms and their activities and function in soil ecosystems. For more detailed information readers are referred to a number of recent publications (Burges and Raw, 1967; Swift et al., 1979; Eisenbeis and Wichard, 1987; Edwards and Stinner, 1988; Paul and Clark, 1989; Wood, 1989; Dindal, 1990; Hatfield and Stewart, 1994; Pankhurst et al., 1997).

The assemblage of organisms that spend at least part of their life cycle in or on the soil is referred to as the *soil biota*. The soil biota is extremely diverse and includes hundreds of thousands of species representing the five biotic kingdoms, including many different animal phyla and all known types of microorganisms (Swift et al., 1979; Paul and Clark, 1989; Hendrix et al., 1990; Walker, 1992). These organisms range in size from less than one micrometer (bacteria) to more than several centimeters in diameter (snails). The relative size scale of the soil biota is presented in Figure S21.

The field of soil biology cuts across many disciplines (Table S5) and includes, but is not limited to, studies of the biological and functional diversity of the soil biota, the biogeochemical processes mediated by the soil biota, the population dynamics and interactions of the biota, and the general

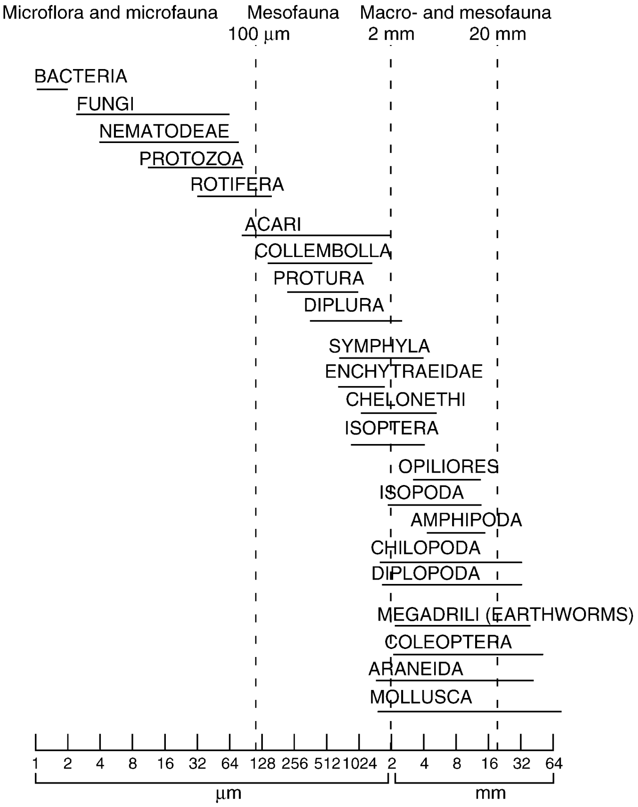


Figure S21 Size classification of soil organisms by body width (from Swift el al., 1979).

ecology of the soil ecosystem. Recent interest in the sustainability of ecosystems, particularly terrestrial ecosystems such as agro-ecosystems, has revitalized interest in soil biology, under the theme of soil ecology, and promoted collaboration among specialists in the various sub-disciplines of soil biology; i.e., microbiologists, nematologists, entomologists and others (Hendrix et al., 1990; Coe Klopatek et al., 1992; Walker, 1992).

The biology of soils may be studied at a variety of levels (Table S6). For example, scientists interested in the biological diversity of a soil may enumerate, isolate, characterize and identify organisms representing a given population. Application of new analytical tools such as confocal scanning laser microscopy coupled with organism-specific fluorescent probes has allowed visualization of organisms in microsites and within consortia of organisms. Whereas studies on nutrient cycling within a particular system may require information on the amounts of plant biomass or microbial biomass in soil only, ecologists studying food webs are concerned with the dynamic relationships between different functional groups such as bacteria and bacterivorous nematodes (Hunt et al., 1987). In addition, biologically mediated soil processes such as denitrification may be studied by simply measuring parameters such as gas fluxes or enzyme activities. All these approaches are complementary, and collectively provide the type of information necessary to better understand the biology of soil ecosystems.

Table S5 Some research areas and interactive disciplines of soil biology[a]

	Accumulated knowledge	Present activity	Future potential
Topic			
Soil			
Enzymes	+	+	++
Viruses			+
Structural stability	+		++
Nutrient cycling/utilization	+++	+++	+++
Plant resiude decomposition/composts	+	+	++
Pesticides	++	+	+
Water relations	+	+	++
Free-living N_2 fixation	+++	++	++
Rhizosphere			
Root nodulation	+++	+++	++
Mycorrhiza	++	++	++
General rhizosphere	+	+	++
Iron uptake	++		++
Recognition phenomena		+	+
Biocontrol of pests and diseases	++	++	++
Disciplines			
Agronomy/crop physiology	+	+	+++
Biochemistry	+	+	++
Chemical metabolism	+	+	++
Ecology	++	++	++
Genetics	+	+++	+++
Entomology/zoology	+	+	++
Mathematical modelling	+	+	+
Microbial physiology	+	+	++
Mineralogy/pedology	+		++
Physics	+	+	+
Plant nutrition	++		+++
Population biology	+	+	+++
Root physiology	++	+	++
Virology			+

[a] Relative activity by number of + marks, no entry indicates little or no activity. Adapted from Lynch (1987).

Table S6 Levels at which soil biology may be studied

Level	Example
Organism	
Population	Microbial biomass
Functional group	Nematophagous fungi
Species	*Azotobacter chroococcum*
Activity	
Total	Soil respiration
Process	Fertilizer recovery
Enzyme	Urease

Adapted fom Wood (1989).

Soil biota undertake a wide range of functions in natural ecosystems and may be arranged into several *functional groups* (Table S7). The soil microflora (i.e., fungi, bacteria and actinomycetes) are the dominant soil organisms both in numbers and biomass. These organisms attack complex organic materials, converting them into simpler molecules and byproducts. For example, as bacteria and fungi decompose crop residues they

Table S7 Influences of soil biota on soil processes in ecosystems

	Nutrient cycling	Soil structure
Microflora e.g., bacteria, fungi	Catabolize organic matter Mineralize and immobilize nutrients	Produce organic compounds that bind aggregates Hyphae entangle particles into aggregates
Microfanua e.g., protozoans, nematodes	Regulate bacterial and fungal populations Alter nutrient turnover	May affect aggregate structure through interactions with microflora
Mesofauna e.g., mites, collembola	Regulate fungal and microfanual populations Alter nutrient turnover Fragment plant residues	Produce fecal pellets Create biopores Promote humification
Macrofauna e.g., amphipods, centipedes, earthworms	Fragment plant residues Stimulate microbial activity	Mix organic and mineral particles Redistribute organic matter and microorganisms Create biopores Promote humification Produce fecal pellets

Adapted from Hendrix et al. (1990).

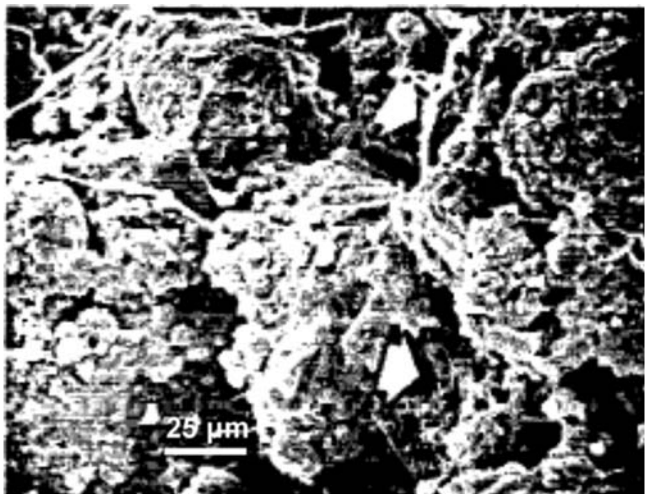


Figure S22 Microbial colonization of microsites and subsequent binding of soil particles to form a macroaggregate (from Gupta and Germida, 1988).

assimilate (i.e., immobilize) some nutrients into new cell biomass, while at the same time mineralizing and releasing other stored nutrients into inorganic forms that serve as a principle source of nutrients for plant growth. Some of these soil microorganisms also serve as the primary catalyzers in the biogeochemical cycling of N, P and S, and may be viewed as regulators of nutrient availability to primary producers. Not only do soil microflora influence soil processes, they also play an important role in maintaining the physical structure of the soil. For example, bacteria and fungi produce chemical exudates that bind primary soil particles together to form micro-aggregates. These micro-aggregates may be further assembled into macro-aggregates (Figure S22) through the binding action of fungal hyphae (Tisdale and Oades, 1982; Gupta and Germida, 1988). The hyphae of mycorrhizal fungi are especially important in stabilizing soil aggregates in cropped terrestrial ecosystems (Miller and Jastrow, 1992).

Small animals that feed upon microflora and organic particles are classified as the soil microfauna. This group consists primarily of protozoa, nematodes, and some small mites and springtails (Collembola). The population dynamics of this group often fluctuates dramatically in response to food availability and to wetting and drying cycles in soil. An important function of this group is regulation of population densities and activities of the microflora.

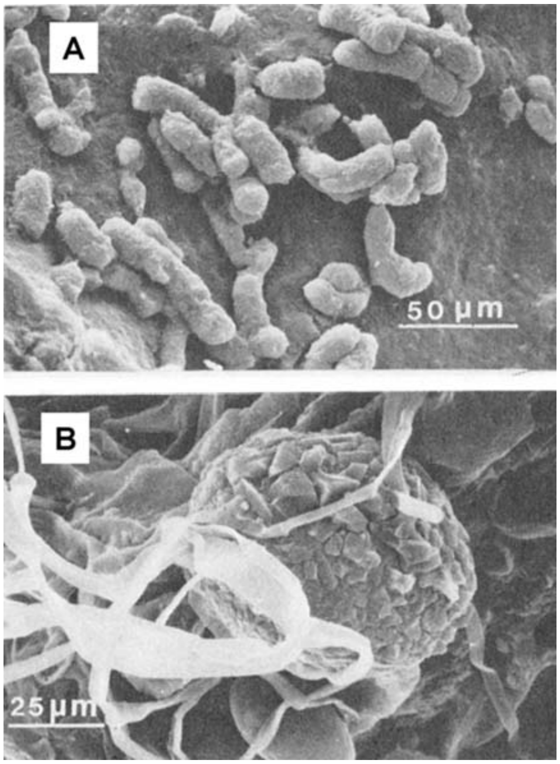


Figure S23 Examples of fecal pellets found in soil; (a) fecal pellets at the entrance of a soil tunnel; (b) rounded fecal pellet surrounded by fungal hyphae (from Cho and Mermut, 1992).

The soil mesofauna are composed of mites, collembola and other small soil insects which display a wide variety of feeding habits, including microbivory, saprobivory, omnivory and predation. The functional roles of these animals in soil processes are numerous and they are considered to be important in regulating microbial populations and in reworking the feces of larger fauna.

Large and conspicuous soil animals such as amphipods, isopods, centipedes and millipedes, adult and larval insects, earthworms and mollusks are considered the macrofauna and megafauna of soil. Fragmentation and redistribution of plant residues in soil is the principle activity of these soil animals. Their activities enhance decomposition of residues by increasing substrate surface area for microbial activity. They also affect soil structure by physically mixing the soil, forming soil pores and excreting fecal pellets (Figure S23). The activities of soil animals (e.g., burrowing, mixing organic and mineral particles, etc.) result in the formation of soil organic matter and the maintenance of soil aggregates and soil structure. Thus the functional importance of these organisms in soil ecosystems is directly related to their ability to regulate primary production through their effects on nutrient cycling and soil structure.

Conclusion

Soil biology deals not only with the biological and functional diversity of soil, but also with the interrelationship of soil organisms with their environment and each other. Living organisms are a critical component of terrestrial ecosystems. The biotic component of soil is important for organic matter decomposition, nutrient cycling, and the maintenance of soil structure, and is critical to the maintenance of the quality and health of soil ecosystems.

James J. Germida

Bibliography

Burges, A., and Raw, F., eds., 1967. *Soil Biology.* London: Academic Press, 532 pp.

Cho, H.D., and Mermut, A.R., 1992. Pedogenesis of two forest soils (Kandiustults) derived from metamorphosed granite in Korea. *Soil Sci. Soc. Am. J.*, **56**: 517–525.

Coe Klopatek, C., O'Neil, E.G., Freckman, D.W., Bledsoe, C.S., Coleman, D.C., Crossley, D.A., Jr., Ingham, E.R., Parkinson, D., and Klopatek, J.M., 1992. The sustainable biosphere initiative: a commentary from the U.S. soil ecology society. *Bull. Ecol. Soc. Am.*, **73**: 223–228.

Dindal, D.L., 1990. *Soil Biology Guide.* New York: John Wiley & Sons, 1349 pp.

Edwards, C.A., and Stinner, B.R., 1988. Interactions between soil inhabiting invertebrates and microorganisms in relation to plant growth and ecosystem processes: an overview. *Agric. Ecosyst. Environ.*, **24**: 1–3.

Eisenbeis, G., and Wichard, W., 1987. *Atlas on the Biology of Soil Arthropods.* New York: Springer, 437 pp.

Gupta, V.V.S.R., and Germida, J.J., 1988. Distribution of microbial biomass and its activity in different soil aggregate size classes as affected by cultivation. *Soil Biol. Biochem.*, **20**: 777–786.

Hatfield, J.L., and Stewart, B.A., eds., 1994. *Soil Biology: Effects on Soil Quality.* Boca Raton, FL: Lewis Publishers. 169 pp.

Hendrix, P.F., Crossley, D.A., Jr., Blair, J.M., and Coleman, D.C., 1990. Soil biota as components of sustainable agroecosystcms. In Edwards, C.A., Rattan, L., Madden, P., Miller, R.H., and House, G., eds., *Sustainable Agricultural Systems.* Ankeny, IA: Soil and Water Conservation Society, pp. 637–654.

Hunt, H.W., Coleman, D.C., Ingham, E.R., Elliott, E.T., Moore, J.C., Rose, S.L., Reid, C.P.P., and Morley, C.R., 1987. The detrital food web in a shortgrass prairie. *Biol. Fertil. Soils*, **3**: 57–68.

Lynch, J.M., 1987. Soil biology: accomplishments and potential. *Soil Sci. Soc. Am. J.*, **51**: 1409–1412.

Miller, R.M., and Jastrow, J.D., 1992. The role of mycorrhizal fungi in soil conservation. In Bethlenfalvay, G.J., and Linderman, R.G., eds., *Mycorrhizae in Sustainable Agriculture.* ASA Spec. Pub. No. Madison. WI: American Society of Agronomy, Crop Society of America and Soil Science Society of America, pp. 29–44.

Pankhurst, C.E., Doube, B.M., and Gupta, V.V., eds., 1997. *Biological Indicators of Soil Health.* New York: CAB International, 1997 pp.

Paul, E.A., and Clark, F.E., 1996. Soil Microbiology and Biochemistry. 2nd edn. San Diego, CA: Academic Press, 340 pp.

Swift, M.J., Heal, O.W., and Anderson, J.M., 1979. *Decomposition in Terrestrial Ecosystems.* Berkeley, CA: University of California Press, p. 327.

Tisdale, J.M., and Oades, J.M., 1982. Organic matter and water-stable aggregates in soils. *J. Soil Sci.*, **33**: 141–163.

Walker, B.H., 1992. Biodiversity and ecological redundancy. *Conserv. Biol.*, **6**: 18–23.

Wood, M., 1995. *Soil Biology*, 2nd edn. London: Blackie, 150 pp.

Cross-references

Biogeochemical Cycles Fauna
Plant Nutrients
Rhizosphere
Soil Chemistry
Soil Microbiology

SOIL CHEMISTRY

Soil chemistry is the branch of soil science that deals with the structure, composition and chemical properties of substances in the soil, and the transformations, which they undergo. It provides the basis for the solutions of problems as diverse as soil fertility and plant nutrition, disposal of organic and inorganic wastes, ground-water quality, corrosion or degradation of underground structures such as pipelines, and reclamation of disturbed land. This entry presents an overview of some of the important chemical properties and processes in the soil. Many of the specific topics are discussed in greater detail in other sections of this encyclopedia.

Soils from different climatic regimes and those originating from different parent materials vary considerably in chemical composition and properties; also, there can be considerable variation with depth and lateral location, often over distances as short as 1 cm. It is this variability that contributes to the chemical complexity of soils.

Soil is a three-phase system, consisting of solid, liquid and gaseous components. The solid phase, which comprises about 50% of the total soil volume, includes inorganic and organic compounds. Mineral matter usually accounts for more than 95% of the solid phase, except in the peat and muck soils, which are composed predominantly of organic matter.

Mineral composition and properties

The mineral phase (Dixon and Schulze, 2002) is commonly separated into three particle-size fractions: clay (less than 0.002 mm particle diameter), silt (0.002–0.05 mm), and sand (greater than 0.05 mm). The clay fraction, because of its large surface area and its surface charge and adsorption properties, is the site of many important chemical reactions occurring in soils. The principal clay-size inorganic components are the phyllosilicate minerals (kaolinite, smectite, vermiculite, illite and chlorite) and the oxides of iron (goethite, hematite and ferrihydrite), manganese (bimessite), aluminum (gibbsite) and silicon (allophane and immogolite; these minerals also contain Al). Important minerals in the sand and silt fractions include quartz, feldspar, mica, calcite and gypsum. The structures of each of these minerals are discussed more extensively in other sections of this book. The techniques that are used to identify and quantify the specific mineral components of a soil, including X-ray diffraction, infrared spectroscopy, differential thermal analysis, petrographic microscopy, electron microscopy and selective extraction procedures, are each important tools of the soil chemist. Three classes of compounds deserve further mention because of their unique chemical properties, which influence the chemistry of the soil.

Phyllosilicates

The 2:1 phyllosilicates (Gieseking, 1975; Greenland and Hayes, 1978; Dixon and Schulze, 2002), smectite and vermiculite, are characterized by their permanent negative charge and their property of shrinking and swelling. The chemistry of these minerals in the soil (e.g., cation retention and swelling properties) is strongly influenced by the following structural variables (Bohn et al., 2001): (1) layer charge density, (2) site of charge deficit (octahedral versus tetrahedral layer), (3) dioctahedral versus trioctahedral mineral, and (4) the iron content of the octahedral layer. The latter property is important since a change in redox potential of the environment may influence the oxidation state of the iron and hence the layer charge density of the clay (Stucki, 1988). The negative charge of the phyllosilicate (which is usually expressed as cation exchange capacity) is balanced by exchangeable cations, which exist predominantly between the internal swelling layers but also on the external surfaces and edges of the clay particles. These cations are usually capable of reversible ion exchange, e.g.,

$$\text{clay]-Na}^+ + \text{K}^+ \rightleftharpoons \text{clay]-K}^+ + \text{Na}^+$$

In spite of this reversibility, the phyllosilicate minerals exhibit a relative order of preference for the different cations, which decreases as follows: $A1^{3+} > Ba^{2+} > Ca^{2+} > K^+ > Mg^{2+} > Na^+ > Li^+$. The more highly charged ions are more tightly held, and of those of equal valence, the ions with smaller hydrated radii are more tightly held. Some cation retention reactions are irreversible; for example, vermiculite will fix K^+ and NH_4^+ and prevent or greatly reduce ion exchange of these cations with other mono- or di-valent cations (Greenland and Hayes, 1981). The fixation is attributable to the high permanent charge and site of charge deficit (Si tetrahedral layer) of vermiculite (see discussions of clay minerals) and the ability of K^+ and NH_4^+ to dehydrate and key into the surface of the mineral. These fixation reactions strongly influence the availability of the essential plant nutrients N and K to plants growing in some soils.

>Soils may be either acid or alkaline. (Acid soils usually have appreciable quantities of Al^{3+} (and sometimes Mn^{2+}) on the ion-exchange complex. Alkaline soils and calcareous soils are dominated by the presence of exchangeable Ca^{2+}, Mg^{2+} and Na^+. The exchange ion composition may influence soil properties in several ways. Aluminum and Mn are toxic to plants in some situations; also, A^{3+} is an acidic buffer that may control the pH of a soil and hence influence the charge properties and binding properties of soil colloids. The exchange cation composition will also influence the flocculation and dispersion of soil colloids, as discussed below. The soil chemists can evaluate the exchange ion composition of a soil by extraction with an indifferent electrolyte, such as $NH_4C_2H_3O_2$ or $BaCl_2$, and subsequent analysis of the extract by atomic absorption spectroscopy.

Oxides

Iron, Mn and Al oxides are characterized by a variable surface charge and by an ability to specifically adsorb certain anions and cations (Mott, 1981; Theng, 1980; Sposito, 1984; Sposito, 1989) Examples of these reactions are:

$$\text{Fe Oxide-OH}_2 + \text{HPO}_4^{2-} \rightleftharpoons \text{Fe Oxide-O-PO}_2(\text{OH})]^{2-} + \text{H}_2\text{O}$$

$$\text{Fe Oxide-OH} + \text{Zn}(\text{H}_2\text{O})_n^{2+} \rightleftharpoons \text{Fe Oxide-O-Zn}(\text{H}_2\text{O})_{n-1}]^+ + \text{H}_2\text{O} + \text{H}^+$$

The surface charge of these minerals is determined by the adsorption of H^+ and OH^-, which is influenced by the pH of the surrounding solution, and by the specific adsorption of cationic or anionic species such as those shown above. The relative affinities of the different metal oxides for metals in the environment follow the approximate order (McBride, 1989):

- amorphous Fe hydroxide:

$$Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+} > Sr^{2+} > Mg^{2+}$$

- Al hydroxide:

$$Cu^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+} > Mg^{2+} > Sr^{2+}$$

- silanol group of silica:

$$Pb^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+} = Cd^{2+} > Sr^{2+} > Mg^{2+}$$

Even though oxides are usually present in the soil in low concentrations, they have a dominating influence on retention of anions and trace metals in the soil.

Carbonates

The solid phase carbonates, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), which occur predominantly in the fine-silt and coarse-clay fractions, also exert a significant influence on soil properties, due to their alkalinity, pH buffering properties and high surface reactivity. Soils that contain solid-phase carbonates usually have pH values which are buffered between pH 7.5 to 8.5. Carbonates also play an important role in phosphate adsorption and movement, and the retention of certain trace metals including Ba, Cd, Cu, Fe, Mn, Ni, Pb, Sr and Zn. The trace metals may exist either as a solid solution, in which the metal ion replaces Ca or Mg in the carbonate structure, or as a separate occluded mineral phase which is physically associated with the carbonate mineral.

Organic composition and properties

Organic matter in the soil originates from natural plant, animal and microbial biomass and from man-made chemicals such as pesticides, hydrocarbons, plastics and industrial by-products. The components of soil organic matter range from living biomass to simple organic molecules (such as organic acids, amino acids and carbohydrates) to complex polymers (humic and fulvic acids) resulting from the decomposition of plant and animal materials in the soil (Stevenson, 1994). The procedures utilized by soil chemists to investigate the composition and structures of organic matter in the soil include nuclear magnetic resonance spectroscopy, infrared spectroscopy, mass spectrometry, liquid chromatography, elemental analyses and functional group analyses. Even though organic matter is usually present in relatively low concentrations (1 to 5% in most mineral soils), it has a strong influence on soil properties due to its high surface area and high concentration of reactive sites. Soil organic matter, especially the humic and fulvic components, has a high concentration of carboxyl (COOH) and phenolic hydroxyl groups. These groups are important because of their pH-dependent negative-charge character, which influences cation-exchange reactions in the soil, and their ability to specifically bind certain metal cations. The ability of organic matter to bind metal cations decreases according to the following approximate order (Stevenson, 1994): Cu > Ni > Co > Zn > Fe > Mn > Ca > Mg. Organic matter also contains positive charge sites, attributable predominantly to NH_2 and aromatic NH groups. Soil humic acid also has a significant hydrophobic character, which is attributable to aliphatic hydrocarbon chains in the humic structure. These hydrophobic binding sites strongly influence the retention of pesticides, hydrocarbons and organic industrial by-products in the soil (Sawhney and Brown, 1989).

Particle-particle interactions

Because of their charge and adsorption properties the individual particles within the soil interact with each other as well as with ions and molecules in the soil solution (Van Olphen, 1991; Singh and Uehara, 1986). These reactions influence the flocculation and dispersion of individual soil particles and the pore structure of soils. A commonly observed situation is one in which montmorillonite is a dominant mineral component and the soil contains a high proportion of exchangeable Na. Under these conditions, which favor an extended diffuse double layer at the external surfaces of the clay particles, the soil clay can in some cases disperse to such an extent that soil pores are plugged and water movement is prevented or greatly retarded. The use of high Na irrigation water may result in this phenomenon (Levy, 1984). Particle-particle interactions also influence the crusting of soils or the formation of impermeable soil layers. An important aspect of soil chemistry is the study of how particles interact within the soil framework, as well as the application of chemistry to the reclamation of Na-affected, compacted or impermeable soils.

Organic matter in the soil is often found to be intimately associated with the soil mineral components due to the active binding sites in both classes of compounds. Mineral and organic matter can interact directly through charge sites or H-bonding sites or may interact via a cation bridge:

$$\text{Clay]}^- \ M^+ \ {}^-\text{OOC-R}$$

Organic matter also is the major storehouse of nitrogen in the soil and therefore plays a major role in the availability of this essential nutrient to the plant.

Liquid phase

The liquid and gas phases occupy the pore space not occupied by the solid phase. The relative proportion of liquid to gas is variable and is dependent on environmental factors such as rainfall. The liquid phase contains dissolved organic (e.g., simple organic acids, simple carbohydrates, plant exudates, fulvic acid) and inorganic components (e.g., Ca, Mg, Na, K, Cl, SO_4, NO_3). The concentrations of inorganic species are influenced to a large extent by equilibrium relations with the solid phase and adsorbed components (Lindsay, 2001; Sposito, 1981). The principles of thermodynamics and chemical equilibrium allow the prediction of soil-solution composition. Sometimes the theoretical predictions of soil-solution composition will agree with the actual solution composition, but at other times the predicted values will differ substantially from actual values, sometimes by many orders of magnitude. Studies of these equilibrium and disequilibrium relationships represent an important aspect of soil chemistry.

The concentrations of dissolved organic components, and hence of inorganic components that are complexed by the organic components, may be considerably high at the soil-root interface than in the bulk soil, due to the exudation of organic compounds by the plant root. The composition of the soil solution is very different in the vicinity of the plant root (the rhizosphere) than in the bulk soil.

In all cases, the solution phase is in dynamic equilibrium with solid and adsorbed phases. There is considerable interest in the composition of the soil solution phase, since the individual species within this phase arc highly mobile and available for uptake by plants and microorganisms. Also, there is considerable interest in the development of models, which describe the equilibrium relations between solid and solution phases. Samples of the bulk soil solution are usually obtained by either vacuum or pressure extraction or displacement with an immiscible solvent. The solution may then be analyzed by procedures such as those detailed by Sparks et al. (1996): atomic absorption and flame emission spectometry, inductively coupled plasma emission spectometry, neutron activation analysis, X-ray fluorescence spactroscopy, liquid chromatography, differential pulse voltametry, infrared and Raman spectroscopy, electron spin resonance spectroscopy, X-ray photoelectron spectroscopy and X-ray absorption fine structure spectroscopy; as well as by traditional wet chemical procedures (Weaver, 1994). The analysis of rhizosphere solution concentrations remains a very difficult problem.

Gas phase

Since the respiration of plant roots and soil microorganisms results in the consumption of O_2 and the production of CO_2, O_2 concentration of the soil is lower and CO_2 concentration is higher than that of the above ground atmosphere. The depletion of oxygen within the soil will result in a lowering of soil redox potential, which controls the form and concentrations of multi-valent chemical species, such as Fe^{3+}/Fe^{2+} and Mn^{4+}/Mn^{2+} (Sposito, 1981; Sposito, 1989). For example, low redox potentials can result in the transformation of Mn^{4+} to Mn^{2+} and an increased solubility of Mn to a concentration that may be toxic to plants. The rate of replacement of depleted oxygen to the soil is strongly influenced by soil water relations, since diffusion of CO_2 out of the soil and O_2 into the soil are considerably more rapid in the gas phase than in the liquid phase. Low redox potentials are usually associated with flooded and waterlogged soils.

Solid-solution interface

A schematic representation of the inorganic hydroxyl surface as may occur on the Fe or Al oxide is shown in Figure S24 (Sposito, 1984). The coordination spheres of the surface structural cations are completed by either OH or OH_2 groups (layer s). Some cationic and anionic species (ligands) can compete with the surface OH or OH_2 groups to form inner-sphere complexes (layer a) at the oxide surface. In this case the ligand is coordinated directly to the surface structural cation, and the hydration spheres of both the surface structural cation and the ligand are disrupted. The formation of inner sphere

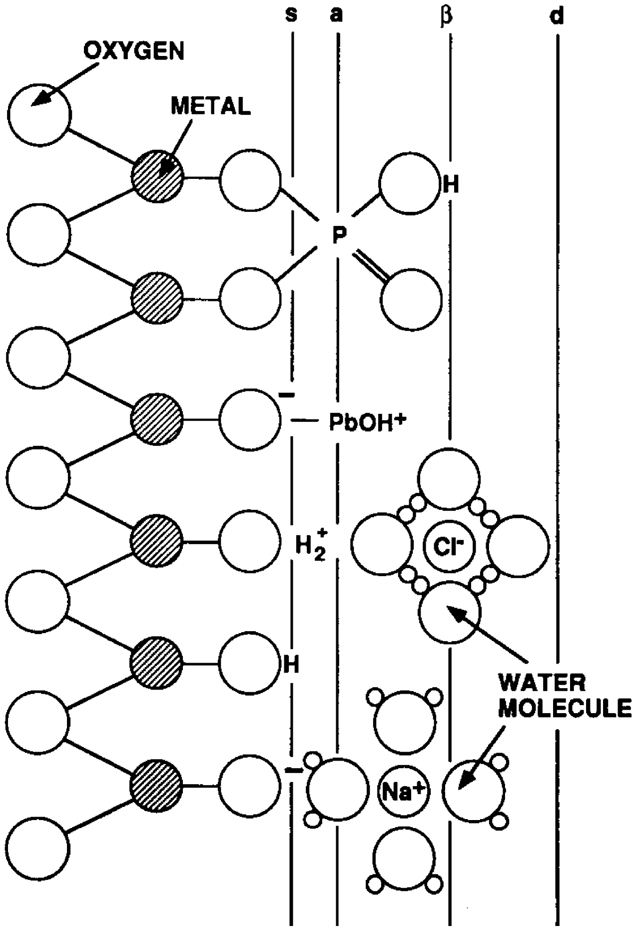


Figure S24 A schematic representation of an inorganic metal hydroxide surface, with surface OH and OH_2 groups (layer *s*), inner-sphere complexes (layer *a*), outer-sphere complexes (layer *β*) and diffuse ions (layer *d*) (Sposito, 1984).

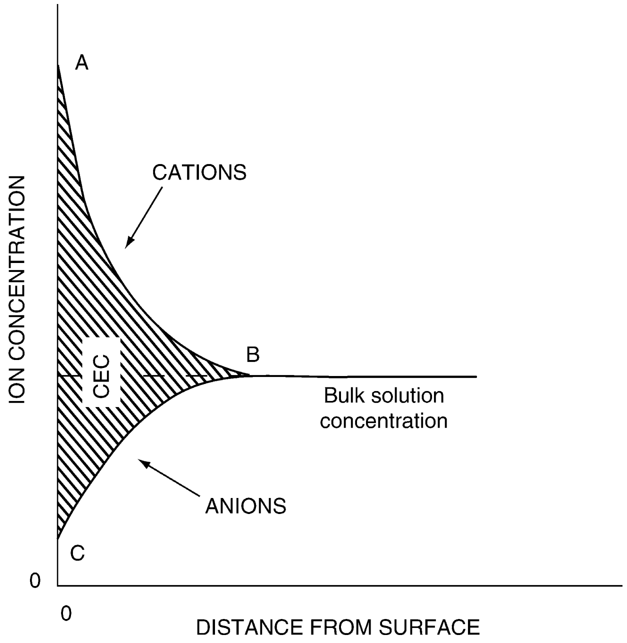


Figure S25 The distribution of cations and anions of a symmetrical electrolyte in the diffuse counter-ion layer of a negatively charged surface, as a function of distance from the surface. Cations are attracted to the surface, and anions are repelled from the surface. At an infinite distance from the surface, i.e., in the bulk solution, the concentration of cation and anion are equal. The area represented by the area *ABC* is equal in magnitude but opposite in sign to the cation-exchange capacity.

complexes has been corroborated by infrared and electron paramagnetic resonance spectroscopy (Mott, 1981). This mode of bonding is especially important with phosphate and controls the retention, mobility and bioavailability of phosphate in many soils. Phosphate will form a binuclear bridging complex with the Fe oxide surface, in which the phosphate ligand is bound to two adjacent surface structural Fe atoms (Mott, 1981). Other examples of inner sphere complexes are complexes between vermiculite and K^+; between Pb^{2+} and alumina; and, between Cu^{2+} and COOH groups of organic matter (Mott, 1981; Sposito, 1984; Sposito, 1989).

In other cases, a ligand may be bound as an outer-sphere complex (layer β), in which case the hydration sphere of the ligand is maintained. There is evidence that in some cases, this type of complex may influence the protonation of surface OH groups and hence the surface charge attributable to the surface OH layer (Singh and Uehara, 1986). Examples of outer-sphere complexes include surface complexes between Ca^{2+} and montmorillonite; between Na^+ and kaolinite; between Cl^- and the protonated aluminol group; between Mn^{2+} and the COOH group of organic matter.

Still other ions are adsorbed by the surface but have sufficient kinetic energy to diffuse some distance from the surface (diffuse layer ions, d layer). The position of the ion is defined by the competing forces of electrostatic attraction and diffusion (Bolt and Bruggenwert, 1976; Van Olphen, 1991; Bolt, 1982; Sposito, 1984; Singh and Uehara, 1986). The distribution of ions with distance from the clay surface (Figure S25) is analogous to the distribution of air with distance from the Earth's surface, which in the latter case is defined by the competing forces of gravity and diffusion.

The components of charge at the surface/solution interface are defined by the following equation (Sposito, 1984; Sposito, 1989):

$$\sigma_0 + \sigma_H + \sigma_{is} + \sigma_{os} + \sigma_D = 0$$

where:

- σ_0 = permanent structural surface charge density
- σ_H = net charge density attributable to OH and OH_2 at the hydroxylated surface
- σ_{is} = net total charge of the ions, other than H^+ and OH^-, which have formed inner-sphere complexes with the surface functional groups
- σ_{os} = net total surface charge of the ions that have formed outer-sphere complexes with the surface functional groups (non-specific adsorption)
- σ_D = net charge density of ions in the diffuse layer

Each of the terms in the above equation may be either positive or negative, but the total net charge of the particle and surroundings must equal 0.

General methodological approaches to studying reactions across phase boundaries

One of the goals of the soil chemist is to understand the reactions that occur across phase boundaries. The processes of precipitation/dissolution and sorption/desorption across the solid-solution boundary are of particular interest because they influence the availability or immobilization of plant nutrients and the mobilization and movement of potential pollutants (Greenland and Hayes, 1981; Sposito, 1984; Sposito, 1989). These reactions are studied by soil chemists in either batch or column systems. In a batch system, a given quantity of reactant is added to an aqueous suspension of the soil. Following a preset reaction time, the solution is analyzed by an appropriate spectroscopic or wet chemical procedure to determine the quantity of reactant remaining in solution and hence the quantity of reactant retained by the solid phase (Weaver, 1994). Equilibrium relationships of the reactant between solution and solid phase can then be evaluated (Sposito, 1981). A series of reactant concentrations can be used to determine the adsorption maximum or to obtain an adsorption isotherm (Mott, 1981). Desorption or dissolution reactions can by studied by procedures similar to those described above.

Sometimes a chemical reaction is evaluated along a time sequence to determine the rate (or kinetics) of a particular adsorption/desorption or dissolution/precipitation process (Sparks, 1989). The evaluation of kinetic processes is an important aspect of soil chemistry because both the uptake of plant nutrients and the mobilization and retention of pollutants are strongly influenced by soil kinetic processes.

In column studies, the reactant is passed through a disturbed or undisturbed soil column (sometimes in the field), and the column eluent is analyzed to determine the kinetics or equilibrium of sorption and the movement of a particular chemical in a soil. Batch and column studies often give very different results, since results in column studies are strongly influenced soil pore distribution, particle aggregation, soil structure, and associated diffusion processes. The choice of batch versus column studies is dictated by whether the researcher's primary interest is in reactions at the particle surface or in reactions in the 3-dimensional soil matrix.

There is also considerable interest in molecular mechanisms of bonding of adsorbents. These reactions are studied by procedures such as infrared spectroscopy, nuclear magnetic resonance spectroscopy, electron paramagnetic resonance spectroscopy and X-ray absorption spectroscopy, as well as by adsorption studies, as discussed above (Stucki and Banwart, 1980; Mott, 1981).

Conclusions

The soil is an extremely complex and heterogeneous chemical system to which the principles and procedures of pure chemistry are used to solve applied environmental, fertility and land resource problems. The science has advanced at a rapid rate along with the advances in pure chemistry, physics and biology, and will undoubtedly continue to do so.

Richard H. Loeppert

Bibliography

Bohn, H.L., McNeal, B.L., and O'Connor, G.A., 2001. *Soil chemistry*, 3rd edn. New York: Wiley, 307 pp.

Bolt, G.H., ed., 1982. *Soil Chemistry.* Part B: Physico-Chemical Models. Amsterdam: Elsevier, p. 479.

Bolt, G.H., and Bruggenwert, G.H.M., eds., 1976. Soil Chemistry. Part A: Basic Elements. Amsterdam: Elsevier, p. 281.

Dixon, J.B., and Schulze, D.G., 2002. *Soil Mineralogy with Environmental Applications*. Madison, WI: Soil Science Society of America, 866 pp.

Gieseking, J.E., 1975. *Soil Components. Vol. 2: Inorganic Components.* New York: Springer.

Greenland, D.J., and Hayes, M.H.B., eds., 1978. *The Chemistry of Soil Constituents.* Chichester: Wiley, p. 469.

Greenland, D.J., and Hayes, M.H.B., eds., 1981. *The Chemistry of Soil Processes.* Chichester: Wiley, p. 714.

Levy, R., ed., 1984. *Chemistry of Irrigated Soils.* New York: Van Nostrand Reinhold, 418 pp.

Lindsay, W.L., 2001. *Chemical Equilibria in Soils.* Caldwell, N.J.: Blackburn Press, 449 pp.

McBride, M.B., 1989. Reactions controlling heavy metal solubility in soils. *Adv. Soil Sci.*, **10**: 1–56.

Mott, C.J.B., 1981. Anion and ligand exchange. In Greenland, D.J., and Hayes, M.H.B., eds., *The Chemistry of Soil Processes.* Chichester: Wiley, pp. 179–219.

Sawhney, B.L., and Brown, K., 1989. *Reactions and Movement of Organic Chemicals in Soils.* Madison, WI: Soil Science Society of America, p. 474.

Singh, U., and Uehara, G., 1986. Electrochemistry of the double layer: principles and applications to soils. In Sparks, D.L., ed., *Soil Physical Chemistry.* Boca Raton, FL: CRC Press, pp. 1–38.

Sparks, D.L., 1989. *Kinetics of Soil Chemical Processes.* San Diego, CA: Academic Press, p. 210.

Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., and Sumner, M.E., (eds), 1996. *Methods of Soil Analysis, Part 3: Chemical Methods*. Madison, WI: Soil Science Society of America, American Society of Agronomy. 1390 pp.

Sposito, G., 1981. *The Thermodynamics of Soil Solutions.* New York: Oxford University Press,

Sposito, G., 1984. *The surface Chemistry of Soils.* New York: Oxford University Press, p. 234.

Sposito, G., 1989. *The Chemistry of Soils.* New York: Oxford University Press, p. 277.

Stevenson, F.J., 1994. *Humus Chemistry: Genesis, Composition, Reactions*, 2nd edn. New York: Wiley, 496 pp.

Stucki, J.W., 1988. Structural iron in smectites. In Stucki, J.W., Goodman, B.A., and Schwertmann, U., eds., *Iron in Soil and Clav Minerals.* Dordrecht: Reidel, pp. 625–675.

Stucki, J.W., and Banwart, W.L., eds., 1980. *Advanced Chemical Methods for Soil and Clay Minerals Research.* Dordrecht: Reidel, p. 477.

Theng, B.K.G., ed., 1980. *Soils with Variable Charge.* Lower Hutt: New Zealand Society of Soil Science. 111 pp.

Van Olphen, H., 1991. *An Introduction to Clay Colloid Chemistry: For Clay Technologists, Geologists and Soil Scientists*, 2nd edn. Malabar, FL.: Krieger Pub. Co., 318 pp.

Weaver, R. W., ed., 1994. *Methods of Soil Analysis.* Part 2. Microbiological and Biochemical Properties. Madison, WIsconsin: Soil Science Society of America, 1121 p.

SOIL COLOR

Color is one of the most obvious soil characteristics. Changes in soil color across a field surface or with depth below the surface are likely to catch the eye before anything else. Such changes may be abrupt; for example, black to gray or yellow to red. Color is a passive soil property – that is, it is a consequence of soil-forming processes and not an agent affecting soil behavior. Nevertheless, several inferences can be made as a result of observing the color of the soil. These inferences may be important in the use and management of soils.

Causes of soil color

Both organic and inorganic materials, separately or in combination determine soil color. Organic matter is largely accountable for the brown and black colors observed in the topsoil. Organic matter varies in its content and stage of decomposition; thus, one must exercise caution when attempting to correlate soil "blackness" with organic matter content. For example, undecomposed raw peat is brown whereas the stable decomposed organic matter, humus, is black or nearly so.

The inorganic compounds that contribute to soil color are principally iron and manganese oxides. Iron oxides occur in all colors ranging from yellow at the one extreme to red at the other. Thus, many brown soils contain relatively large amounts of iron oxides in addition to organic matter. The red color of soils is generally related to unhydrated iron oxide although manganese dioxide may also contribute to the red color. The yellow color in soils is also largely due to iron oxides. The range of colors from red to yellow appears to be related to the degree of hydration of the iron oxide minerals.

Soils may also owe their color to the nature of the parent material in addition to or in place of soil-forming processes. For example, minerals like quartz, kaolin and other clay minerals or carbonates of lime and magnesium often cause gray and whitish colors of soils. Even many of the red soils owe their color to iron oxides present in the parent material (for example red-beds sandstones) and not to soil-forming processes.

Soils with a fluctuating water table exhibit colors due to the persistence of water in the environment. Imperfectly and poorly drained soils are nearly always mottled with various shades of gray, brown and yellow. Where a high water table persists in the presence of large amounts of ferrous iron, soils may appear bluish in color.

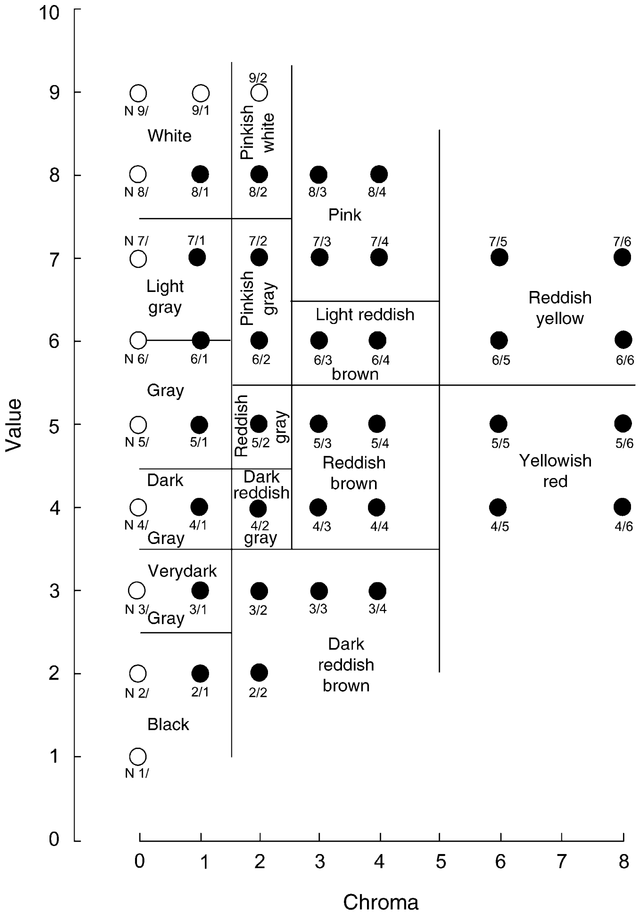


Figure S26 Soil color names for several combinations of value and chroma and hue SYR.

Expression of soil color

Soil colors are most conveniently expressed by comparison with a color chart. The one generally used with soil is a modification of the Munsell color chart, which consists of some 175 different colored chips. The color chips are arranged by hue, value and chroma, the three simple variables that combine to give all colors. Hue is the dominant spectral (rainbow) color. It is related to the dominant wavelength of the light. Value refers to the relative lightness of color and is a function (approximately the square root) of the total amount of light. Chroma is the relative purity or strength of the spectral color.

In the soil color chart all colors on a given card are of a constant hue (Figure S26). Vertically, the value increases as the colors become successively lighter. Horizontally, they increase in chroma to the right. The value and chroma of each color in the chart is printed immediately beneath the color (Figure S26).

The symbol for hue is the letter abbreviation of the color of the rainbow: for example, 'R' for red; 'YR' for yellow-red; 'Y' for yellow. A number from 0–10 precedes the symbol. Within each letter the hue becomes more yellow and less red as the numbers increase. The middle of the letter range is at 5, thus 5YR is in the middle of the yellow-red hue, which extends from 10R to 10YR.

The notation for value consists of numbers from '0' for absolute black to '10' for absolute white. Thus, a color of value '5' is visually midway between absolute white and absolute black. The notation for chroma consists of numbers beginning at '0' for neutral grays and increasing at equal intervals to a maximum of about 8.

In writing the Munsell notation, the order is hue, value, chroma, with a space between the hue letter and the succeeding value number, and a virgule between the two numbers for value and chroma. Thus, the notation for a color of hue '5YR', value '5', chroma '6' is 5YR 5/6 (yellowish-red).

Soil color changes with the moisture content and this is evident in the Munsell color notation. The effect of moisture on color is a phenomenon of the light and is particularly pronounced in soils having low contents of organic matter. Thus, it is often desirable to record Munsell notations on soils in both air dry and moist conditions. Official descriptions for technical use, such as soil series descriptions, should include the moist colors and preferably both dry and moist colors if they are significantly different.

Implications of soil color

Color is particularly useful for making several meaningful predictions about soil conditions. It is an indicator of mineral weathering, the amount and distribution of organic matter and the state of aeration. Thus, soil color is one of several tools used in evaluating the suitability of a given soil for various uses and determining the kinds of soil modifications that need to be applied.

Colors such as red, yellow and reddish-brown are related to well oxidized conditions, which exist when aeration is good. Gray colors predominate in reduced conditions where oxygen is deficient. Poor aeration results when pores remain waterfilled for long periods of time. When this occurs, the chemically reduced forms of iron and manganese impart grayish or bluish colorations to the soil, a condition referred to as gleying. If poor aeration due to excess water is intermittent, iron and manganese that are soluble during the wetter part of the year tend to oxidize during periods of improved aeration and precipitate as more brightly colored oxide coatings over other mineral grains. These coatings frequently appear as red, yellow or brown splotches called mottles. Soils exhibiting gleying and/or mottling usually are inadequately drained for crop growth. Thus, these conditions are often used as field criteria for installing a drainage system. The presence of these stains is a clear indication that the soil is probably waterlogged during at least part of the year and should therefore be avoided as a site for dwellings or other structures with basements, or for septic tanks used for on-site sewage disposal.

There is a definite interrelationship between soil color and soil temperature. Color is one of the influences on the absorption/reflectance of solar radiation in any particular region. Dark soils will absorb more energy than light colored ones. Studies have shown that a difference of as much as 8° centigrade may occur between black surfaces and white surfaces. Red and yellow soils will show a more rapid temperature rise than white ones. Dark soils are warmer during the warm parts of the year. Daily variations in temperature are greater with dark soils. The loss of heat during the night under the darker colors and temperatures between darker and light colored soils are smaller with increasing depth. It is important to keep in mind that those properties, which are responsible for rapid absorption of heat during the day by dark colored objects, also cause rapid emission of heat during the night. Since dark soils absorb more heat from the sun than colored soils, they also lose more water through evaporation and gain more water through condensation at night. It should not be concluded that dark soils are always warmer, though. Actually, the opposite may be true since dark soils usually are higher in organic matter and consequently hold large amounts of water, which warms at a slower rate than the soil solids.

Maurice G. Cook

Bibliography

Baver, L.D., Gardner, W.H., and Gardner, W.R., 1972. *Soil Physics*, 3rd edn. New York: Wiley, 498 pp.

Brady, N.C., and Weil, R.R., 2004. *Elements of the Nature and Properties of Soils.* Upper Saddle River, NJ: Prentice-Hall, 606pp.

Hausenbuiller, R.L., 1985. *Soil Science: Principles and Practice*, 3rd edn. Dubuque, IA: William C. Brown Co., 610 pp.

Staff, Soils conservation Service, USDA, 1996. *Keys to Soil Taxonomy.* Washington, DC: U.S. Government Printing Office, 644 pp.

Cross-references

Carbon Sequestration in Soil
Classification of soils: Soil Taxonomy
Humic Substances
Iron Oxides
Soil
Soil Processes
Soil Variation
Soil Water

SOIL COMPONENTS, ORGANIC

See *Humic substances*; *Carbon sequestration in soil*.

SOIL CONSERVATION SERVICE

See *Conservation*.

SOIL DRAINAGE

Soil drainage is the removal of excess water from the land by artificial or man-made facilities (Fangmeir et al., 2006). Most natural drainage occurs because of land forms and elevation differences that result from geologic erosion. All natural drainage is by gravity flow, even artesian water that moves upward to the land surface. Runoff is a more common term for drainage over the land surface, and seepage or groundwater flow are terms often applied to drainage below the land surface Skaggs and van Schilfgaarde (1999).

Man has improved on nature's drainage systems in order to construct buildings, highways, and other facilities; to improve the growth of more desirable vegetation; and to improve the environment for man, animals, and other organisms. Agricultural soil drainage enhances plant growth by increasing soil aeration and by removing toxic materials such as salts, which impair plant growth. Toxic salts accumulate near the surface in the more arid regions, and when such land is irrigated, either these salts must be removed or chemical amendments must be added to the soil. The most practical method of salt removal is irrigating and draining the excess water from the soil (Schwab et al., 1996). Some drainage method must eventually be provided, either natural or man-made, for leaching irrigated soil. The construction of a suitable drainage system may involve both extensive surface and subsurface drains.

The computed flow rate in an open channel or in a subsurface tube drain with gravity flow is the product of the average velocity and the cross-sectional flow area (Sturm, 2001). The Manning Equation is most commonly used to estimate average velocity. This velocity varies inversely with the roughness of the channel or tube and with the two-thirds power of the length of the wetted surface of the cross-section. It also varies directly with the two-thirds power of the cross-sectional area and with the square root of the hydraulic slope.

Surface drainage

In agricultural land, surface drainage is accomplished by a combination of open ditches, shallow field drains, and land grading.

Open ditches should be built so that neither scouring nor sedimentation will occur, with sufficient flow capacity, with adequate depth, and with stable side slopes. They should have minimum initial cost and minimum long-term maintenance. Figure S27 shows a typical crosssection. Flow capacity will vary with different climatic regions and with the drainage needs of the crop to be grown.

Most big drainage ditches in the USA have been constructed under state laws enacted to facilitate drainage where several landowners are involved. Under such laws the construction and maintenance costs can be equitably distributed to the benefited landowners. Large ditches normally drain too much area and are too costly for a few owners to undertake individually. Regrowth of shrubs and trees in the channel causes reduced flow and is one of the major maintenance problems. In legal organized districts, the trend is toward annual maintenance assessments to assure continued proper functioning of the ditches.

Shallow field drains and land grading are often required in flat or undulating land to improve the flow to the open ditches. Small areas that are flooded even for a day or so may kill young plants or reduce crop yields appreciably. These fields drains may connect several low-lying areas in a random pattern or they may consist of parallel drains at uniform or variable spacing. Between these drains additional surface grading may be necessary to remove shallow water that accumulates on the surface. Such grading may also be required for removal of small ridges or furrows produced by normal tillage equipment. In irrigated areas, land grading is called *leveling*, but for some irrigation, the land is truly leveled as in a flooding system.

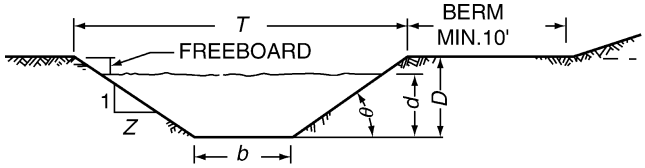


Figure S27 Typical ditch cross-section.

Shallow drains are often constructed with pan scrapers, blade graders, bulldozers, or similar equipment. Lazer-beam equipment for grade control is commercially available and is capable of greater accuracy than operator-controlled machines (Schwab et al., 1996). The system of grade control is the same as for subsurface drains shown in Figure S28.

Subsurface drainage

Subsurface drainage is required in agricultural land to lower the water table. Removing the excess groundwater permits oxygen and carbon dioxide gases to move into and out of the soil, increases the length of the crop growing season by early tillage and planting, removes toxic substances that may retard plant growth and increases the available water-storage capacity of the soil. Drainage of highways and buildings increase the structural bearing capacity of the soil by reducing the moisture content. Flow of water through the soil can be predicted by Darcy's Law, which states that the flow rate is proportional to the soil hydraulic conductivity and the gradient of the flow. For one-dimensional flow, this law can be easily applied, but for subsurface drains the flow is three-dimensional, and the flow region is not well defined. The geometry of the drains, varying soil characteristics, and complex boundary conditions greatly complicate mathematical flow equations and horizontal spacing equations for parallel drains.

Subsurface drains are constructed primarily with clay tile, concrete tile, and corrugated plastic tubing (Fangmeier et al., 2006). Figure S29 illustrates some common types of drain materials and openings. In the early days before such materials were available, drains were made by placing tree limbs, sand or gravel, rocks, and other natural porous material in the bottom of a covered trench. In some special soil and climatic conditions in humid areas *mole drains* (Ede, 1961) were successful. The mole channel was made by pulling a plug through the soil. It was attached to the bottom of a narrow vertical steel blade designed to keep the plow in the soil. Such drains rely entirely

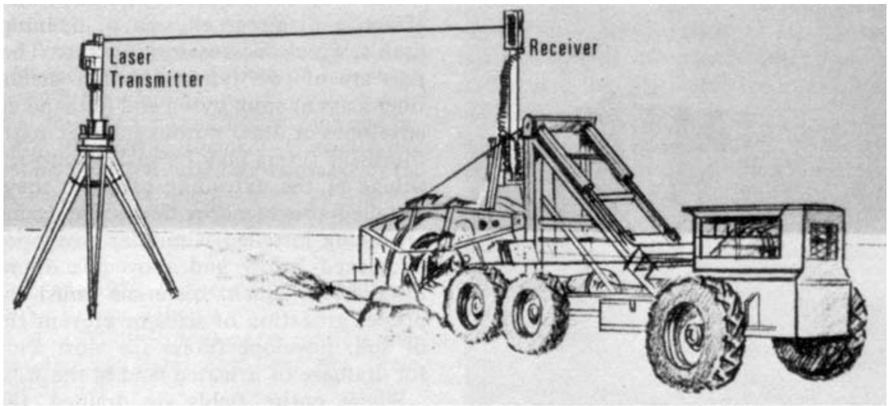


Figure S28 Laser-grade controlled trencher (photo: U.S. Department of Agriculture, Agricultural Research Service).

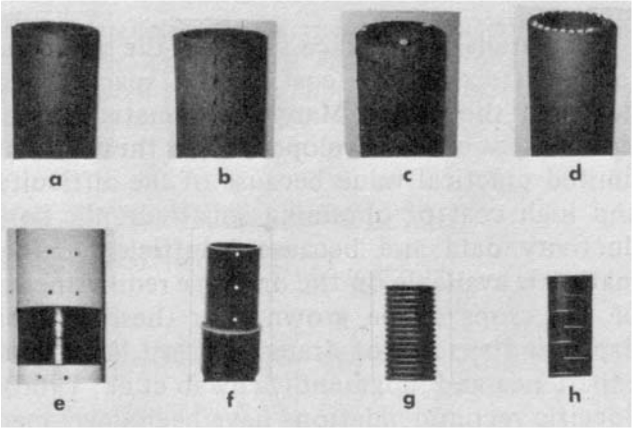


Figure S29 Common types of drain materials and openings; (a) clay tile with 16$^{5}/_{16}$-inch holes per foot in 4 rows; (b) clay tile with 36$^{3}/_{16}$-inch holes per foot in 3 rows; (c) concrete tile with 3 spacer projections on one end, $^{3}/_{32}$-inch joint spacing; (d) clay tile with corrugated ends, $^{1}/_{16}$-inch joint spacing; (e) asbestos cement pipe with 16$^{5}/_{16}$-inch holes per foot in 4 rows; (f) bituminous fiber pipe with 16¼-inch holes per foot in 4 rows; (g) corrugated plastic pipe with 18$^{1}/_{16}$-inch by 1-inch slits per foot in 3 rows; and (h) smooth plastic pipe with 15$^{1}/_{32}$-inch by 1½-inch slits per foot.

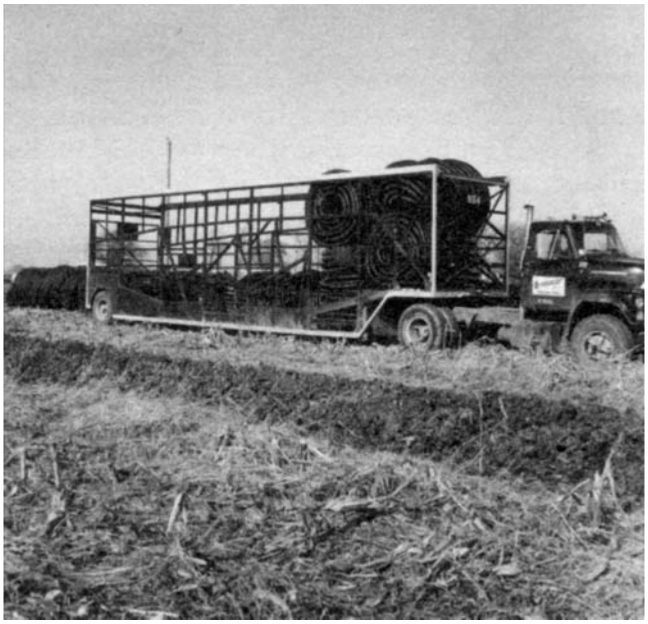


Figure S30 Four-inch corrugated plastic tubing and modern transport method.

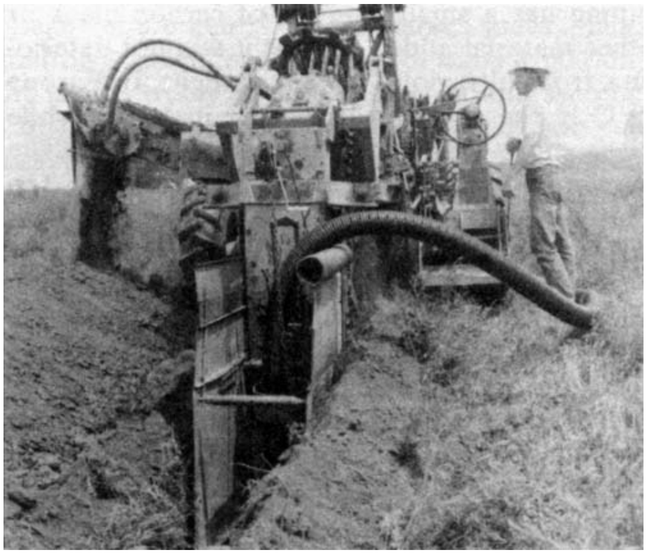


Figure S31 Modern trenching machine installing 4-inch corrugated plastic tubing in Ohio.

on the natural stability of soil to maintain its shape. Although they function for only a few years, mole drainage is still a common practice, primarily in Great Britain and New Zealand.

Clay drain tile (Alpers and Short, 1965) are made from surface clay or shale, which is pulverized, extruded through a die, dried, and then burned in a kiln. Some early clay tile were made on a potter's wheel, while others were shaped from a flat slab of clay into a horseshoe shape. Clay tile are not affected by acid or alkaline soils, but those made from surface clay or poorly burned tile are subject to deterioration by freezing and thawing action. In general, tile installed more than 2 ft (60 cm) in depth are not affected by frost action. Many tile over 100 years old have been found. Good quality tile should last indefinitely in the soil.

Concrete tile, made from sand and gravel aggregate, is generally formed on a packerhead machine and then steam- or water-cured to obtain the desired strength (Manson, 1971). Concrete tile are resistant to freezing and thawing but may be subject to deterioration in acid and alkaline soils. For these soils the tile should be made with cement having special chemical characteristics.

Since the 1960s *thermoplastic tubing* (Figure S30) has become a common drain material (Fouss, 1974). The development of corrugating machines in Germany was largely responsible for the rapid expansion of plastic tubing. High-density polyethylene (PE) and polyvinylchloride (PVC) are the two most common plastics. PE tubing has a small amount of carbon black or other material added so that it will not deteriorate from ultraviolet rays in sunlight. In Europe PVC is the most widely used material, while PE is more common in the United States. The maximum size produced commercially in the United States is 457 mm (18 inch) diameter. Corrugated plastic tubing, unlike concrete or clay tile, is a flexible material and will deflect vertically when soil is backfilled in the trench (Figure S31). As it deflects, the sides of the tubing move outward horizontally into the surrounding soil. The circular tubing changes to a slight oval shape, which becomes stabilized because the soil on the sides of the tubing resists the outward movement.

Corrugations in the tubing provide sufficient stiffness to resist the initial soil load. They also reduce the amount of plastic required to make the tubing as well as provide flexibility, which permits the smaller-size tubing to be coiled into a compact package.

Corrugated plastic tubing weighs only 1/25 of concrete or clay tile, resists practically all soil chemicals, and can be installed in a continuous length (saves labor). Its stiffness decreases with increased temperature. Compared to concrete and clay tile, greater care is required in placing soil around plastic tubing because of deflection, and it is more difficult to locate the plastic lines with a steel probe.

Filter materials (Skaggs and van Schilfgaarde, 1999) are sometimes placed around subsurface drains primarily to prevent the inflow of soil into the drains, which may cause failure, and/or to increase the effective diameter or area of openings in the drains, which increases inflow rate. These materials are of two types: (1) thin sheets such as fiber glass or spun nylon and (2) sand and gravel envelopes or other porous granular material. The thin-sheet filters may be sealed onto the plastic tubing at the extruding plant, or they may be installed above and/or below the drains as they are being installed. Granular envelopes should be placed below and above the drains during installation. Such materials must have the proper gradation of sizes to prevent the inflow of soil. Envelope filters are most widely used for drainage of irrigated land in the West.

Where entire fields are drained, the lateral lines are laid out parallel to each other, and a main drain is connected to each lateral at one end to carry the water into an outlet ditch. Where only low wet areas are drained, a system of random lines through the wet spots may suffice. Large systems may include a combination of random and parallel drains laid out so as to best fit the surface topography of the land. Where surface water is to be removed by the subsurface drain, vertical risers are installed to allow the water to enter the buried drain. In some areas where the level of water in the outlet ditch is too high, automatic pumping plants are required. On more sloping land, subsurface drains may be installed to intercept groundwater that causes springs or side-hill seeps. In such cases the drain is placed at the proper depth and location in relation to the seepage area.

For parallel subsurface systems, the principle factor affecting the cost is the spacing and depth of the drains. Many mathematical equations have been developed, but they are of limited practical value because of the difficulty and high cost of obtaining soil hydraulic conductivity data and because insufficient information is available on the drainage requirements of the crops to be grown. For these reasons depth and spacing of drains is based largely on experience and judgment (Schwab et al., 1996). Specific recommendations have been developed in each of the states where drainage is a major problem.

G. O. Schwab

Bibliography

CIGR. 1999. Handbook of Agricultural Engineering: edited by CIGR, the International Commission of Agricultural Engineering. St. Joseph, MI: American Society of Agricultural Engineers. 5 volumes.

Ede, A.N., 1961. Floating-beam mole plough trails, *Farm. Mech.*, **13**(144): 274–275.

Fouss, J.L., 1974. Drain tube materials and installation. In Van Schilfgaarde, J., ed., *Drainage for Agriculture.* Madison, WI: American Society of Agronomy, Monograph, Vol. 17, 147–177.

Manson, P.W., 1971. Specifications for concrete drain tile, *Proc. Am. Soc. Agric. Eng. Conf. Nat. Drain. Symp.*, pp. 29–31.

Fangmeier, D.D., Elliot, W.J., Workman, S.R., Huffman, R.L., and Schwab, G.O., 2006. *Soil and Water Conservation Engineering*, 5th edn. Clifton Park, NY: Thomson Delmar Learning, 502 pp.

Schwab, G.O., Fangmeier, D.D., and Elliot, W.J., 1996. *Soil and Water Management Systems*, 4th ed., New York: Wiley, 371 pp.

Skaggs, R.W., and van Schilfgaarde, J. eds., 1999. *Agricultural Drainage.* Madison, WI: American Society of Agronomy, Monograph 38. 1328 pp.

Sturm, T.W., 2001. *Open Channel Hydraulics*, Vol. xiii. Boston, MA: McGraw-Hill, 493 pp.

Cross-references

Conductivity, Hydraulic
Flow Theory
Irrigation
Leaching
Pudding
Salt Leaching
Water Movement

SOIL ENGINEERING

Soil engineering, in its broad sense, can be defined as the study and description of all kinds of effects exerted on the soil with relation tilling. It involves engineering solutions to the theoretical problems of soil mechanics, changes in the physical properties of the soil under the effect of external forces, and the effect of these properties on biological processes.

Introduction

Under natural conditions, with no human interference, the soil environment is determined by the effect of the plant cover, air, water, climate, and soil organisms. The dynamics of the changes are slow and may stabilize for particular periods of time. On arable soils, human intervention becomes an additional factor. The mechanization of tillage disturbs natural soil processes and initiates a number of biological processes that change the soil environment. Apart from desirable and controlled effects, adverse side effects of tillage may arise. The working parameters of tillage implements should be selected such that the physical, chemical and biological properties of the soil are affected in such a way as to increase crop yield, and to allow any destructive effects to be neutralized naturally or with the help of subsequent tillage treatment. Increase in tillage mechanization result in the soil becoming not only a medium of plant vegetation, but also a running surface for tractors, and other agricultural machines and means of transportation, (Baver et al., 1972; Byszewski et al., 1977; Håkansson et al., 2000; ISTRO, 2002; Marshall et al., 1979; Soane et al., 1994).

Knowledge of the mechanism of soil response to forces applied is necessary to solve the problems of tillage technology, of wheel and implement design, and of the selection of suitable parameters of their movement. Deformation of soil subjected to intensive tillage results primarily in changes in soil physical properties, and an accurate assessment of those changes determines the possibility of controlling the effective productivity of the soil. All forecasts concerning the behavior of the soil consist in determining the fundamental stress-strain relation, in a broad range of values, taking into consideration the great variety of soil material.

Machine-soil

The soil subjected to strain is a crumbled, multiphase, polymineral material, containing organic matter. Under natural conditions it occurs within broad ranges of moisture and temperature values. Every agricultural machine moving over a field causes volumetric and shear strain. Volumetric strain is characterized by an increase in soil density (i.e., compaction) while retaining similarity of every element of the soil (under comprehensive and uniform pressure); shear strain, on the other hand, involves relative displacement of soil layers (shearing).

Mechanical strain affects the development of plants, both directly and indirectly by changing the physical properties of the soil. Volumetric strain, is dominant throughout the whole process and may constitute up to 90 % of the total strain. Its effect is to change the packing of the solid phase of the soil, thereby changing the volume of the soil pores. This phenomenon is accompanied by filtration, primarily of air, and water movement is slow as compared to the duration of the strain. Shear strain may result in a change in the aggregate structure of the solid phase of the soil, as well as in damage to the root systems of plants (Hillel, 1980; Horn et al., 1990, 1994; Gliński et al., 1990; Soane, 1994).

The process of soil compaction represents the relation between changes in density and stress, taking into account moisture content. Stress caused by contemporary tractors is high and depends primarily on their weight, the tyre-soil contact area and the tyre inflation pressure. The level of stress affects the depth of the tyre groove and the variation of density in the soil profile (Figure S32). In practice, loads are applied to the soil surface repeatedly at short intervals (Smith, 1985, 1987; Soane et al., 1980, 1984; Tijink, et al., 1990).

Another significant effect on density changes within the soil profile is that of the speed at which tractor and machine wheels move over the soil. It has been found that an increase in wheel speed results in a decrease in the value and range of the recorded changes in density (Figure S33) (Karczewski, 1978).

Changes in soil density due to variable loads determine other basic physical values directly related to plant development, e.g., penetration resistance. An increase in penetration resistance results in a reduction of the root length per unit surface area. Such a relationship is observed at various depths in the soil profile throughout the vegetation period, which has been confirmed by a detailed study on winter wheat roots.

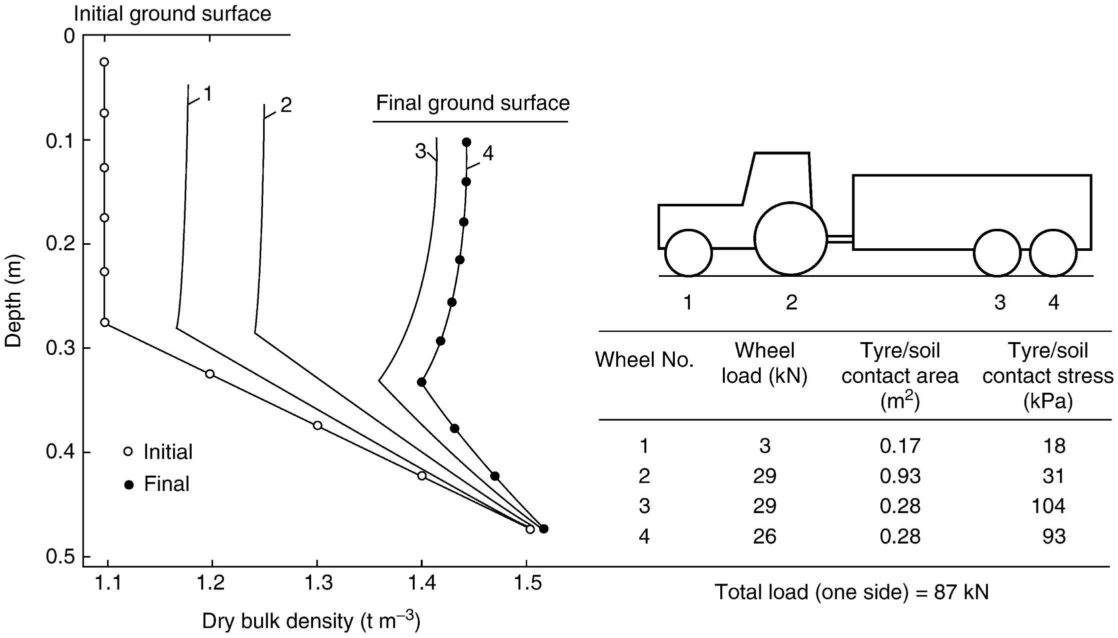
On the basis of numerous result's obtained from field experiments involving various plants and soils, and taking into account the volume of traffic by tractors of various weights, a generally negative effect of the degree of compaction on the crop yield has been established (Figure S34), though there have been instances when the effect was positive. A maximum was observed at a certain range of compaction, which suggests that an increase in crop yield is closely related to the selection of a crop plant suitable for the current physical status of the soil (Håkansson, 1981; Lipiec et al., 2000).

Studies of soil compaction are important not only with relation to the crop yield, but also to the reduction of the costs involved in loosening compacted soil horizons, the compaction extending occasionally down to considerable depths. For example, topsoil to a depth of 30 cm in a typical small plot of 1 hectare weighs no less than 4 000 t, and in a large field of 1 000 ha the mass of topsoil that has to be handled amounts to 4 million t (Hillel, 1980).

Physical properties

Due to rapid changes in external forces acting in the course of soil tillage, accompanied by short periods of application and high strain rates, the problem arises of how to describe the physical properties of the constantly changing soil material which is immediately subjected to subsequent loading.

In the course of soil strain it is primarily the structure of the soil that is subject to change. There are numerous definitions of soil structure, all of which describe the soil as a spatial system of solid phase elements and soil pores (Baver et al., 1972; Bodziony et al., 1993; Kooistra, 1994; Marshall et al., 1979; Niewczas et al., 2003). New micromorphological studies, especially of the changes accompanying various tillage treatments, provide a great amount of information on the structure of



Wheel No.	Wheel load (kN)	Tyre/soil contact area (m^2)	Tyre/soil contact stress (kPa)
1	3	0.17	18
2	29	0.93	31
3	29	0.28	104
4	26	0.28	93

Total load (one side) = 87 kN

Figure S32 Increases in soil dry bulk density resulting from successive wheels of tractor and two axle trailer (Smith,1985).

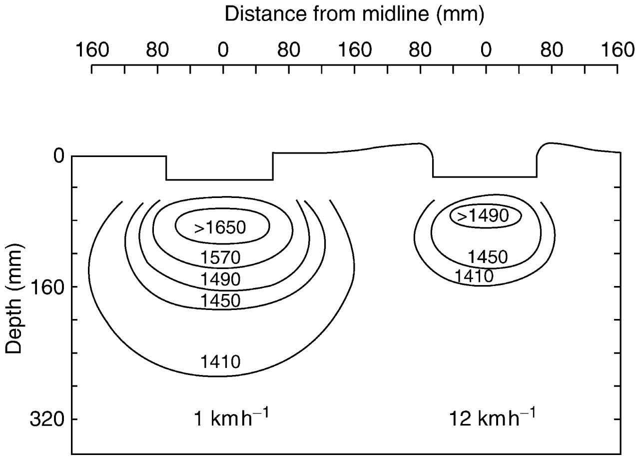


Figure S33 The effect of forward speed on the distribution of soil bulk density below a tractor wheel (Karczewski, 1978).

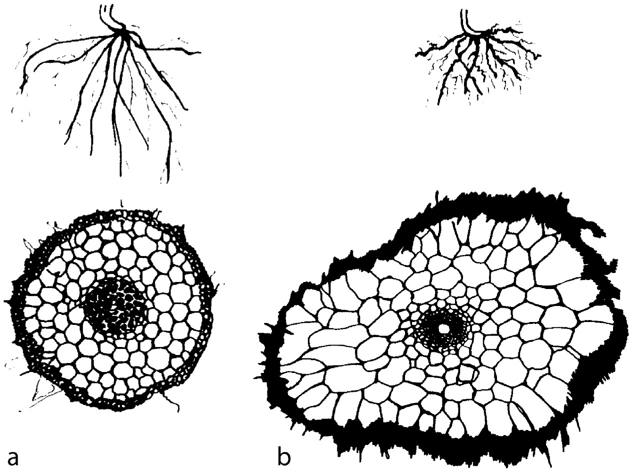


Figure S34 Root system and cross-section of roots grown in loose (a) and compacted (b) silty loam soil (magnification ×150) (Lipiec et al., 1991).

the solid phase of soil and on its pores (Bisdom et al., 1990; Czachor et al., 2001; Hartge, 2000). The relation of such changes to the external forces requires, apart from qualitative assessments, also quantitative determinations, (Guc et al., 1995; Kooistra, 1990, 1994; Lipiec et al., 2003; Pukos, 1994; Tarkiewicz et al., 2000). The structural complexity of soil justifies such an approach, and the treatment of soil structural parameters as random variables may create a possibility of the prediction of their values under constantly changing "momentary" states of the structure of soil subjected to strain.

Soil porosity and moisture

Porosity, like density, can be adopted as a measure of the volumetric strain of the soil. Generally, tillage reduces the porosity of soils, mainly by changing the size of large pores, (Hillel, 1980; Mc Kyes, 1985; CIGR, 1999).

Total porosity is most frequently determined on the basis of the bulk density and dry density at the actual water content. Also used for the purpose are instruments whose operation is based on the Boyle and Mariotte Law. What is being determined is the air capacity at the actual water content (Baver et al., 1972; Mückenhausen, 1975).

The water retention ability of soils, and the filtration of water through soil samples, are also frequently used to determine soil porosity. In such cases the amount of water seeping out of capillary-saturated soil samples is determined at various chosen and gradually increasing, pressure levels, (Baver et al., 1972; Hillel, 1980).

Other methods, e.g., of mercury porosimetry, make use of the behavior of non-wetting liquids in capillaries, giving as a result the relation between the pressure necessary to force mercury into a capillary and the radius of the capillary. In both these groups of methods it is assumed that pores are cylindrical in shape and that the adopted values of surface tension and of liquid-soil contact angle are correct at a given temperature. Laboratory studies show that under the effect of external stress significant changes occur not only in the total porosity of the soil, but also in the volume of pores within the range of radii conducive to water availability in plants, that is within the range of pF values from 2.0 to 3.0. The effect of stress decreases with decreasing initial moisture content (Konstankiewicz, 1977; Lawrance, 1978).

The effect of the type of soil, of the physical properties of its solid phase and compaction on the water retention and hydraulic properties are also significant (Baumgartl, et al., 2000; Dawidowski et al., 1986, Horton, 1994; Walczak, 1977; Sobczuk et al., 1992). Increasing compaction is accompanied by a decrease in the water content at all pF values, and the extent of the effect of hysteresis depends on the type of soil and also decreases with increasing compaction (Figure S35). These effects result primarily from the destruction of large pores which were completely filled with water at pF = 0; in the case of pF = 3.4, when water fills capillaries of small diameters, no changes in soil moisture are observed.

Air and thermal properties

Soil porosity and moisture, taking into account the hysteresis loop, determine the volume of air and the gas exchange in the soil. During mechanical tillage changes in the gas-filled porosity are brought about by simultaneous decrease in porosity and increase in moisture due to the appearance of a considerable number of new small capillaries.

At a low level of gas-filled (air-filled) porosity, the access of oxygen to plant roots is possible mainly by air diffusion through the liquid phase. This process is several thousand times slower than in the gaseous phase. The oxygen diffusion rate (ODR) decreases with increasing moisture content (Gliński et al., 1985). A slight increase in moisture, caused by soil compaction for example, may even cause total stoppage of gas exchange through plant roots. Such adverse effects may be alleviated by a slight loosening of the soil, which causes an increase in the volume of larger-section pores, and of water movement to the subsoil, as well as improving diffusion conditions (Figure S36).

Mechanical strain causes not only changes in water and air conditions in the soil, but also in heat flux. The latter, by virtue of thermodiffusion, evaporation and condensation, in turn also affects water-air relations. The traffic soil have involved the

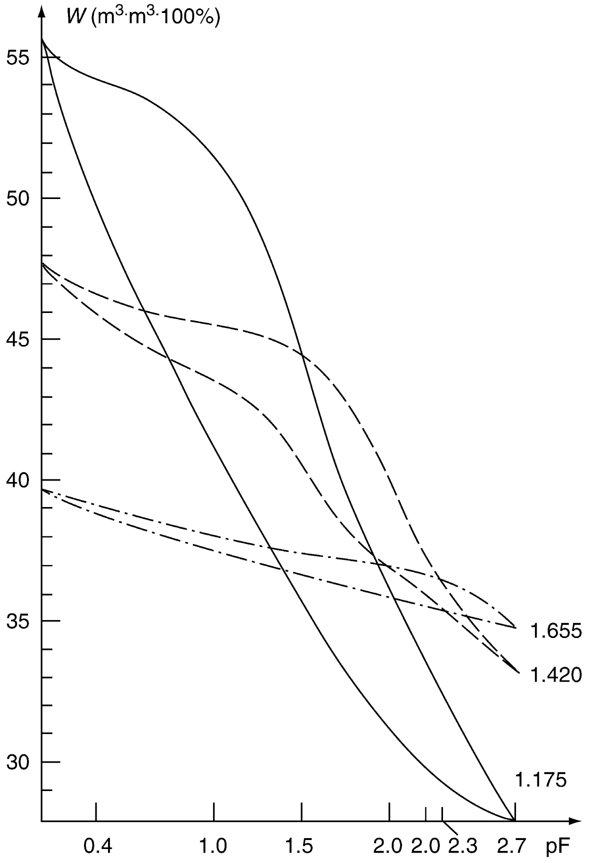


Figure S35 Loops of pF-moisture hysteresis for different compaction of brown soil (Walczak, 1977).

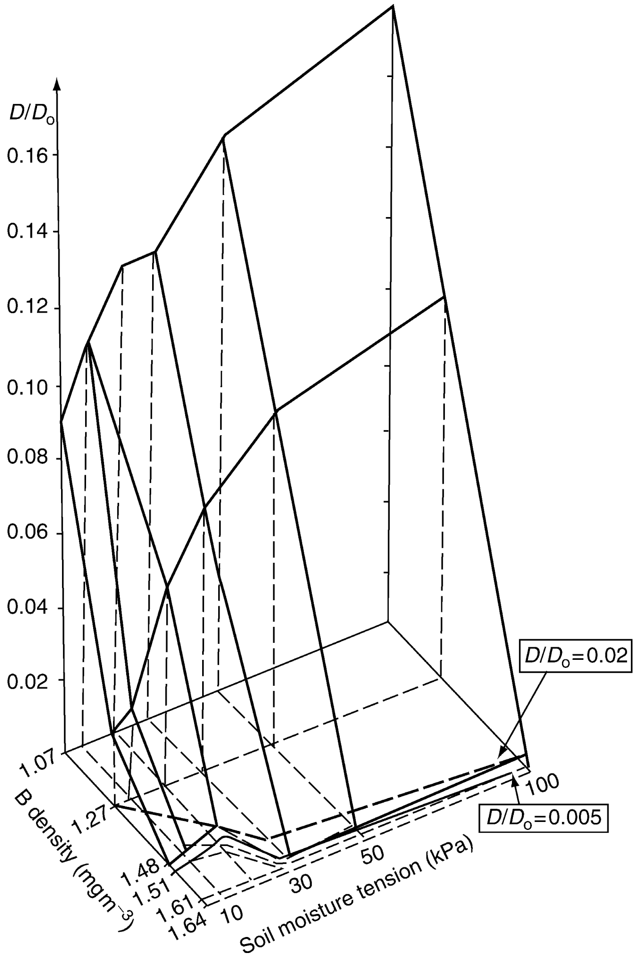


Figure S36 Relationship of diffusion coefficient *D/D* in a loamy textured black earth to soil moisture tension and bulk density (Gliński et al., 1985).

new condition of the mass and energy transfer through the pore system (Usowicz, 2002; Walczak et al., 1994).

Thermal parameters of the soil – temperature, conductivity and heat capacity – are determined primarily by mineralogical composition, porosity and moisture content. Water has the greatest heat capacity of any soil component and therefore has the dominant effect on the heat capacity of the soil. A decrease in porosity in the course of compaction, and an increase in water content, lead to an increase in the heat capacity of the soil, and in consequence to slower rates of warming and cooling of the arable layers of the soil (Gupta et al., 1984; Kossowski, 1991).

Likewise, the heat conductivity of the soil depends primarily on the water and air content in pores. Due to the low heat conductivity of the soil air, soils of high porosity and low moisture content are characterized by low heat conductivity. Even a slight increase in moisture content results in a rapid increase in heat conductivity. In addition, the effect is enhanced by soil compaction, which increases contact between particles of the solid phase, the components of which may have high heat conductivity coefficients.

Mechanical properties – model studies

All the physical properties of soil presented above, and especially changes in their values, are directly determined by the level of soil compaction. Their measurement can be used to assess the physical effects brought about by the work of agricultural implements in the field. Model studies are used to provide detailed knowledge of such physical characteristics, including their quantitative description and interrelationships involved. Studies of this type involve a degree of simplification of reality, but at the same time they allow a given process to be studied under controlled conditions, and permit the effect of selected factors to be assessed.

Modeling is applied to field tillage treatments in which both the parameters of the tractor itself (weight, wheel track and base, on-road load), and also the traffic parameters are selected, including working elements appropriate to the type of soil and plant cultivated (Koolen, 2000; Perdok et al., 1990; Tijink, 1988; Vermeulen et al., 1988, 1989).

In the laboratory, the effect of machines on the soil is simulated, ideally under controlled conditions, by means of suitable equipment e.g., odometer, direct shear apparatus, strength machines (Lerink, 1990; Dawidowski et al., 1986, 1990; Pukos, 1994).

Mechanical model

In the modeling of physical processes in soil, continuity and homogeneity of the medium cannot be assumed. Especially in the case of the stress-strain relationship it is impossible to adopt the assumptions of continuum mechanics.

However, the model of a continuous and homogeneous medium is the oldest one in soil mechanics, and is still in use. It has been adopted directly from civil engineering where, much earlier, it had proved to be of use. Mechanically, problems of soil strain are related to short periods of subjection to stress, to the loose initial condition of the soil, and to high rates of strain (Hillel, 1980; Koolen et al., 1983; Pukos, 1994).

The Coulomb-Mohr hypothesis

The oldest model of soil mechanics assumes that the soil is material with internal friction (Hillel, 1980; Scott, 1980; Feda, 1982). This shows up with the sudden breakdown of structure when a certain level of stress has been reached. The limiting level of stress (shearing strength) is characterized by two basic parameters, cohesion (C) and angle of internal friction (ϕ):

$$\tau_f = C + \sigma_n \tan \phi \tag{1}$$

where: τ_f = shearing stress and σ_n = normal stress (Figure S37).

This theory can forecast forces causing the limiting state (of strength), but it does not provide information on the stress-strain relationship, nor does it take into consideration the time factor. Nevertheless it has been broadly adopted in soil mechanics.

It is commonly assumed that before the soil reaches its limit it behaves like an elastic medium, especially if preliminary compaction has taken place. Such a situation never occurs in practice. In its initial state, the soil is more or less incoherent, and consequently, strain is the most irreversible (non-elastic). Momentary strain constitutes 20 to 50% of the total strain and cannot be neglected. It is not possible to apply the simplest relation between stress and strain that follows from the linear theory of elasticity (Hooke's body). Even simple experiments show that the soil is not an ideally elastic body, and that its strength depends on the manner of stress application, and thus also on time (Huszar, 1976; Söhne et al., 1978; Tijink, 1988).

Strain in the soil stabilizes within several seconds, and the rates at which modern machines and implements act upon the soil reach several meters per second. It is, therefore, necessary to introduce an equation that will describe the mechanical characteristics of the soil subjected to strain (the stress-strain relation) and take into account their variation in time, as well as the effect of other physical parameters of the medium under study. Such a possibility is provided by the application of the

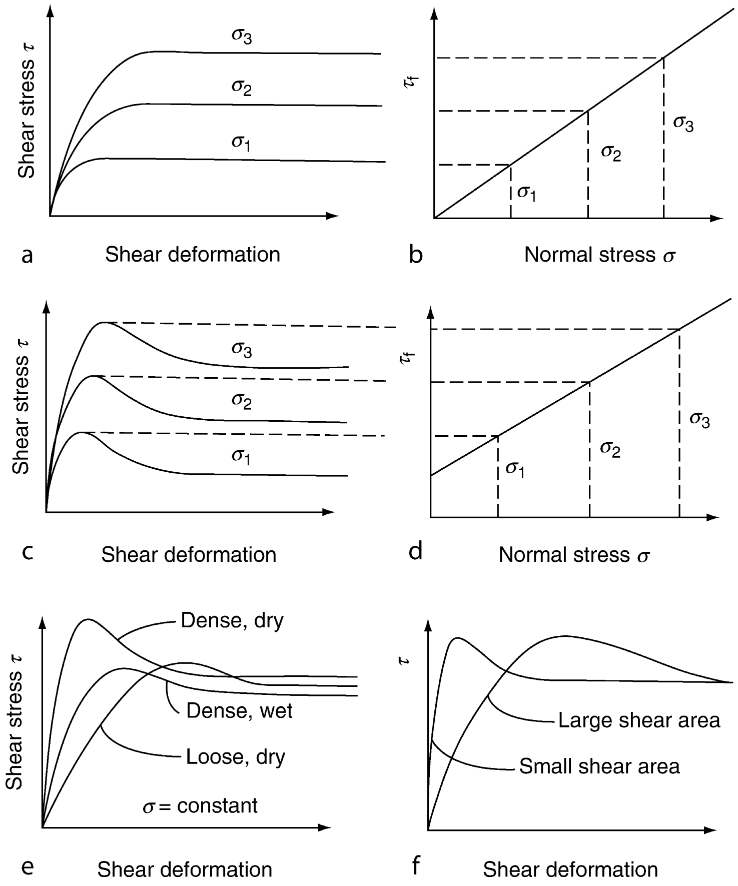


Figure S37 Shear stress-shear deformation relationship for pure sand (a), for cohesive soil (c), for cohesive soil under different conditions (e), and at different shear areas (f). Coulomb's lines for pure sand (b) and for cohesive soil (d) (Söhne et al., 1978).

methods of rheology, with particular emphasis on the visco-elastic theory (Pukos, 1983, 1994).

Rheological models

Rheology studies the mechanical properties of media as a function of time. Rheological models are expressed in terms of differential equations and mechanical analogues. The rheological variables are stress and strain, and the basic parameters are the coefficient of elasticity and the coefficient of viscosity, representing the ideal elastic body and the Newtonian liquid respectively.

In mechanical analogues these occur as combinations of parallel and serial links of springs and dampers, and the general equation describing any number of such elements has the following form:

$$\sigma + \sum_{k=1}^{m} b_k \frac{\mathrm{d}^k\sigma}{\mathrm{d}t^k} = a_0\varepsilon + \sum_{k=1}^{m} a_k \frac{\mathrm{d}^k\varepsilon}{\mathrm{d}t^k} \tag{2}$$

where σ is stress, ε is strain, and a_0, a_k, b_k are constant coefficients related to viscous and elastic phenomena in the soil medium, $m = n$ or $m = n + 1$.

In practice, it is often sufficient to use the above equation with the following limitation to the first time derivatives:

$$f(\sigma, \dot{\sigma}, \varepsilon, \dot{\varepsilon}) = 0 \tag{3}$$

which in its simplest form is a linear differential equation, i.e., its coefficients have constant values. Experimental verification of several of the simplest linear rheological models (Maxwell's, Kelvin-Voigt's, Poynting-Thomson's) was unsatisfactory (Konstankiewicz, 1989). This can be illustrated by an example of the relationship between stress and time, (for sandy soil), obtained experimentally in the strength machine at various rapid strain rates and a hydrostatic stress, and calculated with the assumption of constant coefficients of viscosity and elasticity. Discrepancies were obtained for several soils and for other experiment parameters (Figure S38).

The weakness of classical rheology lies in its assumption of a linear character for equations formulated phenomenologically on the basis of models of ideal bodies.

Substituting for the abstract model of a continuum, a discrete system of structural elements with their physical interactions taken into account, on the basis of the methods of statistical thermodynamics, it is possible to formulate function-type expressions for the coefficients of viscosity and elasticity (Pukos, 1983):

$$\eta = \frac{A\sigma(t)}{\sinh[B\sigma(t)]}; \quad E = \frac{C\sigma(t)}{\operatorname{arcsin\,h}[D\sigma(t)]} \tag{4}$$

where η and E are coefficients of viscosity and elasticity respectively, and A, B, C, D are constants independent of stress.

Examples of the dependence of viscosity and elasticity on stress were obtained in a strength test at various strain rates for several model samples of soil (Figure S39). Verification of the results was performed using the three-parameter visco-elastic model of Poynting-Thomson, assuming the value of $E_2 \sim 10^5$ N m^{-2}.

Probabilistic micromechanics

As the soil consists of a great number of elements differing in size and shape (pores, grains, aggregates), while the interactions between them are extremely complex, it is natural to consider the parameters influencing soil deformation as random variables. In this case the complexity of the soil medium is an advantage, which makes the consideration of its elements as statistical populations (sets, ensembles) possible (Haman, et al., 1996; Pukos, 1994).

Soil structure can be described by 4 random variables the values of which are: (*i*) diameters of the skeletal particles and aggregates, which describe the geometry of a solid phase, (*ii*) pore diameters, deciding which soil grains or aggregates can enter into a given pore during deformation, (*iii*) pore volumes, indicating the soil volume which can enter into a pore under

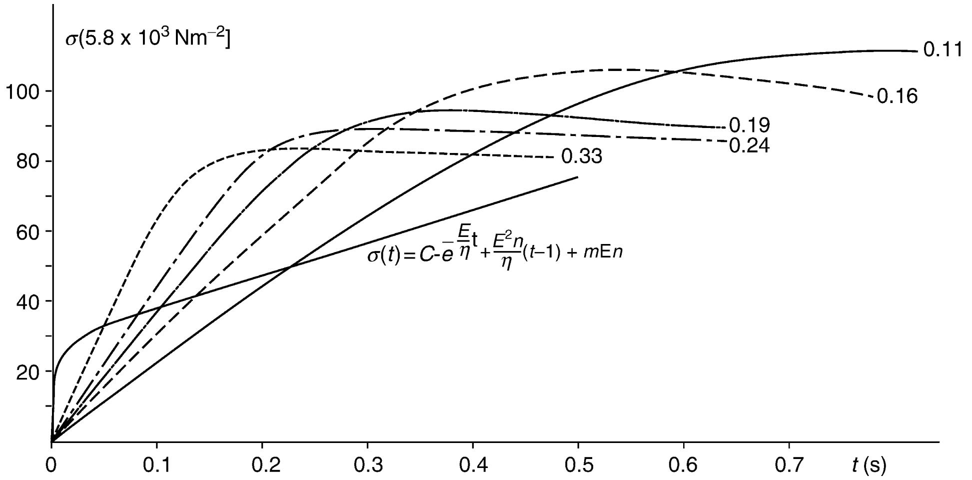


Figure S38 Relationship between stress and time for sandy soil from experimental triaxial test with speed rate of strain and hydrostatic pressure 2.10^4 Nm^{-1} and theoretical solution with constant coefficients of viscosity and elasticity (Konstankiewicz, 1987).

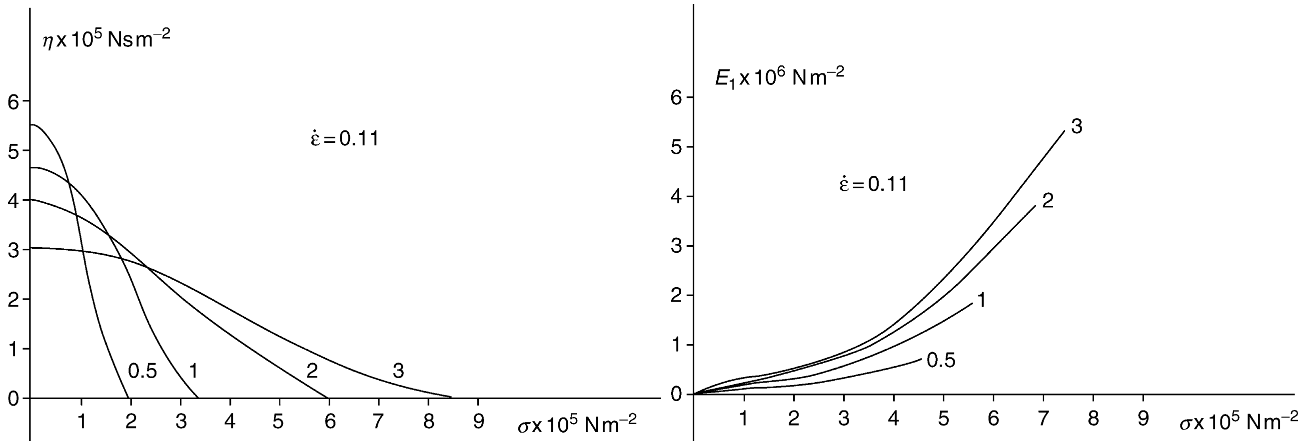


Figure S39 Relationship between coefficient of viscosity and elasticity (– axial stress) at a constant rate of strain = 0.11 s^{-1} and four different spherical stress values for loamy sand (Konstankiewicz, 1989).

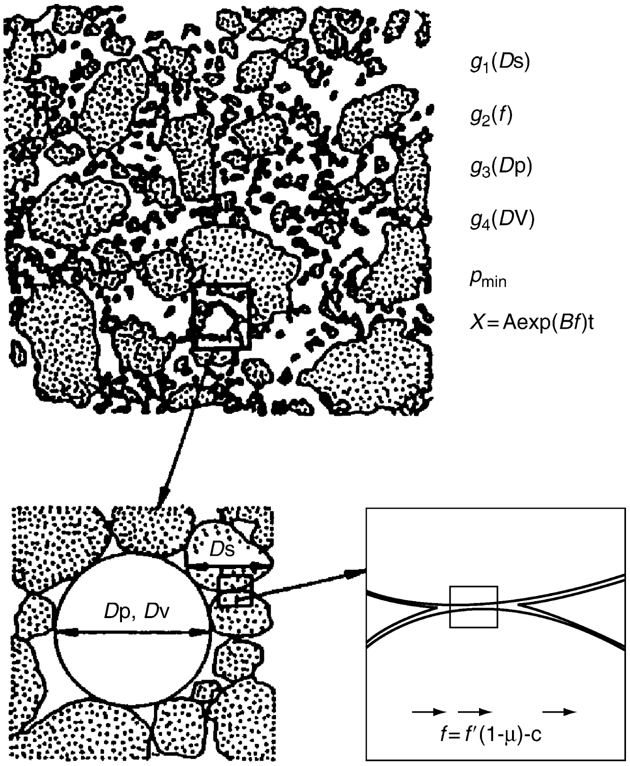


Figure S40 Soil structure and random variables. $g_1(Ds)$ – grain and aggregate size distribution, $g_2(f)$ – distribution of contact forces, $g_3(Dp)$ – pore diameter distribution, $g_4(D_V)$ – pore volume distribution, p_{min} – minimal porosity, $X = A\exp(Bf)t$ – grain motion equation, f, f' – microforces, μ – friction, c – cohesion (Pukos, 1994).

consideration, (*iv*) contact forces, responsible for the stress heterogeneity and instantaneous, irreversible effects, (Figure S40).

This permits the derivation of the probabilistic equation of deformation for a single pore. The equation is then integrated over all sizes of pores, aggregates, particles and contact forces, to give soil deformation as a function of soil structure and its initial condition. The effect of stress and time on the soil strains were taken into consideration as well as dry friction (which depends on deformation velocity and tangential force), cohesion and the initial state of the soil structure in nature.

New measurement techniques

Modeling of mechanical processes in soil under external load, requires experimental data for parameterization and validation of models. Special methods of measurement are in use together with specialized techniques, devices and procedures. The required measures to be determined are: soil stress and soil deformations. Soil stress can be related to soil compaction as well as to forces in wheel-soil or tool-soil systems. Stress in soil is a measure that quantifies the mechanical response of soil to the applied loads. Deformations of soil summarize the global change in soil volume as well as its influence on soil mechanical properties, soil water and air relations and their impact on soil ecology.

Because of the complex structure of soil, where physical and mechanical properties are dependent on numerous factors, it is advisible to carry out experimental studies, and especially to develop new methods for accurate measurements of stress and deformation in soil when loaded.

Methods for soil stress determination

The determination of the state of soil stress under loading caused by machinery traffic requires the use of stress transducers and their proper installation at different depths and distances from the centerline of a wheel. Soil stress state is determined by indirectly, with the assumption that the identification of stress with a measured value of pressure at a point within the soil volume. In general, five types of pressure transducer are used: hydraulic, pneumatic pressure transducers, vibrating-wire strain gauges, strain gauge type pressure transducers, and piezzoresistive strain gauges (Horn et al., 1994).

Hydraulic transducers are equipped with a deformable diaphragm (membrane), which separates the surrounding soil from an intermediate fluid (water, oil) or gas (air, nitrogen, argon) for

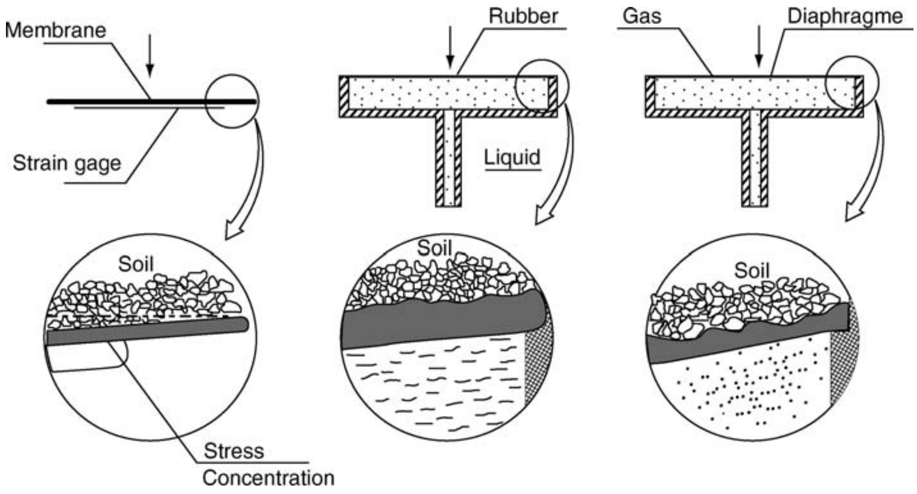


Figure S41 Interactions between soil and pressure transducers: (a) strain gage type transducer, (b) hydraulic transducer, (c) pneumatic transducer.

pneumatic transducers. A pressure sensitive element (piezzo, semiconductor or strain gauge) can be installed outside the soil volume.

In vibrating-wire strain gauges soil pressure causes vibrations of a wire, connected to a diaphragm. These transducers have long-term stability, are robust and resist external electrical noise. They have non-linear characteristics and a relatively slow response, and so are not suitable for dynamic measurements.

Strain gauge type pressure transducers are designed as elastic membranes with a sensing element-strain gauge (usually four constantan resistors in a Wheatstone bridge configuration) glued on. Elastic membranes would not deform and metals are used as a construction material (steel, aluminum, titanium). These are the most accurate pressure transducers and are suitable for static and dynamic measurements, although static long-term measurements can be affected by a possible zero-drift. Temperature changes, power supply voltage fluctuations can also influence the data obtained. Output signals from the sensing elements are electric signals of low level and usually require conditioning units (amplifiers, filters).

Hydraulic pressure transducers tend to measure soil pressures lower than real values. This can be explained as the effect of membrane deformation (the membrane stiffness moduli are lower then soil stifness moduli). Strain gauge measured soil pressure may be higher than real values, because of higher value of metal membrane stiffness moduli and stress concentration. Thus, under- and over-estimation occurs (Horn et al., 1992). A schematic action of three types pressure transducers, strain gage, hydraulic and pneumatic is shown in Figure S41.

Material of a membrane influences sensor characteristics, especially sensitivity, progressivity (or regressivity) and hysteresis. Rubber, silicon or plastic membranes ensure the best sensitivity, whereas steel or aluminum membranes usually have a higher sensitivity threshold (they are less sensitive because of a high elastic modulus). The use of softer membranes results in sensor regressivity while stiffer membranes result in progressivity. Some measurement errors may depend on the membrane material hysteresis, which is higher for rubber, silicon and plastics than for steel or aluminum.

The performance of a soil pressure sensor system depends on calibration methodology and it is desirable to calibrate such sensors under controlled laboratory conditions that will simulate in situ properties of an investigated soil. The transducer response is assumed to be influenced by the mechanical properties of the medium to be investigated. Consequently, the best results are obtained when the calibration is performed in soil which will be subjected to pressure measurements. Soil for the calibration should also have similar or the same moisture content and level of compaction.

Installation of stress transducers into soil always causes soil disturbances and soil structure damage, dependent on soil type as well as on sensor size and shape. The smaller the transducer, the less significant influence on soil stress measurements is seen. By contrast, in non-aggregated or non-cohesive sandy soils the presence of an extrinsic, rigid or deformable body of a sensor may cause only minor errors of soil stress by under- or over-estimations (Horn et al., 1994). The whole sensing surface of a transducer must be in contact with the soil particles to prevent stress concentrations on the transducer. Many researchers have reported the installation of sensor systems in light textured soil, excavating and then refilling an already disturbed soil

Determination of spatial stress in soil

In general, external loads on the soil surface, from agricultural, off-road and military vehicles cause a complex, three-dimensional stress state in soil. The assumption of one- or two-dimensional stress state is therefore erroneous. A three dimensional determination of stress state is required. A stress state transducer (SST) enables such a complete stress state in soil to be determined i.e., major normal stresses, S1, S2 and S3 and the direction cosines for these stresses (Bailey et al., 1987). Optionally, stress state can be described by means of two stress invariants: MNS (mean normal stress) and OCTSS (octahedral shear stress) in the so-called octahedral stress system (Figure S42). The typical SST consists of six pressure transducers positioned to obtain soil pressure values needed for calculation of S1, S2, S3 and MNS, OCTSS. Several SST designs are in use (Bailey et al., 1987; Horn et al., 1992; Pytka

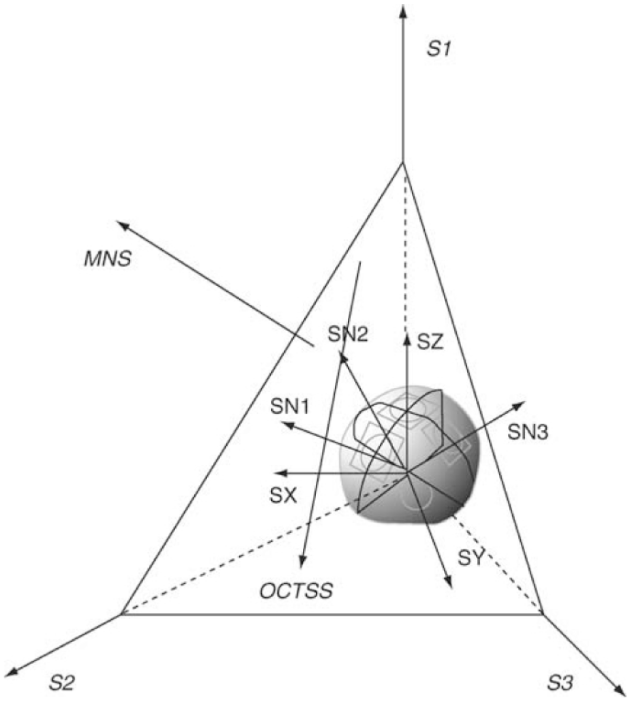


Figure S42 Stress state and geometry of stress state transducer. Outer vectors: *S1, S2, S3* – major stresses, *MNS* and *OCTSS* – mean normal and shear stresses in octahedral stress system. Inner vectors: *SZ, SY, SX* – three major planes of pressure transducers, *SN1, SN2, SN3* – mutually orthogonal planes of pressure transducers in the SST.

et al., 2002). The SST can also be connected to soil deformation transducers (Horn et al., 1994; Pytka et al., 2002), thus enabling the determination of soil stress and deformation state in simultaneous measurements.

Methods for soil deformation determination

Determination of soil deformations can be performed by measuring changes in soil sample volume and shape or, by investigation of displacements of sensing elements installed in a deforming soil volume. The former enables determination only of the global deformation of relatively small soil samples (usually 10 × 2 or 5 × 5 cm). More informative results can be obtained by the use of the second kind of method. These methods enable the determination of isolines of deformation in a soil volume as well as their time dependent curves. Spatial or planar displacements of sensing elements are monitored. Various sensing elements are used: sticks (van den Akker, 1988), colored soil layers (Yo Qun et al., 1992), rigid probes (Pytka et al., 2002) or pressure transducers as deformation sensing elements (Horn et al., 1994; Pytka et al., 2002). There are several methods for the monitoring the displacement of the sensing elements: mechanical – the use of arm-gear-potentiometer systems (Horn et al., 1994), photogrammetric (van den Akker, 1988), electro-optical (laser projectors, semitransparent shield, camera) (Pytka et al., 2002), hydrostatic (determination of changes in hydrostatic pressure caused by vertical movements of a sensing element) (Arvidsson et al., 1996) and inertial (determination of sensing element acceleration) (Pytka et al., 2002).

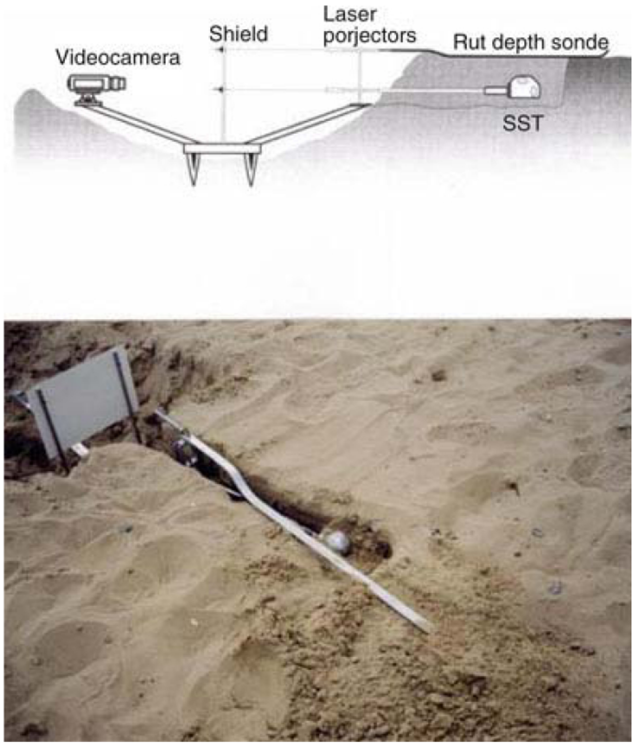


Figure S43 A schematic view (*upper*) and field installation (*lower*) of the measuring system for soil stress and deformation determination.

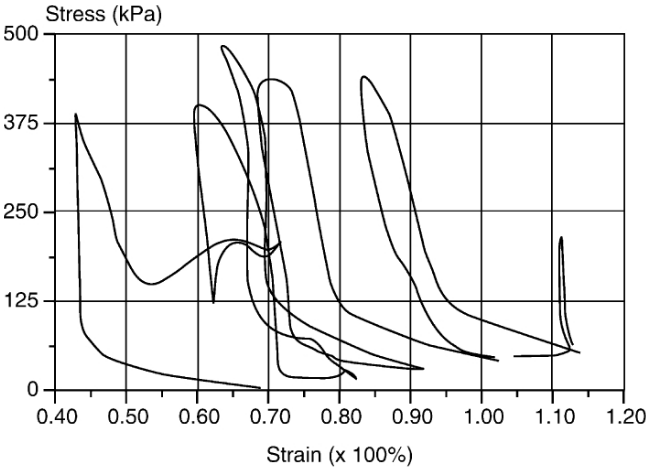


Figure S44 Stress – strain relationship for sandy soil loaded by a tracked vehicle obtained in a field experiment.

Simultaneous measurements of stress and deformation in soil

A mechanical characterization of soil is possible by means of stress-strain relationship analysis. Such data can be obtained experimentally by the simultaneous measurement of both the state of soil stress and the deformation of the soil (Figure S43). Some of the measuring systems described above are capable of such measurements (Horn et al., 1994; Pytka et al., 2002). The final results of soil stress and deformation measurements may be plotted in the form of a stress-strain relationship. An example of an experimental stress-strain relationship obtained for a sandy soil loaded by a tracked 6-wheeled vehicle is presented in Figure S44. Analysis of such relationships provides information on soil strength, hysteresis behavior of soil mechanical properties, values of the so-called pre-compression stress and others. Detailed analysis and data reduction can be performed to evaluate new models of soil-wheel or soil-machine interactions, especially soil compaction models and trafficability studies.

Krystyna Konstankiewicz and Jarosław Pytka

Bibliography

van den Akker, J.J.H., 1988. *Model computation of subsoil stress distribution and compaction due to field traffic*, Wageningen, Report 23. Institute for Land and Water Management Research.

Arvidsson, J., and Ristic, S., 1996. Soil stress and compaction effects for four tractor types. *J. Terramech.*, **33**(5): 223–232.

Bailey, A.C., Nichols, A., and Johnson, C.E., 1987. A stress state transducer for soil. *Trans. ASAE*, **30**: 1237–1241.

Baumgartl, T., Rostek, J., and Horn, R., 2000. Internal and external stresses affecting the water retention curve. *Adv. Geoecol.*, **32**: 13–21.

Baver, L.D., Gardner, W.H., and Gardner, W.R., 1972. *Soil Physics.* New York: Wiley.

Bisdom, E.B.A., Tessier, D., and Schoute, J.F.Th., 1990. Micromorfological techniques in research and teaching (submicroscopy). In Douglas, L.A., ed., *Soil Micromorphology.* Amsterdam, The Netherlands: Elsevier, pp. 581–603.

Bodziony, J., Konstankiewicz, K., Młynarczuk, M., and Ratajczak, T., 1993. Assessment of the porosity of soil samples according to the method of stereological analysis. *Int. Agrophys.*, **7**(1): 35–46.

Byszewski, W., and Haman, J., 1977. Gleba-maszyna-roslina, Warszawa: PWN.

CIGR, 1999. *Handbook of Agricultural Engineering.* A Five Volume Series. St. Joseph, USA: ASAE (//www.asae.org) (on CD).

Czachor, H., and Góźdź, A., 2001. Modelling of granular and cellular materials. *Trans. ASAE*, **44**(2): 439–445.

Dawidowski, J.B., and Koolen, A.J., 1986. Changes of soil water suction, conductivity and dry strength during deformation of wet undisturbed samples. *Soil Till. Res.*, **9**: 169–180.

Dawidowski, J.B., and Lerink, P., 1990. Laboratory simulation of the effects of traffic during seedbed preparation on soil physical properties using a quick uni-axial compression test. *Soil Till. Res.*, **17**: 31–45.

Feda, J., 1982. *Mechanics of Particulate Materials.* Prague: Academia.

Gliński, J., and Lipiec, J., 1990. *Soil Physical Conditions and Plant Roots.* Boca Raton, FL: CRC Press.

Gliński, J., and Stępniewski, W., 1985. *Soil Aeration and Its Role for Plants.* Boca Raton, Florida: CRC Press.

Guc, A., Czachor, H., and Konstankiewicz, K., 1995. Effect of stress on stereological parameters of polished sections of soil samples. *Int. Agrophys.*, **9**: 4.

Gupta, S.C., Larson, W.E., and Allmares, R.R., 1984. Predicting soil temperature and soil heat flux under different tillage-surface residue conditions. *Soil. Sci. Soc. Am. J.*, **48**: 223–232.

Håkansson, J., 1981. Effects of heavy traffic on soil conditions and crop growth. In Seventh International Conference on ISTVS Calgary, Canada.

Håkansson, I., and Lipiec, J., 2000. A review of the usefulness of relative density values in studies of soil structure and compaction. *Soil Till. Res.*, **53**: 71–85.

Haman, J., Konstankiewicz, K., and Pukos, A., 1996. Probabilistic micromechanics of three-phase media. ASAE International Meeting, Phoenix, Arizona (USA), July 14–18.

Hartge, K.H., 2000. The effect of soil deformation on physical soil properties – a discourse on the common background. *Adv. Geoecol.*, **32**: 32–43.

Hillel, D., 1980. *Fundamentals of Soil Physics.* New York: Academic Press.

Horn, R., and Hartge, K.H., 1990. Effect of short time loading on soil strength and some physical properties. *Soil Till. Res.*, **15**: 247–256.

Horn, R., and Lebert, M., 1994. Soil compactability and compressibility. In Soane, B.D., and Van Ouwerkerk, C., eds., *Soil Compaction in Crop Production.* Amsterdam, The Netherlands: Elsevier, pp. 41–96.

Horn, R., Johnson, C., Semmel, H., Schafer, R., and Lebert, M., 1992. Raumlische Spannungsmessungen mit dem Stress State Transducer (SST) in ungesattigten aggregierten Boden – theoretische Betrachtungen und erste Ergebnisse. *Z. Pflanzenren. Bodenkunde*, **155**: 269–274 (in German).

Horton, R., Ankeny, M.D., and Allmaras, R.R., 1994. Effects of compaction on soil hydraulic properties. In Soane, B.D., van Ouwerkerk, C., eds., 1994. *Soil Compaction in Crop Production.* Amsterdam, The Netherlands: Elsevier, pp. 141–166.

Huszar, I., 1976. Soil mechanics in the agriculture. *Z. Probl. Post. Nauk. Roln.*, **168**: 3–18.

ISTRO, 2002. Curent trends in the research of soil environment. Proceedings of International Conference, Brno, Czech Republic.

Karczewski, T., 1978. Wpływ prędkości przejazdu na zmiany zagęszczenia gleby przez koła maszyn rolniczych. *Z. Probl. Post. Nauk Roln.*, **201**: 69–74, (in Polish).

Konstankiewicz, K., 1977. The influence of pore distribution on water potential in soils subjected to consolidation. *Z. Probl. Post. Nauk Roln.*, **197**: 79–97.

Konstankiewicz, K., 1989. Viscosity and elasticity coefficients of selected soils. *Zesz. Probl. Post. Nauk Roln.*, **378**: 69–74.

Kooistra, M.J., 1990. The future of soil micromorphology. In Douglas, L.A., ed., *Soil Micromorphology.* Amsterdam, The Netherlands: Elsevier, pp. 1–7.

Kooistra, M.J., and Tovey, N.K., 1994. Effects of compaction on soil microstructure. In Soane, B.D., van Ouwerkerk, C., eds., *Soil Compaction in Crop Production*, pp. 91–112.

Koolen, A.J., and Kuipers, H., 1983. *Agricultural Soil Mechanics.* Berlin, New York: Springer.

Koolen, A.J., and van den Akker, J.J.H., 2000. On the use of agricultural soil data required in soil deformation models. *Adv. Geoecol.*, **32**: 118–125.

Kossowski, J., 1991. Differentiation of temperature in arable layer under the influence of soil compaction. *Z. Probl. Post. Nauk Roln.*, **396**: 75–80.

Lawrance, G.P., 1978. Stability of soil pores during mercury intrusion porosimetry. *J. Soil Sci.*, **29**: 299–304.

Lerink, P., 1990. Prediction of the immediate effects of traffic on field soil qualities. *Soil Till. Res.*, **16**: 153–166.

Lipiec, J., and Håkansson, I., 2000. Influeces of degree of compactness and matric water tension on some important plant growth factors. *Soil Till. Res.*, **53**: 87–94.

Lipiec, J., and Hatano, R., 2003. Quantification of compaction effects on soil physical properties and crop growth. *Geoderma*, **116**: 107–136.

Lipiec, J., Hakansson, I., Tarkiewicz, S., and Kossowski, J., 1991. Soil physical properties and growth of spring barley as related to the degree of compactioness of two soils. *Soil Till. Res.*, **19**: 307–317.

Marshall, T.J., and Holmes, J.W., 1979. *Soil Physics.* Cambridge: University Press.

Mc Kyes, E., 1985. *Soil Cutting and Tillage.* Amsterdam, The Netherlands: Elsevier.

Mückenhausen, E., 1975. Bodenkunde. Frankfurt: DLG.

Niewczas, J., and Witkowska-Walczak, B., 2003. Index of soil aggregates stability as linear functionvalue of transition matrix elements. *Soil Till. Res.*, **70**(2): 121–130.

Perdok, U.D., and Tijink, F.G.J., 1990. Developments in IMAG research on mechanization in soil tillage and field traffic. *Soil Till. Res.*, **16**: 121–141.

Pukos, A., 1983. Thermodynamic interpretation of soil medium deformation. *Z. Probl. Post. Nauk Roln.*, **22**: 367–399.

Pukos, A., 1994. Quantitative description of structural changes in soil and plant materials during deformation. *Int. Agrophys.*, **8**: 103–112.

Pytka, J., and Konstankiewicz, K., 2002. A new optical method for soil stress and strain investigation. *Soil Till. Res.*, **65**: 243–251.

Scott, C.R., 1980. *An Introduction to Soil Mechanics and Foundations.* London: Applied Science.

Smith, D.L.O., 1985. Compaction by wheels: a numerical model for agricultural soils. *J. Soil Sci.*, **36**: 621–632.

Smith, D.L.O., 1987. Measurement, interpretation and modelling of soil compaction. *Soil Use Manag.*, **3**: 87–93.

Soane, B.D., and van Ouwerkerk, C., eds., 1994. *Soil Compaction in Crop Production.* Amsterdam, The Netherlands: Elsevier.

Soane, B.D., Blackwell, P.S., Dickson, J.W., and Painter, D.J., 1980/81. Compaction by agricultural vehicles: a review. II Compaction under tyres and other running gear. *Soil Till. Res.*, **1**: 373–400.

Soane, B.D., Campbell, D.J., and Dickson, J.W., 1984. Avoiding compaction. *Aspects of Applied Biology*, **7**: 313–342.

Sobczuk, H., Plagge, R., Walczak, R., and Roth, C., 1992. Laboratory equipment and calculation procedures to rapidly determine the effect of hysteresis on soil hydrophysical properties under nonstationary conditions. *Z. Pflanzen. Bodenk.*, **155**: 157–163.

Söhne, W., and Stubenbock, H., 1978. Theoretische Grundlagen der Mechanik der Bodenbearbeitung. *Berichte Landwirtschaft*, **56**: 390–414.

Tarkiewicz, S., and Lipiec, J., 2000. Methods for simultaneous recording of stresses and displacements in soil under wheels of agricultural machinery. *Adv. Geoecol.*, **32**: 154–168.

Tijink, F.G.J., 1988. Load-bearing processes in agricultural wheel-soil systems. Doctoral Thesis, Wageningen: Agricultural University.

Tijink, F.G.J., Perdok, U.D., Vermeulen, G.D., and Arts, W.B.M., 1990. Agricultural Engineering research on field traffic systems in the Netherlands. In Proc. 10th Int. Conf. ISTVS, Kobe, Japan, pp. 557–566.

Usowicz, B., 2002. The universal model of mass and energy transfer in a porous medium. 17th WCSS, Soil Science: Confronting New Realities in the 21st Century, 14–21 August, Thailand, //www.17wcss.ku.ac.th.

Vermeulen, G.D., and Arts, W.B.M., 1989. True-scale field traffic simulation to investigate soil and crop response. Proc. 4th European Conf. ISTVS, Wageningen, The Netherlands.

Vermeulen, G.D., Arts, W.B.M., and Klooster, J.J., 1988. Perspective of reducing soil compaction by using a low ground pressure farming system selection of wheel equipment. Proc. 11th Conf. ISTRO, Edinburgh, Scotland, Vol. 1, pp. 329–334.

Walczak, R., 1977. Model investigations of water binding energy in soils of different compaction. *Z. Probl. Post. Nauk Roln.*, **197**: 11–43.

Walczak, R., and Usowicz, B., 1994. Variability of moisture, temperature and thermal properties in bare soil and crop field. *Int. Agrophys.*, **8**: 161–168.

Yo, Q., Shen, J., and Dai, X., 1992. Camera tracing and image processing system for soil deformation, *J. Terramech.*, **29**(4/5): 423–431.

SOIL FERTILITY

The potential of a given site to produce is referred to as productivity, whereas the contribution of soil to productivity is called *fertility*. This is a comprehensive definition that covers physical, biological and chemical aspects of soils. A more restricted definition of soil fertility limits it to soil nutrient status and *soil productivity* then refers to all soil factors that determine the capacity to produce crops (see Havlin et al., 2005). The more comprehensive definition is followed here, but discussions of aspects other than nutrient status will be brief.

Soil physics and fertility

Texture (see *Particle-size distribution*)

The *texture* of a soil refers to the size-composition of elementary grains in a soil. The texture affects productivity in several ways. Sandy soils are said to be “light” and clays “heavy”. These terms originated from the number of horses needed to pull a plow. The texture is an important factor determining the amount of pores and the pore size distribution, two properties that are of fundamental importance for water relations, aeration and root penetration and thus for soil fertility. Sandy soils have large pores so that infiltration rates and permeabilities to water are high, and they retain little water (Table S8). In contrast, clays have low infiltration rates, low permeabilities, retain much water in available as well as in unavailable form, and may be poorly drained. Specific surfaces and ion exchange capacities (CEC) of sands are low as compared to clays although clay mineralogy is another factor to be considered for the CEC. Aeration is good in sandy soils and fair to poor in clays, depending on their structure. Roots penetrate sands more easily than clays. Soils of intermediate textures such as loams are also intermediate in porosity, water retention, and drainage. The general tendency is for productivity to be better on medium-textured soils consisting of a mixture of sand, silt, and clay than on soils that are light, heavy or mainly silty. The texture is one of the most important soil properties affecting fertility. It is easily estimated by feeling the soil: sandy soils feel gritty, intermediate soils more silky and clays are cloddy or plastic. More accurate laboratory methods involving sieving and sedimentation of elementary particles are also used. Management of texture is usually not economical. However, consequences of poor texture can often be partially alleviated by improving soil structure.

Structure

The arrangement of elementary particles into aggregates is considered *structure*, which, in combination with texture, governs porosity of the soil and thus affects water relations, aeration, root penetration, and the metabolic activities of soil flora and fauna. The binding among elementary particles occurs through unbalanced charges at broken edges of clay particles, through bi- and polyvalent ions that neutralize charges of two different clay particles and thus form a bridge to hold the particles together through iron, calcium carbonate or silicate cements and through organic matter. Water too is a potent “glue” due to the fact that water in small pores is under a lower pressure than atmospheric. Therefore, the atmospheric pressure acting on the particles presses them together and gives them stability. There is no agreement as to how to describe and measure structure (see *Structure*). In a large number of soils it is important to manage soil structure. Many difficulties of extremely light and extremely heavy soils can be overcome. For example, poor water infiltration and permeation of heavy soils can be overcome by an adequate soil structure allowing for enough pores for an adequate flow of water and air. Application of solid animal manure is a good way to improve soil structure. Synthetic organic chemicals that have an effect on soil structure have appeared on the market. Water: Plants require much larger amounts of water than mineral nutrients. Most of the water simply passes through the plant and is lost into the atmosphere through stomatal openings on the leaf surface. These openings are necessary for the entry of CO_2, which is utilized in photosynthesis. Only a small quantity of the water is used for biochemical and other processes such as maintenance of turgidity. Important aspects of soil water are the availability and its buffering capacity.

The state of water in soils is – in modern terminology – described by the soil water potential which is equivalent to the chemical potential of water and is measured in energy units per unit mass (e.g., J kg^{-1}). Incorrect pressure units (Pa) are often used, corresponding to energy per unit volume. The water potential is relative to the standard state of pure free water at a standard pressure and a reference elevation. The potential is affected by the matrix, which gives the matric component, by solutes, defining an osmotic component, and by the pressure, giving a pressure component. The magnitude of these components depends on the path by which a certain soil system is thought to have been created, e.g., whether solutes are added to the water before or after the matrix. Hence the components are not real properties in contrast to solute concentrations and pressure (Noy-Meir and Ginzburg, 1967; Oertli, 1971). Nevertheless, it is customary and practical to work with potential components. The water potential decreases, as water is lost from soils through transpiration or evaporation from the soil surface. The soils vary in their resistance to such changes. The quantitative measure for this resistance is given by the capacity:

$$\text{Capacity} = \frac{\partial\,\text{water content}}{\partial\,\text{potential}}$$

which actually represents the amount of water that can be removed before the water potential changes by unity. The water retention in soils depends primarily on the porosity. Light soils such as sands have low capacities in the range of water potentials at which plants are usually grown, and they must receive water frequently through irrigation or rain in order to remain productive. Heavy soils are better buffered with available water. Clay soils also contain large quantities of unavailable water. Water is usually considered available for plant consumption between *field capacity* and the *permanent wilting point*. Above field capacity water drains off too rapidly to be of much use to plants, and below the permanent wilting point, effects of the low water potential, e.g., on turgidity, are very deleterious to plant behavior. However, neither field capacity nor permanent wilting point can be considered strictly as scientific properties, but their practical use is nonetheless justified. The water available between field capacity and permanent wilting point corresponds roughly to one fourth of the total porosity but differs widely between light and heavy soils. Field capacity corresponds to about –33 Joules (kg water)$^{-1}$ (about –33 kPa) and the permanent wilting point to –1 500 Joules (kg water)$^{-1}$ (about –1.5 MPa).

Dynamic aspects of water also depend largely on the porosity which itself is governed by soil texture and structure (Table S8).

Table S8 Significance of soil texture on fertility

Property	Light soil	Heavy soil
Water relations		
Infiltration rate	High	Low[a]
Permeability	High	Low[a]
Plant-available water	Low	High
Unavailable water	Low	High
Runoff	Low	High[a]
Mechanical resistance		
Tillability	Easy	Difficult
Root penetration	Easy	Difficult[a]
Erosion		
Water detachability	High	Low
Transport in water	Short distances	Long distances
Wind erodibility	High	Low
Nutritional status	Low	High
Cation exchange capacity	Low	High, modified by type of clay tendency to high
Soil nutrients	Tendency to low	

[a] Strong modifying influence by structure possible.

Aeration

The oxygen necessary for respiration of plant roots is largely provided by an exchange of gases between the soil and the atmosphere. That exchange depends primarily on pores that drain rapidly after water is added by rainfall or irrigation. The lower limiting diameter of such pores is about 0.06 mm (Kohnke, 1968). In addition to the exchange of gases through soil pores, oxygen is also provided to roots through the interior of plants.

Whether aeration is good or poor greatly affects soil fertility. An adequate oxygen supply is necessary for respiration of roots. It affects plant metabolism, which in turn affects the uptake of nutrients. Poor aeration can have harmful effects through the reducing conditions that follow. Solubilities of iron and manganese may reach toxic levels; nitrates can be reduced to nitrites or even to nitrous oxide and nitrogen gas. This not only represents the loss of a valuable nutrient, but it may also have environmental impacts (see *Fertilizers, inorganic*).

Sulfates can be reduced to the harmful hydrogen sulfide. The synthesis of toxic levels of ethylene, a plant hormone, of alcohol, and of methane may be induced. Oxygen is required for the decomposition of organic residues originating from plant production. Under extreme anaerobic conditions, decomposition of organic matter can be retarded sufficiently to produce peats and mucks. Conversely, when organic soils are drained and used for crops or pasture, organic substances are oxidized rapidly and disappear and the land subsides, as has happened in a number of places in the past. Hence, drainage of organic soils must be done carefully.

The air-filled volume of a soil varies between 0 and 40% depending on texture and water content. At field capacity the air volume of sandy soils is 30 to 40%, that of clays only 5 to 10%. The oxygen content of the soil air is lower than in the free atmosphere, and levels of 10% and higher are considered sufficient. The concentration of CO_2 is higher than in the atmosphere and may reach 20%. These high contents of CO_2 are apparently not injurious. Microbial and root respiration together produce on average about 8 000 kg CO_2 per hectare and year. Oxygen enters the soil by convection induced by barometric changes and local changes in pressure caused by the movement of water (Scheffer and Schachtschabel, 2002). Diffusion is considered a more important mechanism of gas exchange. The ability to supply oxygen to plant roots is expressed by the oxygen diffusion rate which is usually higher in well structured upper horizons and sandy soils than in compact deeper horizons and clay soils.

Temperature

Effects of soil temperature on soil fertility are both direct and indirect; direct because of its effect on growth and development of plants, indirect because of its effect on the development of soil properties. The metabolic rates of all organisms are affected by temperature. Low temperatures slow down metabolic rates and reduce the uptake of water and nutrients. Wilting of plants, for example, can be induced by irrigating with cold water. Germination of seeds may be retarded by temperatures that are above or below an optimum. Furthermore, low temperatures can also retard the growth of seedlings and thereby keep them susceptible to attacks by pests for longer periods. Maximum and minimum temperatures rather than temperature means tend to determine the distribution of plants over the world by their effects on species survival. Temperature is an important factor of soil formation. Release of nutrient elements as a result of rock weathering affects fertility, the release being faster under high temperatures. The decomposition of soil organic matter, which releases nutrients, especially nitrogen, in a plant-available form, is favored by higher temperatures. Therefore, the organic matter content in soils of warmer climates is often lower (Jenny, 1941).

The temperature of the soil surface increases during the day as radiation energy is transferred to the soil. Through thermal conduction, heat energy is transferred to lower soil layers. In the evening, the input of radiation energy declines. Energy is still lost to the atmosphere through radiation, convection and evaporation of water. Thus the surface temperature declines. As a consequence of these energy transfers toward greater depth and into the atmosphere, a heat wave moves downward and, at the same time, the amplitude decreases and the wavelength increases. It will take many hours until the heat wave reaches the subsoil.

Soil temperature can be managed to some extent through mulching and irrigation. Keeping the soil covered with vegetation lessens these fluctuations. In modern agriculture, covers of transparent plastic are used to increase soil temperature in order to give plants an early start. These covers permit the passage of solar radiation but greatly reduce radiation losses from the soil.

Soil biology and fertility

Biology has many effects on soil fertility. The plants being grown must compete with but also benefit from weeds and microorganisms. Various species of the latter participate in many reactions in the soil, which may be beneficial, neutral, or harmful to the crop plants being grown. Similarly, the fauna living in soils may also be harmful or beneficial to soil fertility.

Weeds interfere with the growth of desirable plants by competing for light, water, nutrients, and space. Under certain circumstances, weeds may consume half of the water applied in irrigation. Alternately, a removal of excessive water after long periods of heavy rain can improve soil aeration and be beneficial to crop plants such as orchard trees. Weeds may also damage crop plants by exuding toxic substances, i.e., by allelopathic interactions (Macías, 2004). Weeds may harbor pests that attack crops, but they may also harbor insects that prey on the pests. Weeds may lead to unfavorable microclimatic conditions that result in frost damage, but they may also dampen extremes of soil temperatures. Weeds, like all plants, will improve soil physical conditions and protect soils from erosion. The extent of weed control must, therefore, be adjusted to the individual situation. In orchards in temperate climates with abundant rain, weeds are often left between rows and only removed around trees in order to control rodents. In a dry climate where water is generally deficient, it might be beneficial to apply a more general weed control, provided that erosion is not a problem. Weeds can be controlled chemically (herbicides), mechanically and by other management procedures like placing fertilizers in such a way that growth of the crop plant is favored over weeds.

Microorganisms (see *Soil microbiology*) and soil fauna participate in transformation of organic and many inorganic substances in soils that affect soil fertility. Decomposition of organic residues is due in large measure to bacteria, fungi, actinomyces, and soil fauna. The breakdown of organic residues changes the chemical composition and gives rise to humus. These chemical processes run continuously and may release or immobilize nutrients. In soils with organic matter of a high carbon to nitrogen ratio quantities of released nitrogen are insufficient for microorganisms, which then make use of inorganic nitrogen, thus competing with crop plants for this important nutrient. This problem arises e.g., after fertilizing with straw, which has a very high C:N ratio. Organic matter with C:N ratios below 20 to 25 can be expected to release nitrogen to crops, whereas nitrogen is immobilized at a ratio above 40. The fraction that can be mobilized is sometimes designated as N_{mob}. A number of bacteria are active at other positions of the nitrogen cycle. Some fix atmospheric nitrogen (diazotroph bacteria) and thereby incorporate it into the soil. Important fixers of atmospheric nitrogen are (*a*) free-living forms such as the organotroph *Azotobacter* which derives its energy from utilizing soil organic matter and the phototroph *cyanobacteria* which uses light energy, (*b*) associated diazotrophs (*Azospirillum*) living in the rhizosphere of some plants, especially C_4 grasses, i.e., grasses which have a special pathway of photosynthesis and (*c*) bacteria of the genera *Rhizobium* and *Bradirhizobium* living symbiotically on legumes, and *actinomycetes* living symbiotically in roots of various plant groups such as *Alnus-Casuarina*. Certain groups of bacteria convert ammonium to nitrite and nitrate (*nitrification*) and still others partly reverse this reaction (*denitrification*) (see *Fertilizers, inorganic*). Other forms of bacteria are involved in redox reactions such as the sulfur cycle (see *Sulfur transformations and fluxes*), oxidation of ferrous to ferric iron, and oxidation and reduction of manganese compounds.

A large number of fungi and bacteria are pathogens of crop plants and must be controlled. Pesticides, crop rotation and other management procedures are available for this purpose.

The *soil fauna* comprise a large number of species ranging from microorganisms to mammals. Their function may be useful or harmful. They also play an important role in the physical and chemical decomposition of plant detritus. Beneficial effects attributed to some species of earthworms have often been emphasized. The intensive mixing of organic and inorganic materials in the digestive tract of the earthworm, combined with chemical changes and vertical transports in the soil profile, leads to improved soil physical conditions. Casts of earthworms may, however, be undesirable on certain lawns and anaerobic conditions in the interior of casts may favor denitrification. Soil fauna contain a number of species that are important pests in crop production and must be controlled.

Soil chemistry and fertility

Availability, intensity-extensity relations, potentials, and capacities

The soil is a reservoir of essential mineral nutrients and occasionally of toxic chemicals. However, a total analysis of a nutrient element or a chemical compound has little value for evaluating soil fertility. Soils may contain large quantities of a certain element that could fill the needs of vegetation for thousands of years, but plants growing on such soils may suffer from deficiencies of this very nutrient. Nutritional aspects of soil fertility are thus determined by the *status of nutrients* in soils, i.e., by their *availability* together with the amount of nutrients present at a certain availability level, namely, the *quantity*. The status of nutrients is an *intensive* property, the expression of the quantity an *extensive* property.

The *intensive factor*, the *availability*, is an expression of the ease with which a nutrient is taken up by plants. Schofield (1955) attempted to characterize the availability of nutrient elements by their chemical potentials. For phosphorus, he suggested the chemical potential of calcium phosphate, which, in the p-form, is

$$0.5\mathrm{pCa}^{2+} + \mathrm{pH_2PO_4^-}$$

where p is, analogous to the pH designation, the negative logarithm of the respective ion concentration or activity. Similarly, the availability of potassium was given by

$$\mathrm{pK}^{+} - 0.5\mathrm{pCa}^{2+}$$

These terms for the availabilities refer to a removal of phosphate as calcium phosphate from the soil solution and of potassium in exchange for calcium. Neither process describes correctly the uptake by plants. Moreover, the quantitative terms are strongly influenced by calcium concentrations. Availabilities must refer to the nutrient uptake process, which depends on root morphology and physiology. This makes availabilities plant-oriented features. Therefore, no soil property alone is likely to be a universal expression of availability. For example, to maintain electroneutrality, potassium may be taken up in exchange for hydrogen or together with nitrate or sulfate etc. Many or all of these processes occur simultaneously. Each process, however, defines a different nutrient potential and, hence, it will hardly ever be possible to express availability by single-valued terms that depend only on soil properties. Numerous uptake studies have shown a dependence of the uptake rate on the nutrient concentration in the solution. As an approximation, the concentration in the soil solution can thus be taken as a measure of availability. This criterion does not take into account nutrient interactions such as ion competition or the counter-ion effect. Further problems arise from differing soil water contents through which, due to ion exchange, the concentration in the soil solution varies in a complicated manner. The magnitude of gradients at the root surface also depends on the dynamics of water movement.

The *extensive factor*, the quantity, is a measure of the quantity of nutrients present at a certain availability level. The capacity is an expression of the rate of change of the intensity factor, i.e., the availability, when nutrients are removed from the soil through plant uptake. Mathematically, it is the differential quotient

$$\left[\frac{\partial n_i}{\partial \mu_i}\right]_{T,P,nj}$$

where n is the number of moles of component i, μ the chemical potential of i or, generally, the "availability". This tells the amount of a nutrient which can be removed from the soil before the availability (potential) suffers a decrease of one unit. The capacity concept, if applied to ionic nutrients, is as problematic as the potential. Just as the nutrient concentration in the soil solution can serve as an approximation of the intensity factor, the sum of exchangeable and soluble ions of the species i can sometimes be used as an estimate of n. The difficulty in expressing availability of nutrients in quantitative terms is increased, because it is usually not sufficient to describe soil fertility by intensity and extensity factors alone. Consideration must be given to parameters affecting transport of nutrients, including water, from the bulk of the soil solution to the root surface. A plot of the quantity as a function of the availability (a Q/I plot) expresses the buffering of a soil. Soil I in Figure S45 is buffered better than soil II. Suppose e.g., that the availability of both soils be A and for a high productivity it should be B. Evidently a larger quantity D, must be added to soil I than to soil II which needs only (D_2) to achieve the same goal. Conversely, if the availability of both soils is B, then a larger quantity of nutrients can be taken up from soil I before the availability drops to A. Tropical soils rich in iron and aluminum (oxisols) exhibit a high buffering capacity of phosphates. Sandy soils usually have a low buffering capacity for most nutrients.

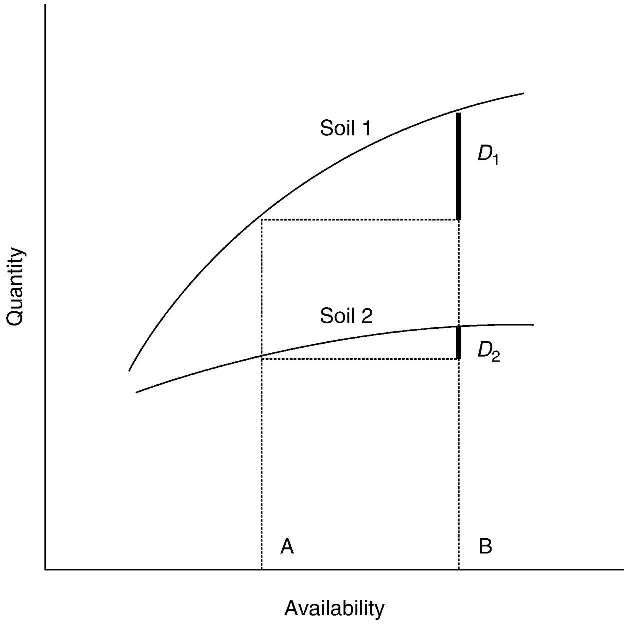


Figure S45 *Q-I* relations of a well-buffered soil I and a poorly buffered soil II. A larger quantity *D*, of a certain nutrient has to be added or removed from soil I in order to bring about a certain change in the availability of the nutrient. The slope of the curves represents the nutrient capacity.

The power of a soil to supply nutrients (nutrient compartments)

The soil is a three-phase system consisting of solid, liquid, and gaseous phases. Nutrients in the liquid phase tend toward an equilibrium with those in the different compartments. Some of the equilibria are established rapidly, for others it takes days, months or years to come even close to equilibrium. Nutrients that are taken up from the soil solution are, to a greater or lesser extent, replaced by those from solid phase. Due to the different reaction rates by which nutrients are released from different compartments there is some arbitrariness as to what is considered "available". A determination of the nutrient capacity of a soil will sometimes depend on the length during which the soil is exposed to the extractant. The most important nutrient compartments are:

Soluble nutrients

Table S9 shows concentration ranges of ions in the soil solution. For some ions, in particular nitrates (but not for total nitrogen), and for chlorides, the amounts in the soil solution represent the total reservoir of the nutrient. Most of the nitrate can be taken up and is therefore available although to different

Table S9 Soil solution composition (after Fried and Broeshart, 1967)

Element	Range	Acid soils	Calcareous soils
Ca	0.5–38[a]	3.4	14
Mg	0.7–100	1.9	7
K	0.2–10	0.7	1
Na	0.4–150	1.0	29
N	0.16–55	12.1	13
P	0.001–1	0.007	0.03
S	0.1–150	0.5	24
Cl	0.2–230	1.1	20

[a] Micromoles per liter.

degrees. Nitrates, however, are continuously produced through mobilization of nitrogen and subsequent nitrification.

Sparingly soluble salts

The solubility of certain compounds is very low and the total amount dissolved in the soil solution at any time will last for only a short period. For example, phosphorus concentrations are usually well below 1 mg l^{-1}. For a crop containing 100 and more times the amount contained in the soil solution the nutrients removed by plants from the liquid phase must be replaced rapidly and continuously through dissolution from the solid form. The concentration of sparingly soluble nutrients tends to be more constant and the amount dissolved changes with the soil water content.

Exchangeable cations

Cations are adsorbed on negatively charged surfaces of clay minerals and by negatively charged functional groups of the soil organic matter. The negative charges on clay minerals originate from electrically unbalanced lattices and from charges originating at broken edges. The latter are partly neutralized by H^+ ions, which, depending on the pH, will dissociate. Charges on broken edges are thus pH-dependent whereas charges due to unbalanced clay lattices are not in the range of biological pH. Charges on the soil organic matter are also pH-dependent. A cation held at any of these surfaces is called *exchangeable*. The total amount of charges that can be held in exchangeable form is called the *cation exchange capacity (CEC)* (see *Sorption phenomena*) Due to pH-dependent charges, cation exchange capacities can be compared only if they are determined at the same pH. They are often defined and determined at pH 7. Occasionally a distinction is made between a *potential CEC* which is determined at a predefined pH (such as pH 7) and an *effective CEC*, determined at the actual soil pH (Scheffer and Schachtschabel, 2002). The latter varies in the course of time. Many rules and laws have been stated and formulated to describe the ion exchange process (Fried and Broeshart, 1967; Scheffer and Schachtschabel, 2002). There is a tendency for the strength of adsorption of ions to follow the Hofmeister series:

$$\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Rb} < \mathrm{Cs}$$

$$\mathrm{Mg} < \mathrm{Ca} < \mathrm{Sr} < \mathrm{Ba}$$

The scientific basis for this rule is the size of hydrated ions. For example, lithium having the largest hydrated ions is, according to Coulomb's Law, adsorbed the least. Coulomb's Law also explains why polyvalent ions are adsorbed more strongly. There are exceptions to these rules for some ionic species and ion exchangers.

It is now assumed that cations are held as a diffuse ion swarm on clay surfaces and that only very close to the surface a regular arrangement, the Stern layer, is found. The distribution of positively charged ions may obey a Boltzman relation,

$$c = c_0 e^{\frac{-ze\Delta E}{\mathrm{k}T}}$$

where c_0 is the equilibrium concentration in the unaffected soil solution, c the concentration where the electrical potential is ΔE with respect to the equilibrium solution, z the valency of ions, e the elementary charge, k the Boltzman constant, and T the absolute temperature. Negatively charged surfaces repel anions (*negative adsorption*).

The *ratio law* of Schofield (1947) states that the equilibrium between ions in the soil solution and exchangeable ions is not disturbed if in the soil solution all monovalent ions are changed in one ratio and all divalent ions in the square and all trivalent ions in the cube of that ratio (see *Activity ratios*).

Numerous attempts have been made to formulate quantitative laws of ion exchange (Fried and Broeshard, 1967). For example, *Donnan equilibrium* considerations for the exchange between mono- and divalent ions give

$$\frac{M^+_{\mathrm{ad}}}{M^+_{\mathrm{solution}}} = \sqrt{\frac{M^{2+}_{\mathrm{ad}}}{M^{2+}_{\mathrm{solution}}}} = 3\sqrt{\frac{M^{3+}_{\mathrm{ad}}}{M^{3+}_{\mathrm{solution}}}} = \frac{A^-_{\mathrm{solution}}}{A^-_{\mathrm{ad}}} = \mathrm{etc.}$$

where M stands for cations, A for anions, and 'ad' for adsorbed. The difficulty is to find satisfactory expressions of the activities of adsorbed ions. Gapon (1933) derived the following equation

$$\frac{M^+_{\mathrm{ad}}}{M^+_{\mathrm{solution}}} = K_1 \frac{M^{2+}_{\mathrm{ad}}}{\sqrt{M^{2+}_{\mathrm{solution}}}}$$

Adsorbed quantities are measured in me l^{-1}, soluble ions in mMol l^{-1}. Vanselow (1932) and others derived the relation

$$\frac{M^+_{\mathrm{ad}}}{M^+_{\mathrm{solution}}} = K_3 \sqrt{\frac{M^{2+}_{\mathrm{ad}}(M^{2+}_{\mathrm{ad}} + M^+_{\mathrm{ad}})}{M^{2+}_{\mathrm{solution}}}}$$

in which activities of adsorbed ions are expressed by their mole fraction. Over limited ranges of concentrations, ion exchange equations are useful for predicting soluble and exchangeable ion concentrations and, in this way, they assume a role in describing fertility relations. The process of ion exchange is fundamental for soil fertility. Large quantities of nutrients can thereby be kept in soils in an available form without causing salinity. The nature of exchangeable ions has other effects besides its role in plant nutrition. Clay platelets, containing high amounts of exchangeable sodium, are often highly dispersed, causing poor soil structure, which in turn is a major cause of infertility in alkali soils.

Anion exchange

Anions are repelled by negatively charged surfaces. This phenomenon is called *negative adsorption* (see *Exchange phenomena*). However, soils also exhibit anion exchange capacities. Some anions (nitrates, chlorides) are adsorbed weakly or not at all, whereas phosphates interact strongly with the solid phase and sulfates take an intermediate position.

Anion exchange occurs at positively charged sites resulting from the association of H ions with clay minerals and iron and aluminum hydroxides as well as at positively charged NH_2^+ and NH_3^+ groups of soil organic matter. Besides this non-specific adsorption, certain nutrients such as phosphates are held very tightly due to an exchange of ligands. In the following example the phosphate exchanges for the –OH_2 group:

$$(\mathrm{Al,Fe})\text{-}\mathrm{OH_2} + \mathrm{H_2PO_4} \rightleftharpoons (\mathrm{Al,Fe})\text{-}\mathrm{O\text{-}PO(OH)_2} + \mathrm{H_2O}$$

Non-exchangeable, fixed nutrients

Potassium and ammonium ions, due to their ionic size, are fixed between layers of illitic and, to a lesser extent, between some other 2:1 clay minerals. These fixed ions are no longer exchangeable but are slowly released to the soil solution over periods in the order of months and thus add to the nutrient supply of plants. Cesium is strongly fixed by the same mechanism, which greatly reduces groundwater contamination or plant uptake after nuclear fallout. The term *fixation* is also applied when other nutrients react with soil constituents, which renders them more difficultly available. Phosphate fertilizers are fixed through reactions with calcium, aluminum, and iron compounds and fixation processes are also a problem with micronutrients.

Minerals of the parent material

In many soils large quantities of nutrient elements persist in forms originally present in soil parent materials. These nutrients become available only slowly through the decomposition of minerals. This group of nutrients was the principal source for the native vegetation, but the processes of release are too slow to furnish adequate nutrients for crop production.

Airspace

The airspace is also a nutrient compartment. It contains nitrogen gas for biological nitrogen fixation – probably never deficient – and oxygen for respiration – which can be lacking (aeration).

Organic matter

Nutrients can be released from and immobilized by soil organic matter. The two processes are referred to as *mobilization* and *immobilization* (see *Nitrogen cycle*; Figure S46). Soils contain between 600 and 12 000 kg ha^{-1} nitrogen of which usually about 98% is in organic form. With an annual release rate of 2.5%, a substantial fraction of the crop's requirement could temporarily be supplied by the organic fraction. In order to sustain the soil nitrogen level, however, an amount of nitrogen equivalent to all losses (crop removal, leaching, denitrification) must be added through fertilization, biological nitrogen fixation, influx via air pollution etc. Whether mobilization or immobilization occurs depends on the C:N ratio of the organic matter). Both mineralization and plant growth are stimulated by high temperatures.

Various methods have been proposed to assess in advance the amount of nitrogen that could be mobilized. Various extractants such as solutions of potassium permanganate, electroultafiltration (EUF), incubations and mathematical models have

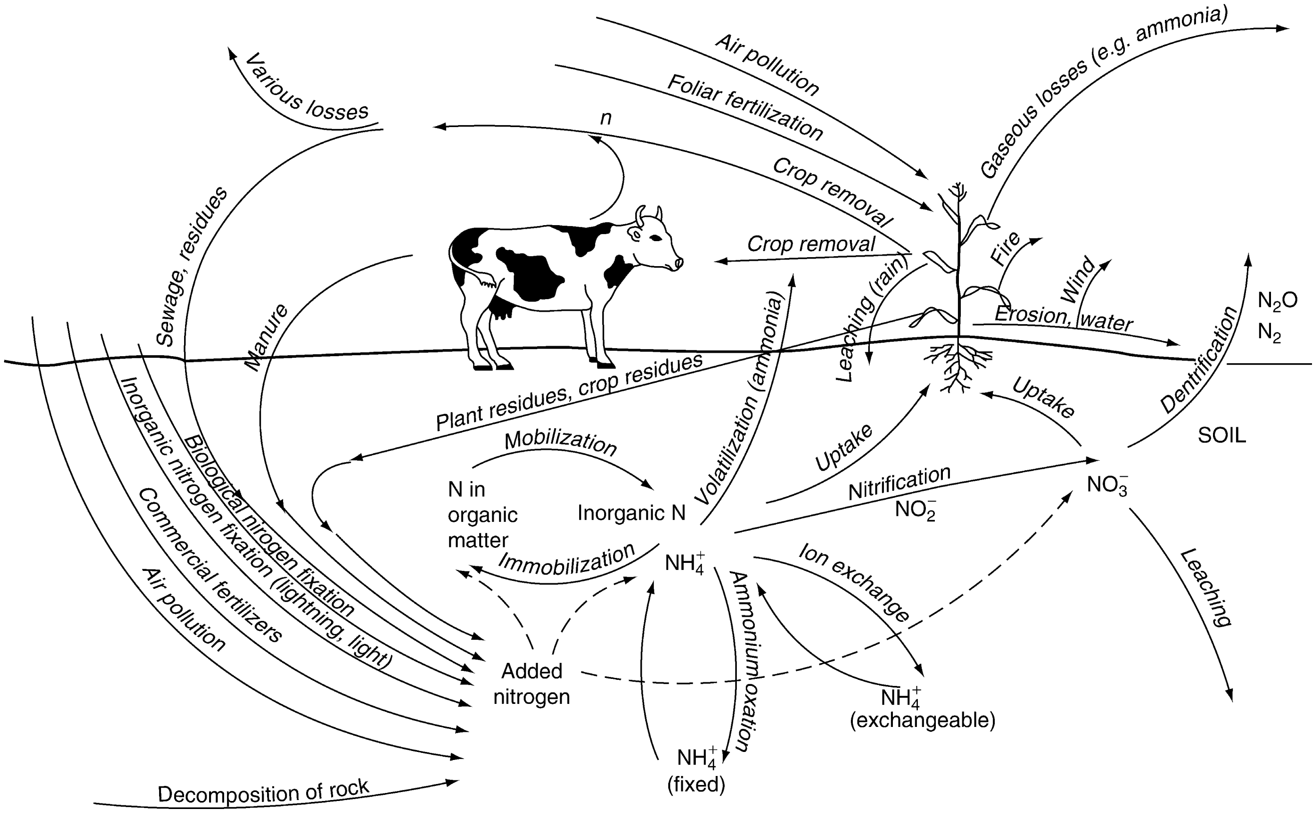


Figure S46 The nitrogen cycle. Processes are indicated in *italics*.

been suggested, none of which is fully satisfactory. A first order reaction is usually used for calculations to describe the mineralization rate of nitrogen:

$$\frac{dN}{dt} = -kN$$

where N represents the nitrogen content and t the time. If nitrogen is added to the soil as organic debris, manure or compost, a term kA has to be added to the above equation, where k represents the fraction of the added organic nitrogen A that eventually ends up in humus. This equation states that the rate of mobilization is proportional to the concentration of organic nitrogen. Effects of climate, soil type etc. are included in the rate constant.

A zero order equation has also been proposed (Paul and Clark, 1996):

$$\frac{dN}{dt} = k$$

This equation describes a situation in which mobilization is independent of the concentration of organic matter. It applies to a situation in which a constant concentration of microorganisms is found in an abundance of substrate. Reaction rates would then be saturated.

pH-fertility relations

Plant communities on basic soils are strikingly different from those on acid soils. These associations could be due to the different hydrogen and OH ion concentrations that interfere with plant metabolism, but most effects of differing acidity result from changes in physical, chemical and biological conditions of soils. Consequently, pH is one of the most valuable indicators of soil fertility. The pH is a measure of the hydrogen ion concentration [H^+] or, more precisely, of hydrogen ion activity (H^+). It is defined as

$$p\text{H} = -\log(H^+)$$

The pH is measured either electrometrically with the glass electrode or colorimetrically with dyes which dissociate in the pH range to be measured and which have differently colored undissociated and dissociated forms. The measured pH increases with the water:soil ratio (suspension effect). In European countries, the pH is often measured in a salt solution (e.g., 0.01 m $CaCl_2$, 1 m KCl). These values are usually lower by about half a pH unit than the pH(H_2O). They are designated as pH(KCl) and pH($CaCl_2$).

Practically all soils fall in the pH range of very strongly acid (pH 3) to moderately basic (pH 9) with rare extremes as low as 2 and as high as 11 (see *Acidity*; *Reaction*).

Soil acidity develops from the ion exchange of protons originating from the dissociation of water with cations of the parent material and a subsequent leaching of the released cations. This process is greatly enhanced when water contains dissolved CO_2 and when CO_2 is given off by respiration of roots and soil microorganisms. Plant detritus e.g., of spruce and pine tend to acidify soils through organic acids. Oxidation of inorganic compounds such as iron sulfides to sulfuric acid sometimes cause problems in rice soils when they dry out before harvesting. Fertilization too can produce acidities. When nitrogen is fertilized in the ammonium form, most nutrients are supplied and taken up as cations. Electroneutrality is maintained in the soil solution by an increase in protons. If, on the other hand, the ammonium is nitrified, acidity is also produced. At extremely low pH values (below 4.5 to 4), direct plant injury through interactions with hydrogen ions is suspected. For example, hydrogen ions interfere with the uptake of essential nutrient elements such as potassium.

In strongly acid soils, concentrations of aluminum, manganese and iron can reach toxic levels. For example, the solubility of iron or aluminum increases a thousand fold for each unit drop of pH. In acid soils, aluminum, not hydrogen, is believed to be the dominating exchangeable cation. Aluminum causes injuries to roots, and relatively little is usually translocated to plant tops. It interferes with the nutrition of many other elements, in particular phosphorus, and also induces wilting of intact plants. On the other hand, it improves the keeping quality of cut flowers. Sometimes concentrations of manganese reach toxic levels below pH 5. In contrast to aluminum, manganese is readily translocated into leaves. Symptoms of manganese toxicity often resemble those of iron deficiency. Because root growth is reduced through aluminum and manganese toxicity, unfavorable nutritional conditions prevail in acid soils, not only because of a reduced availability of nutrients, but also because plants exploit smaller volumes of soil. Increased acidity resulting from air pollution (acid rain, e.g., sulfate, nitrate) and higher availability of Al and Mn has been suggested as a cause for the forest decline in several countries.

Levels of nutrient cations (calcium, magnesium, and potassium) are also characteristically low in acid soils. Most such soils have been strongly leached and are generally of low fertility. The degree of base saturation is low, possibly below critical levels required for optimum crop production. Indications are that yields of sensitive crops such as alfalfa and many other legumes are reduced in some soils if base saturation is below 70%. Penetration of the soil by plant roots is also restricted by very low levels of calcium.

High pH values are found in dry climates when exchange sites on clays are covered with alkali ions, usually Na ions with soil solutions often containing bicarbonate as an anion.

The solubility (availability) of many nutrients is a function of pH. In moderately to strongly acid soils, phosphates become less available through interactions with iron and aluminum compounds. At high pH values, phosphates become increasingly insoluble because of interactions with calcium forming apatites and other precipitates. Consequently, the highest solubility of many other nutrients is also affected by pH. Most become more soluble (available) under acid conditions (zinc, copper, manganese, iron). Molybdenum is an exception with its availability increasing with increasing pH. Many biological processes depend on the soil pH. Nitrogen fixation (see *Nitrogen cycle*) and nitrification are largely but not completely inhibited at low pH values. Bacteria dominate the soil flora at neutral and basic pH values, whereas the relative importance of fungi increases in acid soils. Adjustment of soil pH can even be used to control plant diseases. Potato scab, caused by an actinomycete, is less severe under acid conditions. Earthworms disappear when calcium is leached and soils become acid.

In practice, the pH is increased by liming. Dolomitic limestone also improves the status of magnesium in soils. Soils of excessively high pH are remedied by adding sulfur, sulfuric acid, suitable fertilizers and other compounds that produce acidity. There is no single optimum pH value for soils. Liming to produce too high a pH might induce manganese deficiency and excessive decomposition of organic matter. Light sandy soils should not be limed to above a pH of about 5.5, whereas a heavy soil can be adjusted to pH 6. Factors like potato scab must be considered.

Soil organic matter and fertility

Although soil organic matter is not essential for plant growth and development – plants can be grown equally well in hydroponic systems – experience and research data point to an eminently important role of soil organic matter. Productivity often increases with the content of soil organic matter. This is well illustrated by simultaneous declines in productivity and soil organic matter after the native forest and grassland vegetation in North America had been cleared for the cultivation of crops (Doran and Smith, 1987). Increased erosion and reduced nutrient supplies were two of the consequences. Whereas the latter problem can be remedied through chemical fertilizers, the former is difficult to overcome through simple management procedures. It is not only the quantity but also the quality that is relevant for the effect of soil organic matter. Functions of soil organic matter are manifold and usually beneficial for crop production and soil conservation.

Effect on soil physical conditions

Organic matter is an important binding agent through which elementary soil particles are joined to form larger aggregates. The resulting ameliorated porosity improves soil water relations, aeration and root penetration. The risk of erosion is reduced and, due to the generally darker color, soils may be warmer which is often beneficial.

Nutritional aspects of soil organic matter

Plant nutrition profits in many respects from soil organic matter:

Ion exchange

Soil organic matter is a potent ion exchanger of equal importance to that of clays. Large quantities of nutrients can be held in a readily exchangeable, and thus available, form without causing salinity problems. The exchange capacity is pH dependent. Cation exchange is more important, but exchange sites for anions also exist.

Mobilization-immobilization of nutrients

Decomposition of soil organic matter by microorganisms frees nutrients, which are then available for plants. The major interest is usually in soil nitrogen, but soil organic matter also stores other nutrients such as phosphorus and sulfur. The CO_2 released during decomposition diffuses out of the soil and may be taken up by plant leaves and used for photosynthesis before escaping into the free atmosphere. Immobilization of nutrients, i.e., incorporation of nutrients into insoluble soil organic matter by microorganisms, reduces leaching losses, especially of nitrate, and volatilization losses (especially of ammonia). On the negative side of the mobilization-immobilization cycle, there is an increased risk of losses after mobilization and a deficiency of nutrients after immobilization.

Complex formation

Some nutrients, in particular zinc, iron, and copper, form water-soluble complexes with low molecular organic substances.

Biological nitrogen fixation (BNF)

A most important function of living soil organic matter is the fixing of atmospheric nitrogen by certain microorganisms, thus making it available for higher plants.

Factor of soil formation

Soil organisms are an important factor of soil formation and, therefore, also modify the nutrient supply pattern. Respiration, be it from soil microorganisms or from roots, acidifies the soil and enhances the release of nutrient cations from original soil minerals. These processes are intensified by complexing and chelating substances exuded from living soil organic matter.

Fixation of nutrients

Some nutrients, especially copper, can be held very tightly by soil organic matter. These processes are probably more often deleterious since they may result in nutrient deficiencies.

Pests, pathogens, beneficial organisms

Living soil organic matter comprises a large number of species, which are detrimental to crop production and thus affect soil fertility in a negative way. Aside from the above-mentioned beneficial nutritional effects, many species of soil microorganisms interfere with pests and pathogens and are thus an important aspect of soil fertility.

Breakdown of toxic organic substances

Nearly all-organic substances are decomposed by soil organisms. The soil, therefore, plays an important role in the sanitation of the environment.

Salinity, alkalinity and soil fertility

Salinized soils cover about 7% of the Earth's surface. More important, however, is that about half of the irrigated land is salinized or is threatened to become so. Irrigation is usually applied in dry climates, where otherwise excellent growing conditions exist. Investments are high in irrigated agriculture. Hence, salinization poses a serious threat to a valuable production system. Soils become saline when excessive soluble salts are added to soils and not removed by leaching or other means. Decomposition of parent material, especially of marine origin, and import by river systems or by rainfall near oceans can lead to salinity. In irrigated agriculture, many tons of salts can be added yearly to each hectare of land and cause salinity if salts are not periodically removed by leaching and drainage. The groundwater often rises in irrigated soils to a level where the capillary rise of water becomes important. Water evaporates at the soil surface leaving salts behind resulting in a saline crust. In humid regions, salinity may result from applications of deicing salts to snow-covered highways. Excessive local applications of fertilizers have also caused salt injuries to plants. Saltwater intrusion along sea shores may also cause occasional salinity problems.

Saline and *nonsaline* soils are distinguished on the basis of electrical conductivity of the saturation extract (water is added until soil pores are just filled; the solution is then extracted, and the specific electrical conductivity is measured). Units for the specific conductivity are now S m^{-1}, formerly Mhos m^{-1}). A conductivity of 2 mS cm^{-1} (= 2 dS m^{-1}, deci-S per meter), or sometimes even less, is sufficient to cause yield reductions in the most sensitive plants. In an *alkali* soil, more than 15% of the cation exchange capacity is saturated with alkali ions, most often sodium. These critical values have been established, because experience showed that in alkali soils the structure deteriorates and impedes crop production when these limits are exceeded. The critical value of 15% for exchangeable sodium is not universally valid since the stability of soil structure also depends on the concentration of solutes in the soil solution.

On average, the electrical conductivity (EC) is related to the osmotic pressure (OP) according to the following empirical relation:

$$OP = 0.036 \times EC$$

where OP is measured in MPa and EC in mS cm^{-1}. For the total amount of dissolved solids (TDS) in mg l^{-1} the following approximate relation is used

$$TDS = 640 \times EC$$

In reality, deviations from this rule can be expected. The assessment of soil salinity has become easier and more efficient through the development of remote sensing methods (Lesch et al., 1992).

Plant responses

Salinity first causes a general reduction of growth, followed by a foliar necrosis starting at the leaf tip and margins. Based on yield reductions (by 10, 25, or 50%), tolerance classifications have been established by the U.S. Salinity Laboratory. A selection of them is shown in Table S10. Among fruit crops, date palms are highly tolerant; pomegranate, fig, olive, grape and cantaloupe have medium tolerance; pear, apple orange, grapefruit, prune, plum, almond, apricot, peach, strawberry, lemon, and avocado show low salt tolerance (Rai and Takabe, 2006). More recently salt injury is expressed in terms of a threshold value and percentage yield decrease with increasing salinity after the threshold has been exceeded. Threshold values of 1 to about 9 mS cm^{-1} and slopes from about 3 to 30 percent per mS cm^{-1} have been reported (Rhodes and Loveday, 1990). A high threshold and a low slope indicate a tolerant plant. At least part of the salinity injury can be attributed to unfavorable water relations. Ion competition during uptake of essential nutrients is another possible mechanism of salt injury. Excessive sodium and chloride concentrations within plant cells may interfere with the normal course of biochemical and biophysical processes.

Table S10 Salt tolerance of crops

EC[a] with 50% yield reduction	Field crops vegetable crops	Forage crops
19		
18	Barley	Crested and tall wheat grass, Bermuda grass
17		
16	Sugar beet, cotton	
15		
14	Safflower, wheat	Tall fescue
13		Barley hay
12	Sorghum	Perennial rye, Harding grass
11		Beardless wild rye
10	Soybean, sesbania	Birdsfoot trefoil
9	Rice	
8	Spinach, tomato, broccoli	Alfalfa, orchard grass
7	Corn	
	Cabbage	
6	Broadbean, flax	Meadow foxtail
	Potato, corn, sweetpotato	
5	Lettuce, bell pepper	
4	Onion, carrot	Clover, alsike and red
3		Bean
2		Bean

[a] EC – electrical conductivity in mS cm^{-1}.

The hazards of alkali (sodic) soils are the unfavorable chemical and physical conditions rather than excess sodium. Growth is usually inhibited and plants are stunted, but the foliage is often dark green, although chlorotic leaves can also be observed. Sodic soils tend to be dispersed (deflocculated) so that the primary soil particles are separated from each other and aggregation is poor. Water penetration rates into soil are smaller by several orders of magnitude in comparison with soils low in sodium. Aeration is poor, and plant roots suffer from oxygen deficiency. The pH values of sodic soils are frequently high resulting in unfavorable chemical conditions for soil fertility. Concentrations of carbonate ions reach levels, which are high enough to induce calcium deficiency through precipitation of calcium carbonate. At pH values above 10.5, direct injuries from high OH-ion levels may be expected, and aluminum toxicity is possible due to the formation of aluminate anions. Iron, zinc, and phosphorus deficiencies are not uncommon. The oxidation of nitrite to nitrate is inhibited more than that of ammonium to nitrite leading to temporary accumulation at toxic levels of nitrites after fertilization with ammonium-nitrogen.

Some injuries can be attributed to specific ions. For example, chloride causes necrotic tips in leaves of avocado trees. Excessive amounts of boron occasionally cause necrosis in tips, margins and interveinal areas of leaves. This toxicity is also associated with arid climates. However, boron concentrations in the soil solution are too low to have a substantial effect on the soil water potential.

Assessment of irrigation water quality

River and ground water in arid climates often contain substantial amounts of salts. It is necessary to predict salinization and alkalinization hazards from the concentration and composition of the irrigation water. A problem of salinization may be anticipated for sensitive plants with electrical conductivities exceeding 0.25 mS cm^{-1} corresponding to a total salt content of 160 mg l^{-1}. The sodium adsorption ratio (*SAR*) has been found useful for the alkalinization risk:

$$SAR = -\frac{\mathrm{N}a}{\sqrt{\frac{\mathrm{Ca}+\mathrm{Mg}}{2}}}$$

According to the Gapon Equation, the *SAR* fixes the exchangeable sodium percentage when equilibrium is established. Thus, an analysis of Na, Ca, Mg permits a prediction of the alkalinization hazard. *SAR* values below 10 are adequate under nonsaline conditions, whereas *SAR* values above 18 require chemical amendments. Gypsum is used most frequently to supply calcium for ion exchange.

Management

Management practices to prevent and correct salinity and alkalinity are of prime importance to irrigated agriculture in warm arid regions. As a rule, excess water must be added above that required for consumptive use by plants in order to leach salts below the root zone. Formulas to estimate leaching requirements are available (see *Leaching*). The rise of the water table into the root zone must be prevented through adequate drainage. Many existing saline soils can be improved by leaching. A low exchangeable sodium percentage and a high solute concentration of the soil solution favor a good soil structure. Therefore, special care is required in improving saline soils by leaching salts, because removal of soluble salts without first reducing the exchangeable sodium percentage can lead to highly undesirable soil structures. The exchangeable sodium percentage can be lowered before (or during) leaching by adding calcium salts (gypsum) or acid formers (sulfur, sulfuric acid, iron sulfates, organic matter), which dissolve calcium carbonates that are often, present in such soils.

Economic losses can sometimes be avoided, or at least minimized, by other management practices in crop production. Use of salt tolerant crops has met with limited success. Planting of a crop can also avoid soils with the highest salinity. Saline conditions are usually patchy or spotty, as, for example, the concentration of salt due to capillary rise may occur at the tops of ridges between irrigation furrows. The sides of ridges or furrows, where salts accumulate to a lesser extent, should be used for planting crops.

Toxic elements

Almost every element can be toxic to plants if available in high enough concentrations in soils. Toxic levels of elements in soils are due to natural sources and/or to human activity (see *Pollution*).

Examples of more commonly occurring toxic elements: boron toxicity is a common problem in arid and semiarid regions. Boron concentrations in the soil solution of 1 mg l^{-1} can be harmful and cause foliar injuries in older leaves. However, crop plants seem to tolerate higher levels of boron before substantial yield reductions are observed. Irrigation waters from wells that penetrate marine deposits are often high enough in boron to cause problems. Aluminum, iron, and manganese may be toxic in strongly acid soils. Selenium can be toxic to animals in semiarid regions where it may be found in concentrations of up to 1% in certain plants, e.g., species of *Astragalus*, *Xylorrhiza*, *Oonopisi*, and *Stanleva*. Animals grazing on such soils suffer from what is called "alkali" disease. Concentrations of molybdenum are occasionally high enough to cause diseases that are known locally under various names such as the "teart disease". Nickel toxicity, and less frequently chromium toxicity, contribute to the low productivity of soils derived from serpentine. Low phosphorus and molybdenum and high magnesium-calcium ratios also contribute to the low fertility of such soils.

Toxic concentrations of some elements originate in soils from human activities. Repeated applications of Bordeaux sprays as fungicides have resulted in copper toxicity in places. Similarly, arsenic toxicities have followed continued application of arsenical sprays and dusts. Heavy metals such as lead, cadmium and zinc have been added to soils near smelters, and fluorine toxicities have been reported near installations processing aluminum, iron and phosphate ores. Awareness has grown during the past two decades of the need to protect soils from contaminants in fertilizers. Depending on the source of the ore, rock phosphate fertilizers may contain from 1 to 90 mg kg^{-1} cadmium. Municipal sludge is another important source of soil contaminants not only of cadmium but also of lead, chromium, copper, nickel, mercury, zinc and many organic substances. Many countries have passed legislation in order to protect soils. The U.S. Environmental Protection Agency (EPA) set application limits for various pathways by which pollutants can accumulate in the final destination (human, animal on a pasture, organism in the soil [earthworm], a plant, etc.). For each pathway the risk assessment is based on the most exposed individual (MEI). Examples of such pathways are (U.S. Environmental Protection Agency. 1992):

sludge → soil → plant → human

sludge → soil → plant → animal → human

sludge → soil → plant

There are difficulties in applying this method (Page et al., 1991). Pollutants behave differently depending on the soil; plant uptake and plant sensitivities varying with species and cultivars. It may, therefore, be better to set limits depending on the individual situation (National Research Council, 2002).

Nutrient cycles

In an established, natural soil–plant system, nutrients move through cycles (see *Carbon cycling and formation of soil organic matter*; *Nitrogen cycle*; *Phosphorus cycle*; *Sulfur transformations and fluxes*). For example, Figure S46 represents the most complicated of these cycles, namely the nitrogen cycle. It also serves as a summary for many processes discussed above. The elements are removed from the soil by plant roots, and many are transported and deposited in leaves from whence some nutrients are remobilized and retranslocated to other parts of the plant (mobile nutrients); some are even transferred back to the soil. Additional nutrients are returned to the soil through leaching of plant tissues (by washing out of substances by rain and by falling guttation drops). Substantial quantities are returned to the soil surface in dead plant remains such as annual leaf fall or plant debris from harvests from which nutrients may be leached or liberated by decay. Through resynthesis of organic substances and through renewed decomposition, nutrient elements are kept in a never-ending secondary cycle. Nutrients are also moved about within the soil by water, by animals such as earthworms and insects.

Contents of nutrient stores in different parts of such a cycle differ greatly depending on the type of vegetation. For example, the amount of nitrogen stored in a natural grassland soil (mollisol-udoll) greatly exceeds the nitrogen content in plants growing on these sites, whereas in a tropical rain forest the bulk of nutrients is contained in living trees, and soil storage is minimal. After deforestation of a native tropical rain forest, soil fertility can only be maintained by immediate and adequate fertilization.

Soil-plant communities are open systems. Nutrients are lost permanently through runoff, leaching, and biochemical processes gains result from decomposition of rocks, mobilization through microorganisms, oxidation of atmospheric nitrogen through lightning, and influx from other communities from where it has been eroded or volatilized. In crop communities, some of these net gains and losses are much enhanced; for example, large quantities of nutrient elements are removed in harvested crops. If natural supply sources are insufficient, compensation through commercial fertilizers is necessary. Extensive data on nutrient losses and gains are available (Fried and

Broeshart, 1967, Cooke, 1982, Havlin et al., 2005). Crop removal of major elements (see *Fertilizers, inorganic*) are 50 to several hundred kg ha^{-1} of nitrogen, 10 to 50 kg ha^{-1} of phosphorus, and 50 to several hundred kg ha^{-1} of potassium.

Leaching losses from soils depend, among other factors, on the plant coverage (see *Fertilizers, inorganic*), climatic conditions, especially rainfall, and on the form of nutrients in soils. For example, annual losses of nitrogen range from essentially nil to a few hundred kilograms per hectare. They are especially high from barren soils, even when not fertilized, or when grassland or a leguminous crop has been plowed in. Gaseous losses of nitrogen (N_2, N_2O) through denitrification also range from negligible to the entire amount, which was in the fertilizer (Freney, 1992). Gains of nutrients also have a wide range; nitrogen fixation by root-nodule bacteria, for example, fluctuates from a few to many hundred kilograms per hectare per year. Additions of nitrogen through precipitation in industrialized countries often reach several tens of kg ha^{-1} yr^{-1} and may contribute substantially to the nitrogen cycle at some locations. Additions of sulfur from the atmosphere may exceed crop needs in industrialized areas, although recent efforts to combat air pollution have greatly reduced the influx of atmospheric sulfur to soils. Additions of nutrient elements in airborne dust are also important in some parts of the world such as the portion of Africa just south of the Sahara.

Theoretical aspects

Numerous attempts have been made to formulate laws and rules governing the dependence of yield (production) on various growth factors. Knowledge of such quantitative relations would be an immense help in fertility management. In recent years, computer programs have appeared on the market covering various aspects of fertility management, such as nitrate leaching, and it is expected that they will gain in accuracy for predicting future events. A number of general laws persist in the literature:

- *Liebig's Law of the Minimum* (anticipated by de Saussure) states that plant yield is primarily dependent on the factor that is most in the minimum (Liebig; 1855). Subsequently, the law was interpreted as meaning that this single factor determines production and that the yield increases linearly on increase in this factor until another factor, which is now lacking must be corrected. The law, originally restricted to plant nutrients, has since been extended to all growth factors.
- *Law of declining yield improvement*. Already in the 18th century, Turgot (Finck, 2007) and others realized that yield increases were not linear with the increase in one factor. Extensive research led Mitscherlich in 1909 (Mitscherlich, 1956) to formulate a law of declining yield improvement, which states that improvement of a growth factor increases the yield in proportion to the difference between the maximum and the actual yield. Thus, as the yield increases through nutrient additions this difference becomes smaller and the efficiency of a specific fertilizer addition decreases. In mathematical terms the law is:

$$\frac{dy}{dx} = c_0(A - y)$$

where A represents the maximum yield, y the yield, x the amount of added nutrient, and c_0 is a constant for which quantitative values are available. Integration of the equation gives

$$-\log_e (A - y) = c_0 x + C_0$$

$$-\log_{10} (A - y) = cx + C$$

Since for $x = 0$, $y = 0$ and it follows that $C = -\log A$ and

$$y = A(1 - 10^{-cx})$$

Mitscherlich and his students reported for c

- nitrogen: 0.002 ha kg^{-1}
- potassium: 0.0049 ha kg^{-1}
- phosphorus: 0.013 ha kg^{-1}

For these values, nutrients must be expressed as elements and not as oxides and fertilizer additions in kg per hectare. The original belief of Mitscherlich that these values of c are independent of plant species and other growth factors could not be verified.

The above equations have also been used to determine the content of an available nutrient in soils. Suppose this content be b, then

$$\log(A - y) = \log A - c(x + b)$$

An experiment in which several levels of fertilizer x are applied and the yields y are measured permits a determination of b.

The concept of Mitscherlich has been extended by Baule (Schilling, 1990) to a multiplicity of growth factors with constants $c_1, c_2, \ldots, c_n$:

$$y = A_n(1 - 10^{-c_1x_1})(1 - 10^{-c_2x_2})(\ldots)(1 - 10^{-c_nx_n})$$

A Baule unit is the amount of a factor required to produce 50% of the yield. Further yield increases per Baule unit occur in a geometric fashion; i.e., a Baule unit will increase the yield by half of what is lacking for maximum yield. The simultaneous action of several factors, described by the above Baule rule, states that the fractional yields of each individual factor must be multiplied to give the total yield. Thus if the yield with only factor 1 being deficient is two thirds of the yield under best conditions, the yield with only factor 2 being deficient is three fourths of the maximum, then with both factors 1 and 2 operative at the above levels, the combined effect will give a yield of $y = 2/3 \times 3/4 = 1/2$.

Various improvements of the original Mitscherlich concept have been proposed. For example, the decline in yield with excessive fertilizer applications has been described with a correction factor:

$$y = A(1 - 10^{-cx})10^{-kx^2}$$

Michaelis-Menten kinetic, mathematically identical with Langmuir's adsorption isotherm, also describes a non-linear response with saturation kinetics

$$y = \frac{k_1 x}{1 + k_2 x}$$

where y represents the yield, x the growth factor, and k_1 and k_2 constants.

Success in formulating general laws to show the dependence of yield on growth factors such as quantities of nutrient elements has been modest thus far. These difficulties serve to emphasize the complexity of the soil–plant system, but this should not discourage scientists from making renewed attempts.

A synopsis of individual nutrient fertility aspects

Nitrogen (Figure S46). Content 0.02 to 0.4% in upper soil horizon (20 cm) equal to 600 to 12 000 kg Nha^{-1}, of these usually 95 to 98% in unavailable organic forms. Nitrate and ammonium are the forms taken up by plants. Dynamics: mobilization changes unavailable organic N into available inorganic ammonium-N, immobilization describes the incorporation of ammonium and nitrate nitrogen into unavailable organic N. Critical for the two processes is the C:N ratio. Nitrification is the oxidation of ammonium to nitrite and nitrate by soil bacteria, denitrification the reduction of nitrate to nitrous oxides (laughing gas) and nitrogen gas. In ammonium fixation ammonium ions are held on clays in a non-exchangeable form. In nitrogen fixation, the nitrogen gas of the atmosphere is changed by microorganisms into a plant-available form. Exchangeable ammonium in arable soils is usually low except after fertilization. Gains in nitrogen occur through nitrogen fixation, addition of plant detritus, inorganic and organic fertilizers and rain containing nitrogen compounds from industry and lightning. Losses occur through plant uptake and crop removal, leaching of nitrate, denitrification, volatilization (of ammonia) and erosion.

Phosphorus. Content 0.01 to 0.1% (300 to 3 000 kg ha^{-1}), about half in organic form. The soil solution contains only 0.02 to 0.1 mg l^{-1} P that suffices only for a few hours for plant uptake. Phosphorus must continuously be dissolved and/or mobilized. In acid soils, phosphates are rendered insoluble through reaction with iron and aluminum compounds, in basic soils through precipitation of calcium salts.

Potassium. Content 0.2 to 3% (6 000–90 000 kg ha^{-1} in upper 20 cm), higher in some alkali soils. Concentration in soil solution 1 to 100 mg K l^{-1}, exchangeable K about 100 times larger, usually a few percent of the CEC. Equilibrium usually rapidly established between exchangeable and soluble potassium. Non-exchangeable potassium is fixed between lattices of certain clays. It is slowly released into the soil solution as is potassium held by original soil minerals (micas, K-feldspars).

Calcium. Content 0.1 to 1.5%, higher in soils with limestone or gypsum, which can supply calcium to the soil solution. Concentration in the soil solution 2 to 450 mg l^{-1}, exchangeable calcium 50 to 100 times higher, at pH values above 5 the major exchangeable ion reaching 75 and more % of the CEC.

Magnesium. Content 0.05 to 0.5%, higher in soils containing dolomitic limestone (which can supply calcium and magnesium to the soil solution) or certain silicates such as serpentine. Exchangeable magnesium 2 to 20% of the CEC.

Sulfur. Content in soils 0.01–0.2%, higher in some saline soils. Numerous compounds are present and interchanged through many reactions (Konopka et al., 1986). In soil solution 10 to 100 mg l^{-1}. Oxidation states: sulfate (SO$_4^{2-}$), which is the usual form present in the soil solution and also the form usually taken up by plants; under anaerobic conditions sulfate in soils is reduced to sulfide, (S^{2-}), by microorganisms (*Desulfovibrio*). It is usually precipitated with heavy metals such as iron, it is toxic as free hydrogen sulfide and suspected to cause plant diseases; sulfur, sometimes added to soils to reduce the pH, is oxidized by sulfur bacteria (*Thiobacillus*) to sulfate; sulfur dioxide (SO$_2$) and sulfite (SO$_3^{2-}$) from air pollution, oxidized to sulfates; organic sulfur comprises 60 to 95% of total S (sulfogroups: –SO$_2$H, thiolgroup –SH) (see *Sulfur transformations and fluxes*).

Chlorine. Content variable, from 10 mg l^{-1} to very high in salinized soils. Almost all water soluble. Deficiencies unknown or extremely rare.

Iron. Content in soil 0.5 to 4%, ions: Fe^{2+} and Fe^{3+}, the latter more stable in well aerated soils at typical soil pHs but practically insoluble in the soil solution, under anaerobic conditions increase of the ferrous ion, possibly to toxic levels. Soluble as iron chelates and complexes with organic compounds.

Boron. Content 5 mg kg^{-1} to high, toxic levels (100), in soil solution usually below 1 mg l^{-1}. At biological pH values mainly present as an undissociated molecule. The p*K* is 9.14 for the dissociation

$$\mathrm{H_3BO_3} \rightleftharpoons \mathrm{H_2BO_3^-} + \mathrm{H^+}$$

The boric acid is adsorbed at the solid phase of soils. Deficiencies prevail in humid, toxicities in arid climates.

Manganese. Contents between 0.02 and 0.4%, in the soil solution as Mn^{2+} in the range of 0.01 to 4 mg l^{-1}. The 3-valent form is not stable

$$3\mathrm{Mn^{3+}} + 2\mathrm{H_2O} \rightleftharpoons \mathrm{Mn^{2+}} + \mathrm{MnO_2} + 4\ \mathrm{H^+}$$

MnO$_2$ is insoluble. The solubility of the manganous ion increases with soil acidity and anaerobic conditions as is evident from the following equation:

$$\mathrm{MnO_2} + 4\mathrm{H^+} + 2\mathrm{e^-} \rightleftharpoons \mathrm{Mn^{2+}} + 2\mathrm{H_2O}$$

Zinc. Contents 10 to 100 mg kg^{-1}, higher in contaminated soils, in soil solution (pH 5 to 7.5) 0.001 to 0.4 mg l^{-1}, more soluble a strongly acid pH, in contaminated soils up to 15 mg l^{-1}. At a neutral pH, most of the soil zinc is organically bound, also some Zn^{++} and some ZnOH$^+$ ions. The inorganic Zn form dominates at a pH below 5.

Copper. Contents 3 to 70 mg kg^{-1}, higher in contaminated soils, in soil solution 0.005 to 0.08 mg l^{-1}, usually not much affected by soil pH, around neutral pH often most of the soluble copper present as organic complexes, in acid soils relatively more inorganic Cu; insoluble organic fractions of humus can bind Cu tightly and fix this nutrient in an unavailable form causing Cu deficiencies.

Molybdenum. Contents 0.2 to 5 mg kg^{-1}, in soil solutions 0.002 to 0.08 mg l^{-1}, main form the molybdate ion, at low pH values also less dissociated forms according to the reactions:

$$\begin{aligned} &\mathrm{MoO_4^{2-}} + \mathrm{H^+} \rightleftharpoons \mathrm{HMoO_4^-} && \mathrm{p}K = 4.0 \\ &\mathrm{HMoO_4^-} + \mathrm{H^+} \rightleftharpoons \mathrm{H_2MoO_4} && \mathrm{p}K = 3.6 \end{aligned}$$

Solubilities of most compounds increase with pH, at low pHs fixed through ligand exchange on Fe and Al oxides similar to phosphates, in contrast to phosphates usually no fixation through Ca at high pH.

J. J. Oertli

Bibliography

Cooke, G.W., 1982. *Fertilizing for Maximum Yield*, 3rd edn. London: Granada Publishing, 465 pp.

Doran, J.W., and Smith, M.S., 1987. Organic matter management and utilization of soil and fertilizer nutrients, Chapter 4. In *Soil Fertility and Organic Matter as Critical Components of Production Systems*. *Soil Sci. Soc. Am. Spec. Publ.*, 19: 53–72.

Finck, A., 2007. *Pflanzenernahrung in Stichworten.* Hirt: Kiel, 253 pp.

Freney, J.R., 1992. Transformations and transfers of nitrogen in the plant–soil system. In *Proceedings of the International Symposium on Nutrient*

Management for Sustained Productivity, Vol. 1. Ludhiana, India: Department of Soils, Punjab Agriculutral University, pp. 334–343.

Fried, M., and Broeshart, H., 1967. *The Soil–Plant System in Relation to Inorganic Nutrition.* New York: Academic Press, 358 pp.

Gapon, E.N., 1933. Theory of exchange adsorption in soils. *J. General Chem. (USSR)*, **3**: 144–158.

Havlin, John L., Tisdale, Samuel L., Nelson, Werner L., Beaton, James D., 2005. *Soil Fertility and Fertilizers*: an introduction to nutrient management. 7th edn., Upper Saddle River, N.J.: Pearson Prentice Hall. 515 pp.

Jenny, H., 1941. *Factors of Soil Formation.* New York: McGraw Hill, 281 pp.

Kohnke, H., 1968. *Soil Physics.* New York: McGraw-Hill, 224 pp.

Konopka, A.E., Miller, R.H., and Sommers, L.E., 1986. Microbiology of the sulfur cycle, Chapter 2. In Tabatabai, M.A., ed., *Sulfur in Agriculture, Agronomy,* Vol. 27. Madison, WI: American Society of Agronomy, pp. 23–55.

Lesch, S.M., Rhoades, J.D., Lund, L.J., and Corwin, D.L., 1992. Mapping soil salinity using calibrated electromagnetic measurements. *Soil Sci. Soc. Am. J.*, **56**: 540–548.

von Liebig, J., 1855. *Die Grundsatze der Agrikulurchemie*, 2nd edn. Braunschweig. Mitscherlich, E.A. 1956. Ertragsgesetze. Berlin: Akademie-Verlag.

Macías, Francisco A. 2004. *Allelopathy: chemistry and mode of action of allelochemicals*. Boca Raton, FL: CRC Press. 372 pp.

National Research Council, 2002. *Biosolids Applied to Land. Advancing Standards and Practices*. Washington, D.C.: The National Academies Press, 345 pp.

Noy-Meir, I., and Ginzburg, B., 1967. An analysis of the water potential isotherm in plant tissues. I. The theory. *Aust. J. Biol. Sci.*, **20**: 695–721.

Oertli, J.J., 1971. A whole-system approach to water physiology in plants. *Advances in Frontiers of Plant Science*, New Delhi, India, 283 pp.

Page, A., Chang, A.C., and Logan, T.J., 1991. U.S. ERA standards for the disposal of sewage sludge: present status and suggested revisions. Porceedings second MWRDGC/JSWA technology exchange workshop on municipal sludge management and industrial waste control, Oct. 14–16, Chicago, IL, pp. 69–88.

Paul, E.A., and Clark, F.E., 1996. *Soil Microbiology and Biochemistry*, 2nd edn. San Diego, CA: Academic Press, 340 pp.

Rai, A. K., and Takabe, T. eds., 2006. *Abiotic Stress Tolerance in Plants: toward the improvement of global environment and food.* Dordrecht: Springer. 267 pp.

Rhodes, J.D., and Loveday, J., 1990. Salinity in irrigated agriculture, Chapter 36. In Stewart, B.A., and Nielsen, D.R., eds., *Irrigation of Agricultural Crops. Agronomy,* Vol. 30. Madison, WI: American Society Of Agronomy, pp. 1089–1142.

Scheffer, F., and Schachtschabel, P., 2002. *Lehrbuch der Bodenkunde.* Heidelberg: Spektrum Akademischer Verlag. 528 pp.

Schilling, G., 1990. *Pflanzenernährung und Düngung, Teil 1.* Berlin: Deutscher Landwirtschaftsverlag, 248 pp.

Schjoerring, J.K., 1991. Ammonia emission from the foliage of growing plants, Chapter 12. In Sharkley, T.D., Holland, E.A., and Mooney, H.A., eds., *Trace Gas Emissions by Plants.* New York: Academic Press, pp. 267–292.

Schofield, R.K., 1947. A ratio law governing the equilibrium of cations in solution. Proceedings of the 11th International Congress on Pure and Applied Chemistry, Vol. 3, pp. 257–261.

Schofield, R.K., 1955. Can a precise meaning be given to “available” soil phosphorus. *Soils Fert.*, **18**: 373–375.

United States Environmental Protection Agency, 1992. Technical Support Document for Land Application of Sewage Sludge. Vol. I (Revised). Office of Water. Washington, DC: U.S. Environmental Protection Agency. 821 pp.

Vanselow, A.P., 1932. Equilibria of the base-exchange reactions of bentonites, permutites, soil colloids, and zeolites. *Soil Sci.*, **33**: 95–113.

Cross-references

Acidity
Activity Ratios
Biogeochemical Cycles
Carbon cycling and formation of soil organic matter
Exchange Phenomena
Fertilizers, Inorganic
Fertilizers, Organic
Humic Substances
Labile Pool
Law of the Minimum
Macronutrients
Micronutrients
Nitrogen Cycle
Nutrient Potentials
Particle-size Distribution
Phosphorus Cycle
Plant Nutrients
Reaction
Salt Leaching
Soil Microbiology
Soil Solution
Solute Sorption-Desorption Kinetics
Sorption Phenomena
Structure
Sulfur Transformations and Fluxes
Trace Elements

SOIL HEALTH

See *Health*; *Quality*.

SOIL HORIZON DESIGNATIONS IN THE WRB SOIL CLASSIFICATION SYSTEM

A soil is usually characterized by describing and defining the properties of its horizons. Abbreviated horizon designations, which have a genetic connotation, are used for showing the relationships among horizons within a profile and for comparing horizons among different soils. Horizon designations are therefore an element in the definition of soil units and in the description of representative profiles.

A number of major horizons, known as Master Horizons, are recognized. A distinction must be made between the soil horizon designations used in soil profile descriptions and diagnostic horizons as used in soil classification. The former belong to a nomenclature in which master horizon codes (H, O, A, E, B, C and R) are assigned to the various soil horizons in a soil profile when it is described and interpreted in the field. The choice of horizon code is by personal judgment of the soil surveyor. Diagnostic horizons, on the other hand, are rigidly defined and their presence or absence can be ascertained on the basis of unambiguous field and/or laboratory measurements. Some of the diagnostic horizons in the WRB (World Reference Base) soil correlation system are special forms of A or B horizons, e.g., a ‘*mollic*’ A horizon, or a ‘*ferralic*’ B horizon. Other diagnostic horizons are not necessarily A or B horizons, e.g., a ‘*calcic*’ or a ‘*gypsic*’ horizon.

Master horizons

H

An organic horizon formed or forming from accumulations of organic material deposited on the surface, that is saturated with water for prolonged periods (unless artificially drained). It contains 30 percent or more organic matter if the mineral fraction contains more than 60 percent of clay, 20 percent or more organic

Table S11 Soil horizons

Surface horizons and subsurface horizons at shallow depth	
Anthropogenic horizons	Surface and subsurface horizons resulting from long- continued *'anthropedogenic processes'*, notably deep working, intensive fertilization, addition of earthy materials, irrigation or wet cultivation.
Chernic horizon	Deep, well-structured, blackish surface horizon with a *high base saturation, high organic matter content, strong biological activity and well- developed, usually granular, structure*. Its carbon content is intermediate between a *mollic* horizon and a *histic* horizon.
Folic horizon	Surface horizon, or subsurface horizon at shallow depth, consisting of *well-aerated organic soil material*.
Fulvic horizon	*Thick, black surface horizon* having a *low bulk density* and *high organic carbon content* conditioned by short-range-order minerals (usually *allophane*) and/or *organo-aluminum* complexes
Histic horizon	*(Peaty) surface horizon*, or subsurface horizon occurring at shallow depth, consisting of *organic soil material*.
Melanic horizon	Thick, black surface horizon conditioned by short-range-order minerals (usually *allophane*) and/or *organo-aluminum complexes*. Similar to the fulvic horizon except for a '*melanic index*[1]' of 1.70 or less throughout.
Mollic horizon	Well-structured, *dark* surface horizon with *high base saturation* and *moderate to high organic carbon content*.
Takyric horizon	Finely textured surface horizon consisting of a dense surface crust and a platy lower part; formed under arid conditions in periodically flooded soils.
Umbric horizon	Well-structured, *dark* surface horizon with *low base saturation* and *moderate to high organic matter content*.
Ochric horizon	Surface horizon *without stratification*, which is either *light colored*, or *thin*, or has a *low organic carbon content*, or is *massive and (very) hard when dry*.
Vitric horizon	Surface or subsurface horizon *rich in volcanic glass* and other primary minerals associated with volcanic ejecta.
Yermic horizon	Surface horizon of *rock fragments* ('*desert pavement*') usually, but not always, embedded *in a vesicular crust* and covered by a thin aeolian sand or loess layer.
Subsurface horizons	
Albic horizon	Bleached eluviation horizon with the color of uncoated soil material, usually overlying an illuviation horizon.
Andic horizon	Horizon evolved during *weathering of mainly pyroclastic deposits*; mineral assemblage dominated by short-range-order minerals such as allophone.
Argic horizon	Subsurface horizon having distinctly more clay than the overlying horizon as a result of *illuvial accumulation of clay and/or pedogenetic formation of clay in the subsoil* and/or destruction or selective erosion of clay in the surface soil.
Cambic horizon	Genetically young subsurface horizon showing evidence of alteration relative to underlying horizons: *modified color, removal of carbonates or presence of soil structure*.
Cryic horizon	*Perennially frozen* horizon in *mineral* or *organic soil materials*.
Calcic horizon	Horizon with distinct *calcium carbonate enrichment*.
Duric horizon	Subsurface horizon with *weakly cemented to indurated nodules cemented by silica* (SiO_2) known as '*durinodes*'.
Ferralic horizon	*strongly weathered* horizon in which the clay fraction is dominated by *low activity clays* and the sand fraction by *resistant materials* such as iron-, aluminum-, manganese- and titanium oxides.
Ferric horizon	Subsurface horizon in which *segregation of iron* has taken place to the extent that large mottles or concretions have formed in a matrix that is largely depleted of iron.
Fragic horizon	*Eense, non-cemented* subsurface horizon that can *only* be penetrated by roots and water along natural cracks and streaks.
Gypsic horizon	Horizon with distinct *calcium sulphate enrichment*.
Natric horizon	Subsurface horizon with *more clay than any overlying horizon(s)* and *high exchangeable sodium percentage*; usually dense, with *columnar or prismatic structure*.
Nitic horizon	Clay-rich subsurface horizon with a moderate to strong *polyhedric or nutty structure with shiny ped faces*.
Petrocalcic horizon	Continuous, cemented or induated *calcic* horizon.
Petroduric horizon	Continuous subsurface horizon cemented mainly by *secondary silica* (SiO_2), also known as a '*duripan*'.
Petrogypsic horizon	Cemented horizon containing *secondary accumulations of gypsum* ($CaSO_4 \cdot 2H_2O$).
Petroplinthic horizon	Continuous layer *indurated by iron compounds* and without more than traces of organic matter.
Plinthic horizon	Subsurface horizon consisting of an *iron-rich, humus-poor mixture of kaolinitic clay with quartz* and other constituents, and which *changes irreversibly to a hardpan or to irregular aggregates* on exposure to repeated wetting and drying with free access of oxygen.
Salic horizon	Surface or shallow subsurface horizon containing 1 percent of *readily soluble salts* or more.
Spodic horizon	Dark colored subsurface horizon with *illuvial amorphous substances* composed of *organic matter* and *aluminum, with or without iron*.
Sulfuric horizon	*Extremely acid* subsurface horizon in which *sulphuric acid has formed through oxidation of sulphides*.
Vertic horizon	Subsurface horizon *rich in expanding clays* and having *polished and grooved ped surfaces ('slickensides')*, or *wedge-shaped* or *parallelepiped structural aggregates* formed upon repeated swelling and shrinking.

matter if the mineral fraction contains no clay, or intermediate proportions of organic matter for intermediate contents of clay.

O

An organic horizon formed or forming from accumulations of organic material deposited on the surface, that is not saturated with water for more than a few days a year and contains 35 percent or more organic matter. O horizons are the organic horizons that develop on top of some mineral soils – for example, the "raw humus" mat which covers certain acid soils. The organic material in O horizons is generally poorly decomposed and occurs under naturally well-drained conditions.

A

A mineral horizon formed or forming at or adjacent to the surface that either:

a. shows an accumulation of humified organic matter intimately associated with the mineral fraction, or
b. has a morphology acquired by soil formation but lacks the properties of E and B horizons.

The organic matter in A horizons is well decomposed and is either distributed as fine particles or is present as coatings on the mineral particles. As a result, A horizons are normally darker than the adjacent underlying horizons. In warm, arid climates where there is only slight or virtually no accumulation of organic matter, surface horizons may be less dark than adjacent underlying horizons. If the surface horizon has a morphology distinct from that of the assumed parent material and lacks features characteristic of E and B horizons, it is designated as an A horizon on account of its surface location.

E

A mineral horizon showing a concentration of sand and silt fractions high in resistant minerals, resulting from a loss of silicate clay, iron or aluminum or some combination of both.

E horizons are eluvial horizons, which generally underlie an H, O, or A horizon from which they are normally differentiated by a lower content of organic matter and a lighter color. From an underlying B horizon, an E horizon is commonly differentiated by colors of higher value or lower chroma, or by coarser texture, or both.

B

A mineral horizon in which rock structure is obliterated or is but faintly evident, characterized by one or more of the following features:

a. an illuvial concentration of silicate clay, iron, aluminum, or humus, alone or in combinations;
b. a residual concentration of sesquioxides relative to source materials;
c. an alteration of material from its original condition to the extent that silicate clays are formed, oxides are liberated, or both, or granular, blocky, or prismatic structure is formed.

B horizons may differ greatly. It is generally necessary to establish the relationship between overlying and underlying horizons and to estimate how a B horizon has been formed before it can be identified. Consequently, B horizons generally need to be qualified by a suffix to have sufficient connotation in a profile description. A 'humus B' horizon is designated as Bh, an 'iron B' as Bs, a 'textural B' as Bt, a 'color B' as Bw. B horizons are not defined in the quantitative terms required for diagnostic purposes. B horizons may show accumulations of carbonates, of gypsum or of other more soluble salts. Such accumulations, however, do not by themselves distinguish B horizons.

C

A mineral horizon (or layer) of unconsolidated material from which the solum is presumed to have formed and which does not show properties found in any other master horizon. Traditionally, C has been used to designate 'parent material'. The designation C is therefore used for the unconsolidated material underlying the solum that does not meet the requirements of the A, E or B designations. This material may, however, have been altered by chemical weathering below the soil and may even bc highly weathered ('preweathered').

R

A layer of continuous indurated rock. The rock of R layers is sufficiently coherent when moist to make hand digging with a spade impractical (after Fitzpatrick, 1980).

Diagnostic horizons, properties and materials

The soil classification units of the FAO system are defined in terms of measurable and observable "diagnostic horizons", the basic identifiers in soil classification. Diagnostic horizons are defined by characteristic '*soil properties*' and/or '*soil materials*' (after FAO, 2001) (see Table S11).

Arieh Singer

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. In Driessen, P., Deckers, J., and Nachtergade, F., eds., World Soil Resources Reports #94. Rome: FAO.

Fitzpatrick, E.A., 1980. *Soils – Their Formation, Classification and Distribution.* London: Longman, 353 pp.

SOIL MAPPING AND SURVEY

The *soil universe*, produced by destructive and synthetic forces, is the biochemically altered upper portion of the regolith. The *regolith* is the unconsolidated earthy materials overlying hard bedrock that weathered from the underlying bedrock, *residuum*, or was moved into place by wind, *loess*; by gravity, *colluvium*; by water, *alluvium*; or by ice, *glacial till*. Soil forms the link between the organic and inorganic worlds and provides support for engineering structures; i.e., buildings and roads.

Pedology and edaphology are two approaches to the study of soil (Brady, 1990). *Pedology* (Gr. *pedon,* soil or earth) is the study of soils as geographic bodies produced by physical and chemical actions of climate, organisms, and relief on parent material over a relative period of time. Pedologists observe basic morphological, physical, chemical, mineralogical, and biological properties and use these data to classify and map geographic distributions of specific kinds of soil. *Edaphology* (Gr. *edaphos,* soil or ground) is the study of soil as a medium for plant growth. Edaphologists are interested mainly in soil fertility and water availability. This article considers soil from the pedologist's viewpoint because pedologic data are important considerations in the management of soil for plant growth and for engineering purposes.

Soil mapping

The study of geographic bodies within the soil universe necessitates an evaluation of property distributions rather than the study of natural individuals, such as plants and animals. Soil exists in a multivariate continuous universe because numerous properties vary at different rates from point A to point B with few discontinuities. Therefore, soil lacks natural boundaries and discrete or natural individuals. Consequently, pedologists are forced to create artificial boundaries, individuals, and classes (taxa) by the arbitrary definition of important soil property ranges. Ranges of properties defined for the order, suborder, great group, subgroup, and family categories in Soil Taxonomy (Soil Survey Staff, 1975) are used to define soil series or artificial individuals. Artificially defined soil series within the continuous soil universe are not independent of the observer and contrast sharply with natural individuals within the particulate universes of plants and animals (Knox, 1965).

Soil Surveyors use maximum lateral rates of change in soil and landscape properties to delineate natural soil landscape units or soil map units (Schelling, 1970). An example of using the maximum rates of change in slope gradient to delineate the landscape into natural units of ridge summit, side slope, and toe slope is shown in Figure S47. Boundaries of these landscape units occur naturally at 300 and 700 feet because these maximum rates of change are independent of the observer.

Soils within natural landscape units have the narrowest possible ranges in soil properties because the soil parent material within these units has been subjected to similar physical and chemical actions of climate on similar relief with similar influence of organisms over a relatively similar amount of time. This soil-landscape model forms the basis for the soil-landscape paradigm described by Hudson (1992). For example, ridge summits are the most stable part of the landscape, and soils are relatively older and have greater differentiation of horizons. Side slopes are relatively younger than ridge summits because they are primarily erosional surfaces and generally have soils that lack upper horizons because they have been removed by erosion. Toe slopes generally receive sediments eroded from side slopes and ridge summits. Toe slopes and flood plains are relatively the youngest segments of the landscape, and soils lack well defined horizons. In addition, water moves across these landscape units at considerably different rates. Water runs off the ridge summit and side slopes at different rates, and accumulates on toe slopes. By differentiating soil landscape units, soil surveyors produce soil map units with narrowest possible ranges in soil properties and with considerably different ages, pedon characteristics, and water movements.

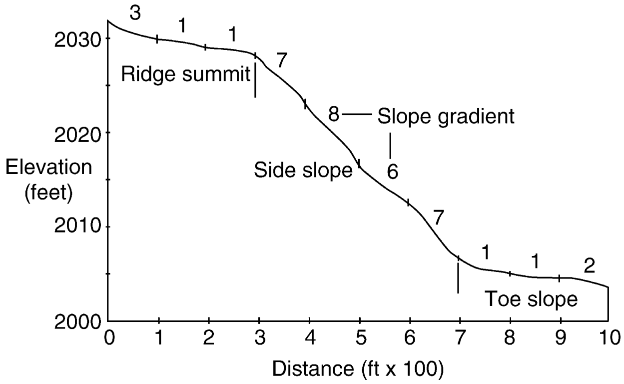


Figure S47 Natural landscape units (ridge summit, side slope, and toe slope) delineated by maximum rates of change in slope gradient at 300 and 700 feet.

An example of a soil map based on the delineation of natural soil landscape units is given in Figure S48, which represents a small area around the village of Midway in Greene County, Virginia (Thomas and Crawford, 1986). Ridge summits are represented by the soil map symbol, E1B – Elioak loam, 2 to 7 percent slope; side slopes by EnC – Elioak clay loam, 7 to 15 percent slopes, severely eroded and by E1C – Elioak loam, 7 to 15 percent slopes; and toe slopes and flood plains by MvB – Meadowville fine sandy loam, 2 to 7 percent slopes.

The map symbol, *E1B*, represents the Elioak soil series, a member of the *clayey, kaolinitic, mesic family of typic hapludults*. The Elioak series is given as an example of an artificial individual created by ranges defined by Soil Taxonomy (Soil Survey Staff, 1975) for (*i*) the *clayey* family particle-size class, the soil has more than 35 percent clay (particles <0.002 mm) in the upper 50 cm of the subsoil; (*ii*) the *kaolinitic* family mineralogy class, the upper 50 cm of the subsoil is dominated by the clay mineral kaolinite; (*iii*) the *mesic* family temperature class, the upper meter of the soil has an annual temperature between 8 and 15 °C and mean summer and mean winter temperatures that differ by more than 5 °C; (*iv*) the *ultisol* order (*ults*), the soil has a subsoil with clay accumulation and low saturation with metallic cations of Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} at 1.25 m below the upper boundary of the subsoil;

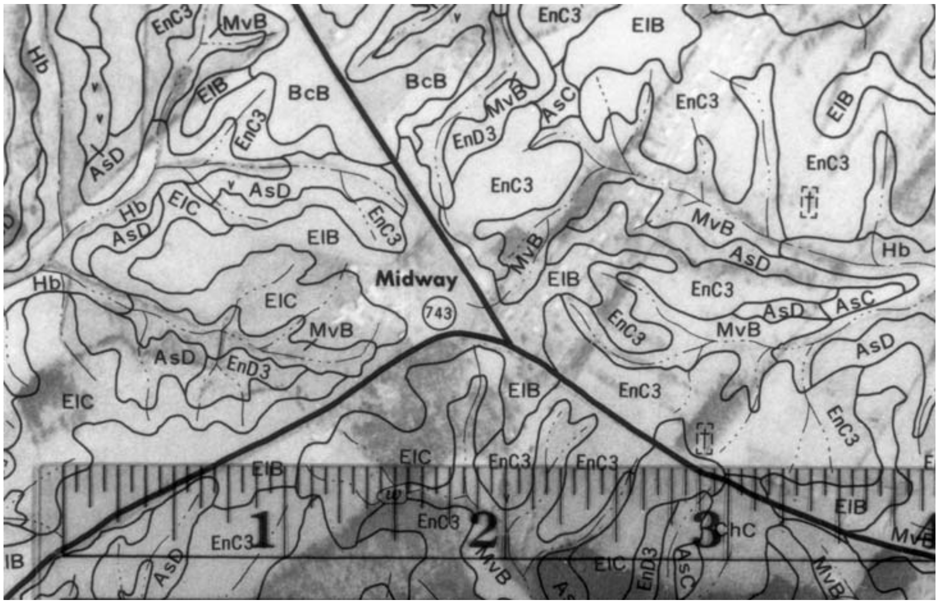


Figure S48 Example of a soil map around Midway in Greene County, Virginia (Thomas and Crawford, 1986). Scale is in inches, and 1 inch represents about 1320 feet on the land surface.

(*v*) the *udults* suborder, the soil has a udic moisture regime; i.e., is moist in most years or are not dry for more than 90 days cumulative; (*vi*) the *hapludults* great group, the soil is a normal representative of the great group; (*vii*) the *typic hapludults* subgroup, the soil is a typical representative of the order.

Soil series

The following properties defined by the Soil Survey Manual (Soil Survey Staff, 1992) are currently used by the National Cooperative Soil Survey to describe landscape features and soil horizons or layers within a soil pedon:

- setting
- slope
- field water characterization
- drainage class
- flooding
  - free water occurrence
  - hydrologic soil groups
  - ponding
- designations for horizons and layers
- depth to and thickness of horizons or layers
- matrix Munsell color
- USDA-particle-size distribution
- mottle Munsell color(s)
- structure
- consistence (dry, moist, wet)
- roots
- pores
- plinthite
- internal surface feature
  - clay films
  - clay bridges
  - sand or silt coatings
  - other coatings (iron, aluminum, or manganese oxides, organic matter, salts, carbonates, etc.)
- stress surfaces (slickensides)
- concentrations
- mica
- rock fragments in the soil or layer
- brittleness
- selected chemical properties
  - salinity
  - sodicity
  - gypsum
  - sulfides
  - reaction (pH)
- boundary of horizons and layers

The following examples of artificial individuals created by human intellect for the purpose of classifying soils are quoted verbatim from Thomas and Crawford (1986):

- *Elioak series:* The soils of the Elioak series are very deep and well drained. They formed in materials weathered from granite, gneiss, phyllite, mica schist, and graywacke sandstone. They are on uplands (ridge summits and side slopes) in the Piedmont physiographic province. Slopes range from 2 to 25 percent.
- *Meadowville series:* The soils of the Meadowville series are very deep and well drained and are in the Piedmont physiographic province. They formed in local alluvium and colluvium weathered from crystalline rocks. They are along small drainage ways and on toe slopes. Slopes range from 2 to 7 percent.

Soil map units

The following properties (Soil Conservation Service, 1983) are currently used by the National Cooperative Soil Survey to characterize each map unit as the basis for their interpretation for agricultural and engineering uses:

- free water occurrence (depth to, kind, and months of the year)
- particle-size distribution
  - USDA-particle-size class
  - fraction >250 mm, 250–75 mm
  - percent passing sieve numbers 4, 10, 40, and 200
  - clay (<0.002 mm)
  - particle-size-superseding characteristics (sapric material, coprogenous earth, cinders, marl, muck, etc.)
- fabric-related analyses
  - moist-bulk density
  - shrink-swell potential
  - saturated-hydraulic conductivity (K_{SAT})
- engineering properties
  - liquid limit
  - plastic limit
- engineering classification
  - unified
  - AASHTO
- chemical properties
  - $CaCO_3$ equivalent
  - cation-exchange capacity
  - gypsum
  - organic matter
  - reaction (pH)
  - salinity
  - sodium adsorption ratio
  - sulfur content

The following interpretations are currently tabulated for each map unit in soil survey reports published by U.S. Government Printing Office (Soil Conservation Service, 1983):

- sanitary facilities
  - septic tank absorption fields
  - sewage lagoon areas
  - trench type sanitary landfills
  - area type sanitary landfills
  - daily cover for landfills
- building site development
  - shallow excavations
  - dwellings without basements
  - dwellings with basements
  - small commercial buildings
  - local roads and streets
  - lawns, landscaping, and golf fairways
- source of construction material
  - roadfill
  - sand
  - gravel
  - topsoil
- water management
  - pond reservoir areas
  - embankments, dikes, and levees
  - excavated ponds, aquifer fed
  - drainage
  - irrigation
  - terraces and diversions
  - grassed waterways

- recreational development
  - camp areas
  - picnic areas
  - playgrounds
  - paths and trails
- capability and yields per acre of crops and pasture with a high level of management for the specific soil survey area
- woodland suitability
- windbreaks
- wildlife habitat suitability
- potential native plant community (rangeland and forest under story vegetation)

Map unit inclusions

Soil map units are named by one taxonomic class. A map unit named by one taxonomic class is a *consociation*. Descriptions of such a map unit contain a paragraph that gives other taxa included within their delineations. The problem of map unit inclusions result from the use of artificial taxa, soil series, to name natural soil landscape units.

Soil map unit inclusions may be *similar* or *dissimilar* and *limiting* or *nonlimiting*. Similar inclusions are soils that share limits of diagnostic criteria and have similar management requirements. Dissimilar inclusions are soils that do not share limits of diagnostic criteria and have different management requirements. Dissimilar soils occur within a natural landscape unit when the two or more kinds of parent material are present within the landscape unit. The definitions of limiting and nonlimiting inclusions are based on specific interpretations for a specific map unit. A limiting inclusion is a dissimilar soil that has properties that limit the use of the soils in a map unit for most land uses. A nonlimiting inclusion can be a dissimilar soil that does not limit a map unit for a specific land use but is limiting for other land uses; e.g., a soil with a seasonal water table at 75 cm below the soil surface mapped in a delineation of a well drained soil with a water table below 1.8 m would be limiting for septic tank absorption fields but not for corn or timber production.

Kinds of map units

When a dissimilar soil or miscellaneous land type constitutes more than 15 percent of the areas delineated by a map unit, the name or taxa used to identify that component is added to the map unit name. Map units named by two or more dissimilar soils or miscellaneous land types are (*i*) *complexes* if the components occur in a regularly repeating pattern and cannot be separated at the scale of the base map, (*ii*) *associations* if the components occur in a regularly repeating pattern and can be separated at the scale of the base map; (*iii*) *undifferentiated group* if the components have similar use and management for common uses.

Summary

Soil maps produced by delineating natural soil landscape units partition the total spatial variability of the multivariate continuous soil universe into the narrowest possible ranges for purposes of making predictions about the responses of the soils to specific use and management requirements. Soil survey reports published by the U.S. Department of Agriculture, Soil Conservation Service, provide the best single source of information concerning the inventory of an important basic natural resource, the soil. Proper use and management of the soil is essential to the production of food, fiber, and shelter and to the maintenance of a clean and wholesome physical environment.

William Joseph Edmonds

Bibliography

Brady, N.C., 1990. *The Nature and Properties of Soils*, 10th edn. New York: MacMillan, p. 621.

Hudson, B.D., 1992. The soil survey as a paradigm-based Science. *Soil Sci. Soc Am. J.*, **56**: 836–841.

Knox, E.G., 1965. Soil individuals and soil classification. *Soil Sci. Soc. Proc.*, **29**: 79–84.

Schelling, J., 1970. Soil genesis, soil classification and soil survey. *Geoderma*, **4**: 165–193.

Soil Conservation Service, 1983. *National Soils Handbook*. Washington, DC: U.S. Government Printing Office, p. 632.

Soil Survey Staff, 1993. *Soil Survey Manual*. Washington, DC: U.S. Government Printing Office.

Soil Survey Staff, 1996. *Keys to Soil Taxonomy*. SMSS Tech. Mono. No. 19, 4th edn. Blacksburg, VA: Virginia Polytechnic Institute and State University, p. 422.

Thomas, S.K., and Crawford, E.D., 1986. *Soil Survey of Greene County*. Washington, DC: U.S. Government Printing Office, p. 131 with maps.

SOIL MECHANICS

See *Soil Engineering*.

SOIL MICROBIOLOGY

Soil microbiology is the branch of soil science concerned with soil-inhabiting microorganisms, their functions and activities (SSSA, 1996). A microorganism is a microscopic organism consisting of a single cell or cell cluster. Microbial cells are different from animal and plant cells which can only exist as part of multicellular organisms. A single microbial cell generally can carry out its life processes of growth, energy generation, and reproduction independently of other cells. Individual microorganisms are invisible to the naked eye, but they are visible collectively. Microorganisms play important roles in elemental/biogeochemical cycling and energy flows on Earth.

Soil microbiology is interdisciplinary and closely linked to soil biochemistry and microbial ecology. It requires an understanding of principles of soil science, microbiology, and the chemistry and physics of biological systems. There are two basic approaches for studying soil microbiology. The first approach is to study the organisms by examining their physiology and taxonomy. The question to be answered here is "*Who are they?*" The second approach focuses on microbial processes, i.e., what microorganisms do in soil.

Major groups of soil microorganisms

Soil is teeming with life, both macroscopic and microscopic. Based on the fundamental structure of the cell, living organisms are either prokaryotic (lacking a nucleus) or eukaryotic (with a true nucleus). Based on the evolutionary relationships among living organisms, all life forms can be divided into 3 domains: Bacteria, Archaea, and Eukarya. The Bacteria and the Archaea are single-celled prokaryotic organisms. The Eukarya are more complex single- or multi-celled organisms with membrane-enclosed (true) nuclei. Soil microbiology includes the study of bacteria (including actinomycetes) (Note: In this entry, the word *bacteria* with lowercase b refers to prokaryotes, while the word Bacteria with a capital B refers to one of the three taxonomic domains.), fungi, algae, protozoa, and the viruses, which are microscopic but not cellular.

Bacteria are the smallest and most numerous cellular organisms in soils. They are usually 0.5 to 1 μm wide and 1 to 2 μm long. The very small bacteria, termed ultramicrobacteria, can be as small as 0.3 μm in diameter with cell volumes less than 0.1 μm^3. In undisturbed soils, at least 50% of the cells are such dwarf cells; less than 5% have volumes above 1 μm^3 (Bakken, 1997). The large bacteria (e.g., a sulfur bacterium, *Thiomargartia namibiensis,* found in sediments off the west coast of Africa) can be as large as 750 μm in diameter, with volumes exceeding the regular bacterial cell volume by several orders of magnitude (Schulz et al., 1999). Although a variety of cell shapes exists for bacteria, including rod, spherical, spiral, and filamentous, the most common cell shape found in soil is short rod (coccoid rod). Some soil bacteria (e.g., *Arthrobacter*) are pleomorphic, having more than one shape. Bacterial biomass found in soil ranges from 300 to 3000 kg ha^{-1} (Table S12). There are approximately 10^8 to 10^9 bacteria in a gram of soil. Most of them (>99%) have not been or cannot be cultured in the laboratory. Common bacterial genera isolated from soil include *Bacillus*, *Arthrobacter*, *Pseudomonas*, *Agrobacterium*, *Alcaligenes*, *Clostridium*, *Flavobacterium*, *Corynebacterium*, *Micrococcus*, *Xanthomonas*, and *Mycobacterium*. In contrast to simply morphology, bacteria have the greatest metabolic diversity. In terms of carbon utilization, there are autotrophs and heterotrophs. In terms of energy consumption, there are chemoorganotrophs, chemolithotrophs, and phototrophs. Aerobic bacteria use oxygen as an electron acceptor; anaerobic bacteria use alternate electron acceptors such nitrate, ferric iron, sulfate, carbonate, and organic matter. Actinomycetes are filamentous bacteria. Most actinomycetes are Gram-positive bacteria and are more abundant in neutral to alkaline soils. The "earthy" smell of soil comes from geosmins produced by *Streptomyces*, an actinomycete. Many actinomycetes produce antibiotics. Cyanobacteria are phototrophic bacteria that are important in soils where light and water are available. Although they may have the capability for movement, most soil bacteria are attached to soil particles and very few can be found in the soil solution. Bacteria reproduce by binary fission – individual cells grow until they divide into two new cells. Bacteria do not exist in isolation; they form small colonies of 2 to 20 cells in soil. Since soil is an oligotrophic (nutrient poor) environment, most bacterial cells are believed to be dormant. The one area in soil where metabolically active microorganisms are commonly found is the rhizosphere, where nutrients are not limiting.

Table S12 Numbers and biomass of major microbial groups found in soil

Organisms	Numbers (per g of soil)	Biomass (kg wet mass per ha)
Viruses	10^{10}–10^{11}	
Bacteria	10^{8}–10^{9}	300–3 000
Actinomycetes	10^{7}–10^{8}	300–3 000
Fungi	10^{5-}–10^{6}	500–5 000
Algae	10^{3}–10^{6}	10–1 500
Protozoa	10^{3}–10^{5}	5–200

Adapted from Sylvia et al. (2005).

Soil fungi are eukaryotic organisms, which can be unicellular, but often are multicellular. Compared to bacteria, fungi have more complex morphologies and life cycles. Yeasts are single-celled fungi that reproduce asexually through budding. Most other fungi have highly branched filaments with strands 2 to 30 μm in diameter and several centimeters long. These filaments are known as hyphae (plural form of hypha). Hyphae are either septate (divided into compartments by cross walls) or nonseptate (long continuous cells without cross walls). Hyphae intertwine together into a filamentous network, called a mycelium. Mycelia may be undifferentiated or organized into a fruiting body that can be greater than 10 cm in diameter. Mushrooms and truffles are examples of fruiting bodies. Fungi commonly reproduce by way of spores, which can be single- or multi-celled and vary in size, shape, color, and surface texture. Reproduction of fungi can be sexual or nonsexual, but commonly both. The classification of fungi has changed over the years and there are many competing classification systems. Most recently, the kingdom of Fungi has been divided into 5 phyla: Chytridiomycota, Zygomycota, Ascomycota, Basidiomycota, and Mitosporic fungi (Deuteromycetes). There is one other phylum in the kingdom of Chromista, the Oomycota, which is closely related to true fungi. Fungi are heterotrophs with the ability to metabolize complex polymers, such as cellulose, hemicellulose, and lignin. Most fungi are aerobic except for yeasts, which can survive in anaerobic environments by fermenting sugars into alcohol. In many ecosystems, fungi constitute the largest biomass of all the soil organisms, ranging from 500 to 5000 kg ha^{-1} (Table S12). An individual fungus can include many fruiting bodies scattered across a large area with extensive underground hyphae. A 1500-year-old fungus, *Armillaria bulbosa,* found in northern Michigan, spreads throughout a 15-hectare woodland, equivalent to the size of 28 football fields (Smith et al., 1992). Fungal hyphae bind soil particles together and stabilize soil aggregates. Fungi also form beneficial mycorrhizal symbioses with almost all terrestrial plants. Mycorrhizal fungi enhance the uptake of mineral nutrients (e.g., phosphorus and zinc) to the plant in exchange for carbon compounds fixed by plant photosynthesis. Lichens are symbiotic associations of a fungus and an alga or a cyanobacterium. They are important soil colonizers that play critical roles in soil formation and stabilization. Some soil fungi are plant pathogens that cause reduced crop yields and economic losses in agriculture. Fungi are also producers of antibiotic compounds such as penicillin and cyclosporins.

Algae are eukaryotic, oxygen-evolving phototrophic organisms that can be found in the upper layers of soil where light and water are available. Although most algae are microscopic, some marine forms are macroscopic, forming 40-meter long seaweed. Algae are either unicellular or multicellular. The latter can be filamentous or forming complex colonies. There are 3 major groups of algae commonly found in soil: green algae, diatoms, and yellow-green algae. Algae are pioneer colonizers in desert and volcanic ash fields where plant growth is limited. They are important in the early stages of soil formation.

Protozoa are unicellular eukaryotic microorganisms that lack cell walls. They are motile heterotrophs that obtain food by ingesting bacteria, yeasts, algae, small protozoa, and organic matter. Free-living soil protozoa fall into 3 categories: flagellates, amoebae, and ciliates. Protozoa regulate bacterial and fungal populations in soil and recycle soil nutrients.

Viruses are genetic elements that can replicate independently of a cell's chromosomes but not independently of cells themselves. Viruses are smaller than bacteria and range in size from 20 to 30 nm in diameter. Viruses are obligate parasites of bacteria, fungi, insects, plants, and animals that inhabit the soil. They regulate soil microbial populations and play a role in the exchange of genetic material between bacterial cells. Viruses can persist in soil as dormant particles for long periods of time.

Distribution of microorganisms in soil

Soil consists of three phases: solid, liquid, and gas. The solid phase of soil is made up of mineral and organic materials. About 50% of the soil volume is taken up by the soil solids. The rest is pore space occupied by either water or air. Filling of the pore space with water diminishes soil aeration and microsites of anaerobiosis develop. Soil is an extremely heterogeneous medium for microbial growth (Figure S49). It contains a wide range of substrates for microorganisms, from simple sugars to the most complex materials, such as humus. Soil also consists of numerous microsites with nutrient, moisture, pH, and E_h levels varying in very short distances (mm or μm) and over time. The consequence of chemical and physical heterogeneity of soil is that soil harbors the greatest diversity of life. Although the inventory of soil microbial diversity remains uncertain, one gram of soil may contain thousands of different microbial species.

Microorganisms are found not only in surface soil, but also in subsurface soil at depths ranging from hundreds to thousands of meters below the ground. Generally, the number of microorganisms declines with increasing depth in the soil profile, primary due to decreases in soil organic matter content. Microbes found in subsurface soil are dominated by bacteria.

Soil microorganisms are not uniformly distributed laterally either. They occur where they can find appropriate nutrients and environmental conditions. Plants, particularly their roots,

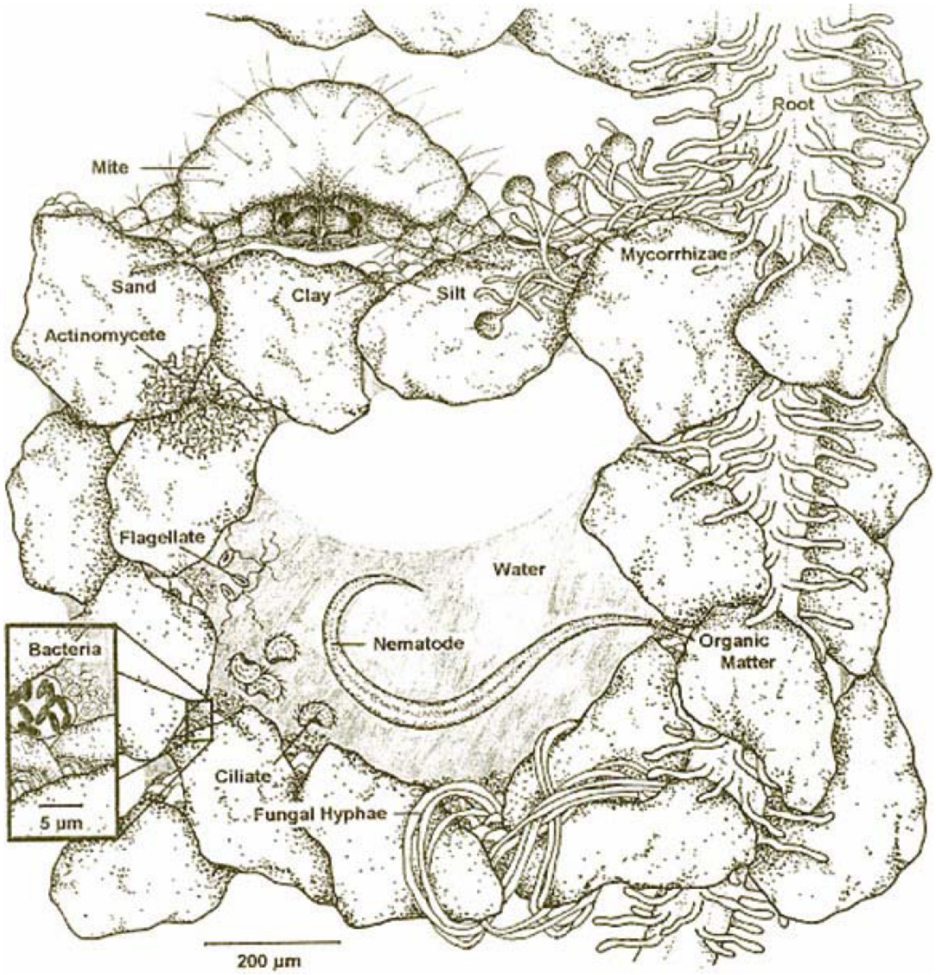


Figure S49 A soil habitat containing mineral soil particles, organic matter, water, plant root with root hairs, and soil organisms. The actual size of the soil in this drawing is slightly greatly than 1 mm^2 (original drawing by Kim Luoma. Courtesy of Peter G. Hartel).

are an important source of carbon and other nutrients to microorganisms. The rhizosphere is the narrow region of soil under the direct influence of plant roots. It usually extends a few millimeters from the root surface. The rhizosphere is a dynamic environment fluctuating with the stages of root growth and senescence. Plant roots release a variety of compounds that support higher microbial populations and activities in the rhizosphere than in bulk soil. These compounds include root exudates, mucilage, and sloughed-off root cells. Mucigel contains plant mucilage, bacterial cells and their metabolic products, as well as clay particles. It maintains contact between the root and the soil as the root shrinks during water stress, permitting continuous uptake of nutrients and water. In the rhizosphere, there is a microbial population distinct from the rest of the soil. Bacteria in the rhizosphere are larger and have higher proportions of Gram-negative and denitrifying bacteria than those in the bulk soil. Rhizosphere fungal populations, abundant in both pathogenic and mycorrhizal species, can be 10 to 20 times higher than those in the non-rhizosphere. Protozoa and other microfauna also thrive in the rhizophere because that is where food is most plentiful. Microbes in the bulk soil often experience long periods of nutrient deprivation; they have different survival strategies in dealing with starvation and stress.

Sand, silt, and clay particles form secondary structures called soil aggregates. Soil aggregation influences microbial distribution and activity as well as soil organic matter turnover. Aggregates held together by polysaccharides, glycoproteins, clays, and fungal hyphae vary greatly in size; so do the pore diameters inside aggregates. Macroaggregates are more than 250 μm in diameter, with pore diameters ranging from 25 to 100 μm. Microaggregates are less than 250 μm in diameter, with pore diameters ranging from 0.2 to 6 μm. Pores most favorable for bacteria are those 0.8 to 3 μm in diameter. Fungi usually do not enter aggregates less than 30 μm in diameter. Microbes in small pores are often protected from their large predators. Interiors of aggregates are often anoxic because of the slow oxygen diffusion rates to the centers. As a result, aerobic bacteria tend to colonize the outer layers of aggregates; anaerobic bacteria are found inside. Aggregates usually contain higher levels of nutrients than soil in general.

Physiochemical and biological factors affecting microbial activities

Microbial growth and activities in soil depend on resources (carbon and other mineral nutrients) available and physiochemical conditions of their habitat. The majority of soil microorganisms are presumably chemoorganoheterotrophic. They use organic compounds as carbon and energy sources. Except for the rhizosphere, soil is an oligotrophic environment for microbial growth. Nutrients, in forms of plant and animal residues, enter the soil in an intermittent fashion; microorganisms are faced with a “feast-or-famine” type of existence. The humic fraction of soil organic matter provides the stable microbial nutrient base for microorganisms, however, humic substances have extremely complex structures and are resistant to decomposition. In addition, humus is associated with mineral particles and forms organo-clay complexes. Therefore, humus only serves as a slow release source of carbon and energy for oligotrophic microorganisms.

Water is essential for soil microorganisms. Soil water affects not only the moisture available to organisms, but also the soil aeration status, soil temperature, and a variety of soil chemical reactions. Generally, microbial activity is optimal at a soil water potential of –0.01 MPa. Extremely wet or dry soils are unfavorable for the growth of most soil microorganisms. Different microbial groups have different tolerance levels of water stress. Algae, protozoa, and anaerobic bacteria are favored by abundant moisture, whereas fungi, actinomycetes, and spore-forming bacteria are more tolerant of greater water stress.

The soil atmosphere generally has a lower level of oxygen and a higher level of carbon dioxide than the outside atmosphere. Because air and water occupy the same spore space, wet soil reduces soil aeration. The oxygen concentration at a particular site depends on the rate of oxygen diffusion and the rate of its use by soil organisms and plant roots. Addition of large amounts of available substrates to soil will reduce the level of oxygen and increase that of carbon dioxide. Aerobes and anaerobes operate side by side in soil. Aerobic organisms deplete oxygen around them when there are high concentrations of available carbon. Anaerobic microsites develop even in well-aerated soils. Soil aeration can be measured in terms of redox (reduction-oxidation) potential (Eh), which is a measurement of the tendency of a compound to gain or lose electrons. In soil, the Eh value represents the sum of numerous oxidation-reduction pairs. The more aerobic a soil becomes, the more positive the redox potential. The Eh values are in the range of 0.4 to 0.7 V for a well-drained soil. The Eh declines to 0.3 to 0.35 V when oxygen is depleted. Waterlogged soils, especially those rich in organic matter, generally have Eh values as low as –0.3 V. Under aerobic conditions, O_2 is the electron acceptor for microorganisms. Under anaerobic conditions, NO_3^-, Fe^{3+}, Mn^{4+}, SO_4^{2-}, CO_2, and organic compounds can serve as electron acceptors.

Soil temperature affects the rates of physical, chemical, and biological processes in the soil. Soil temperature varies diurnally and seasonally. The greatest variation occurs near the soil surface. Temperature change in the subsurface soil lags behind the surface soil and the temperature fluctuation is smaller. Generally speaking, the rates of biochemical reactions double for every 10 °C increase in temperature. All microorganisms have an optimal growth temperature as well as a temperature range within which they are active. The temperature ranges for the psychrophiles, mesophiles, and thermophiles are –5 to 20 °C, 20 to 45 °C, and 45 to 80 °C, respectively. Extremeophiles can growth at a temperature as low as –12 °C and as high as 121 °C. Mesophiles, however, predominate in most soils.

Soil pH values vary greatly, ranging from pH 2 to pH 11. Microorganisms generally cannot tolerate extreme pH values. Under highly alkaline or acidic conditions, proteins may be denatured and enzymes may be inactivated. In addition to the direct effect, soil pH also influences microorganisms indirectly by changing the chemical forms, solubility, and availability of chemical compounds. Bacteria are active in a broad pH range (1–9) although many (i.e., actinomycetes, nitrifiers) prefer a neutral pH. Fungi as a group are acid tolerant; their optimal pH ranges are between 4 and 6. Microorganisms also have the ability to alter soil pH. Acidophilic bacteria, like sulfur-oxidizing *Thiobacillus*, create their own low pH environment by producing acids.

Different soil organisms frequently interact with each other; the interactions can be positive, negative, or neutral. Positive interactions (commensalism, synergism, and mutualism) enhance the abilities of populations to survive within a particular habitat; negative interactions (competition, amensalism, and predation/parasitism) limit the population growth. Some of the most important symbiotic relationships (mutualism) involve interactions between microorganisms and plants, i.e., symbiotic nitrogen fixation and mycorrhizae. Symbiotic nitrogen fixation is essential for plant growth in environments that are deficient in mineral forms of nitrogen. Important symbioses involving nitrogen fixation include the associations between leguminous plants (e.g., soybean, alfalfa) and rhizobia (*Rhizobium* and *Bradyrhizobium*), actinorhizal plants (e.g., alder, bayberry) and the actinomycete *Frankia*, as well as the water fern *Azolla* and the cyanobacterium *Anabaena*. Both rhizobia and *Frankia* induce the formation of nodules on the plant roots, in which the bacterial symbiont converts atmospheric nitrogen to ammonia. *Anabaena,* however, grows within the cavities in the leaf lobe of water fern.

Members of soil biological communities also exert negative effects on one another. Competition for limited resources adversely affects both populations with respect to their survival and growth. Available sources of carbon, nitrogen, phosphate, iron, oxygen, and water are all resources for which microorganisms may compete. For example, heterotrophic microorganisms need ammonium to make amino acids and proteins; ammonia-oxidizing bacteria use ammonium as an energy source. If ammonium is limited, neither population will grow to the extent that it would in the absence of competition. When one microbial population interferes or inhibits competing populations by producing chemical substances, the relationship is referred to as amensalism. Examples of amensalism include antibiotic production by actinomycetes, and acid production by *Thiobacillus*. Predation/parasitism has negative effects on preys or hosts, but positive effects on predators or parasites. Bacteria, such as *Bdellovibrio*, *Myxococcus*, and *Agromyces ramosus*, are known to lyse other bacteria and fungi. Nematode-trapping fungi form specialized mechanisms to catch and digest nematodes. Protozoa and nematodes feed on bacteria and fungi. Feeding activities of microfauna reduce the size of prey populations, but release excess ingested nutrients and accelerate nutrient recycling. In addition to interactions among different groups, microorganisms can interact with members of their own group. Moreover, interactions can also take place at the genetic level, especially for bacteria, resulting in horizontal gene transfer.

Major microbial processes in soil

Soil microorganisms are involved in the cycling of all major elements, e.g., carbon, nitrogen, phosphorus, and sulfur, as well as some minor and trace elements. With carbon and nitrogen cycles, once carbon dioxide and dinitrogen are incorporated into biomass, actively cycled soil carbon and nitrogen are contained in the organic components of the soil. With the cycling of sulfur, phosphorus, and metals, major reservoirs are in the soil mineral fraction.

Both carbon and nitrogen cycle between organic and inorganic forms via biologically-driven processes. Photosynthesis converts carbon dioxide in the atmosphere to organically bound forms of carbon in plants, algae, and cyanobacteria. The vast array of organic matter thus produced is available for consumption by animals and heterotrophic microorganisms. Biological nitrogen fixation carried out by symbiotic and nonsymbiotic nitrogen-fixing bacteria converts dinitrogen gas to ammonia for biological uptake. Plant residues are the primary organic matter input to soil. Other contributors include soil animals and microorganisms. Once in soil, complex organic compounds (e.g., cellulose and lignin) decompose to simple organic constituents. Mineralization is the complete decomposition of organic compounds to inorganic molecules.

$$(\mathrm{CH_2O})n + \mathrm{O_2} \rightarrow n\mathrm{CO_2} + n\mathrm{H_2O} + \text{energy}$$

$$\text{R-NH}_2 \underset{-2\mathrm{H_2O}}{\overset{+2\mathrm{H_2O}}{\rightleftharpoons}} \text{R-OH} + \mathrm{OH^-} + \mathrm{NH_4^+} + \text{energy}$$

Transformation of nitrogenous compounds involves oxidation-reduction reactions. Ammonium, the end product of nitrogen fixation, is assimilated by cells to form proteins, nucleic acids, and cell wall components. This process is referred to as immobilization or ammonium assimilation. Decomposition of dead cells releases ammonium, which can be oxidized by nitrifying bacteria to nitrite and nitrate. This process is known as nitrification. Nitrate can be reduced dissimilatorily to dinitrogen gas, a process called denitrification, or ammonium, a process called nitrate ammonification (dissimilatory nitrate reduction to ammonium).

Soil microorganisms are also intimately involved in the cycling of phosphorus and sulfur. Unlike carbon, nitrogen, and sulfur, the phosphorus cycle does not involve fluxes to and from the atmosphere. In nature, phosphorus occurs almost exclusively in phosphate form (oxidation state of $+5$) and microbial transformation of phosphorus rarely involves oxidation-reduction reactions. Most soil phosphates are insoluble or poorly soluble. Organic phosphorus compounds found in soil include phytates, nucleic acids, and phospholipids. Microorganisms participate in the solubilization of inorganic phosphorus and in the mineralization of organic phosphorus. Dissolved phosphate is taken up directly by soil microorganisms; organic phosphorus is taken up either directly or after being hydrolyzed by extracellular phosphatases. Soil microorganisms are important in the immobilization of available soil phosphorus in the short term.

The soil microbial community is the driving force behind all sulfur transformations. Soil sulfur occurs in both organic and inorganic forms, but mostly is bound in the organic fraction. Microorganisms participate in the mineralization of organic sulfur, immobilization of sulfur compounds (e.g., sulfate, amino acids, and sulfide), oxidation of inorganic sulfur compounds, and dissimilatory reduction of inorganic sulfur. More in-depth discussions on carbon, nitrogen, phosphorus, and sulfur cycling can be found elsewhere in this volume.

Many toxic chemicals have found their way into soil as a result of industrial and agricultural activities. Biodegradation of organic pollutants can be considered a special case of organic matter decomposition. Microorganisms are able to use many organic pollutants as sources of carbon and energy. Microorganisms, especially bacteria, are constantly evolving and adapting their enzyme systems to new substrates and changing environments. This provides a great potential for the use of microorganisms to degrade recalcitrant chemicals and to clean up the contaminated soils.

Summary

Soil is a heterogeneous habitat with constantly changing environmental conditions for microbial growth. Soil microorganisms are present in high numbers and have a wide range of metabolic activities and physiological properties. They play a key role in the cycling of nutrients within the soil and are essential for removal of pollutants from soil. Microbial activity is also responsible for the formation and maintenance of soil structure as well as soil fertility. All life on Earth is dependent on the "service" performed by these invisible organisms.

Yucheng Feng

Bibliography

Bakken, L.R., 1997. Culturable and nonculturable bacteria in soil. In van Elsas, J.D., Trevors, J.T., and Wellington, E.M.H., eds., *Modern Soil Microbiology.* New York: Marcel Dekker.

Schulz, H.N., Brinkhoff, T., Ferdelman, T.G., Marine, M.H., Teske, A., and Joergensen, B.B., 1999. Dense population of a giant sulfur bacterium in Namibian shelf sediments. *Science*, **284**: 493–495.

Smith, M.L., Bruhn, J.N., and Anderson, J.B., 1992. The fungus *Armillaria bulbosa* is among the largest and oldest living organisms. *Nature*, **356**: 428–431.

Soil Science Society of America (SSSA), 1996. *Glossary of Soil Science Terms*. Madision, WI: Soil Science Society of America.

Sylvia, D.M., Fuhrmann, J.J., Hartel, P.G., and Zuberer, D.A., 2005. *Principles and Applications of Soil Microbiology*, 2nd edn. Upper Saddle River, NJ: Pearson.

Cross-reference

Rhizosphere

SOIL MINERALOGY

Scope and significance of soil mineralogy

Soil mineralogy aims to study and understand the soil mineral phase, which makes up about 90% of the solid volume of mineral soils. This scientific discipline encompasses a diverse range of topics including: (*i*) the occurrence and distribution of soil mineral materials, (*ii*) their chemical composition, and crystallographic properties, (*iii*) the stability, transformations, and interactions of soil minerals in natural environments, and (*iv*) their consequent influence on soil physical and chemical properties and regulating air and water chemistry (Dixon and Schultze, 2002).

A *soil mineral* has a unique chemical formulation and crystal structure, though its chemical composition is not always fixed. *Soil minerals* have long been used to indicate weathering rates of surficial materials, determine the age of soils and sediments, elucidate mechanisms of soil formation, and reconstruct paleoenvironmental conditions during pedogenesis (Velbel, 1986; Pavich, 1991; Righi and Meunier, 1995; White, 1995; Scudder et al., 1996; Blanc-Valleron and Thiry, 1997; Borchardt, 2002).

Soil minerals provide a medium to store water and support plants in addition to contributing both an available and a labile pool of plant nutrients that often are the only sources of mineral nutrition, besides atmospheric deposition, in unmanaged (e.g., forest) ecosystems (Fisher and Binkley, 2000). Along with organic matter soil minerals play a major role in regulating the chemistry of natural waters by immobilizing excess agricultural nutrients, pesticides, and hazardous pollutants in the environment, and by neutralizing many of the potentially detrimental effects of atmospheric (acid) deposition (Ellis and Mellor, 1995; Appelo and Postma, 1996; Haygarth and Jarvis, 2002). Through their interactions with soil water, soil minerals are also linked to soil physical properties and behaviors such as plastic or shrink-swell properties, compressive and shear strength, permeability to water and air, and aggregate stability (Quirk, 1996).

The physicochemical properties of soil minerals that regulate these processes are determined in large measure by the nature of the secondary mineral phases that form from the in situ breakdown of *primary silicate minerals* (Table S13), which are inherited from parent materials, during weathering. *Secondary* (or '*clay*') *minerals,* such as the *phyllosilicates* and metal *oxides*, *hydroxides*, and *oxyhydroxides* (Table S14) commonly dominate the clay (<2 μm) fraction of soils, particularly in well-developed soils and those formed in humid-temperate or warmer areas. Secondary minerals normally have small particle sizes, high surface areas, and a net negative surface charge (Table S15), and these colloidal properties render them extraordinary ability to participate in a multitude of interfacial reactions (e.g., ion exchange, adsorption etc.) that involve water molecules, nutrients, organic pollutants, toxic contaminants, and heavy metals (Parker and Rae, 1998; Ford et al., 2001; Johnston and Tombácz, 2002).

In addition to their influence on soil behavior, clay minerals are used commercially as paper coatings, extenders in paints, plastics, and rubbers, as constituents of drilling fluids (for oil/gas exploration) and cracking catalysts in the petroleum industry, as pigments, adhesives, and adsorbents, and as physical barriers to the movements of wastes such as in landfill liners or backfill materials (Rowe et al., 1995; Giese and van Oss, 2002). They are also used extensively in the ceramic industry in the manufacture of glazes, enamels, tiles, and refractories (Grimshaw, 1971; Velde, 1992). Because of the great importance of clay minerals to industry, agriculture, and the environment, and because of their abundance and many unique surface-reactive properties that they impart to soils and sediments, much of the study of soil mineralogy specifically involves *clay mineralogy.*

Minerals in soil environments

Consequences of weathering

Compared with weathered rock, unweathered sediments, or other geological deposits, soils usually exhibit distinct vertical zonation (horizons) that results from relatively intensive *pedogenic* processes that include a complex array of physical, chemical, and biological reactions involving parent materials. The pedochemical weathering of soil parent materials results either in the solid-state transformation of primary minerals (Table S13) to new phases, or their dissolution and subsequent formation as new, more stable, secondary species by recrystallization/precipitation from solution (Table S14; Weaver, 1989; Righi and Meunier, 1995). Weatherable primary minerals are largely unstable in soils (Loughnan, 1969). Even the most resistant primary minerals in soils (e.g., quartz, zircon, and rutile) are altered to some degree (Carroll, 1953), making identification of the more easily weathered minerals considerably more difficult than is the case with fresh, intact geologic specimens. Secondary minerals in soils are typically so finely divided that analysis and identification requires a combination of chemical and instrumental techniques. Moreover, some minerals found in soils have unique properties and are not found elsewhere (e.g., hydroxy-interlayered vermiculites, Al-substituted goethite, etc.). Accordingly, the study of soil mineralogy departs somewhat from traditional petrology or sedimentology and is thus unique in several important aspects.

Compositional and structural variability

Soil minerals typically occur in a polymineralic fashion, and the mineralogical composition of a soil is dependent primarily

Table S13 Common primary (residual) minerals present in soil environments in order of increasing stability (after Feldman and Zelazny, 1998)

Name	Mineral Class	Environment	Ubiquity in soils[a]	Importance
Pyrite[b]	Sulfides	Tidal marshes (reducing conditions) and hard-rock mine tailings (coal and shale beds)	C	Primary mineral (oxidizing conditions) but secondary phase forms in reducing environments; large metal and acidity input to surface waters during weathering
Dolomite	Carbonates	Shallow, young soils formed in limestone	R	Major constituent of limestone parent material; fertilizer source
Pyrophyllite	Phyllosilicates	Low temp. metamorphic and hydrothermal	R	No layer charge - little chemical reactivity; unstable in soils
Talc	Phyllosilicates	Ultamafic rocks	R	No layer charge - little chemical reactivity; unstable in soils
Olivine	Nesosilicates	Basic and acidic igneous rocks	R	Source of Fe, Ca, Mg, and Mn; unstable in highly leached soil
Pyroxenes	Inosilicates	Igneous and contact metamorphic rocks	R	Source of Fe, Ca, Mg, and Mn; unstable in highly leached soil
Amphiboles	Inosilicates	Igneous and metamorphic rocks	R	Source of Fe, Ca, Mg, and Mn; vermiculite precursor
Chlorite (Mg-interlayer)	Phyllosilicates	Metamorphic or igneous rocks	R	Important precursor for 2 : 1 soil clay minerals
Biotite (Fe^{2+}-bearing micas)	Phyllosilicates	Granitic and high-grade metamorphic rocks	R	Stable in only the youngest or least weathered soils; precursor of other 2 : 1 soil clay minerals and Fe-oxides; source of K
Feldspars:	Tectosilicates	Wide variety of igneous/metamorphic rocks; persistence in soils and geologic deposits is related to weathering intensity, and the duration of exposure to weathering		Source of Ca, Na, and K; alteration to secondary products is a function of microenvironment; weathering products can be kaolinite, mica, gibbsite, halloysite, smectite, or amorphous materials
Calcic Plagioclase	Tectosilicates		R	
Sodic Plagioclase	Tectosilicates		C	
K-Feldspars	Tectosilicates		C	
Muscovite	Phyllosilicates	Granitic and high-grade metamorphic rocks	C	Vermiculite, smectite, and interstratified 2 : 1 precursor; K source
Epidote	Sorosilicates	Medium-grade metamorphic and mafic igneous rocks	R	Source of Fe, Ca, Mn; very resistant to weathering
Quartz	Tectosilicates	Nearly all soils and parent materials	U	Concentrated in sand- and silt-fractions; soluble in clay fraction
Garnets	Nesosilicates	High-grade metamorphic/acid igneous rocks	R	Source of Fe, Mg, Ca, Al, and/or Mn; precursor of Fe-oxides
Tourmaline	Cyclosilicates	Granites and pegmatites; detrital sediments	R	Stable in soils, but may alter to secondary 2 : 1 clay minerals
Rutile	Oxides	Igneous and metamorphic rocks; detrital sediments; quartz inclusion	C	Very stable in soils, but some mobility of Ti; rarely alters to other oxides
Zircon	Nesosilicates	Acid and basic plutonic, metamorphic rocks	C	Very resistant; Used as 'index mineral' in pedologic studies

[a] U = ubiquitous or dominant, C = common, R = rare or minor.

[b] Primary mineral in oxidizing conditions.

Table S14 Common secondary silicates and nonsilicates present in soil environments in order of increasing stability (after Feldman and Zelazny, 1998)

Name	Mineral class	Environment of formation	Ubiquity in soils[a]	Importance
Halite	Halides	Arid, saline/sodic soils	C	Highly soluble; adverse osmotic effects on plants
Gypsum	Sulfates	Arid soils	C	Moderately-high solubility; used to reclaim sodic soils
Jarosite	Sulfates	Acid sulfate soils: mine overburden, coastal wetlands	C	Product of pyrite oxidation resulting in large production of acidity and toxic metals
Calcite	Carbonates	Arid soils; very limited leaching	C	May act as cementing agent; high P sorption
Pyrite[b]	Sulfides	Tidal marshes (reducing conditions) and hard-rock mine tailings (coal and shale beds)	C	Primary mineral (oxidizing conditions) but secondary phase forms in reducing environments
Allophane/Imogolite	Paracrystalline	Soils derived from volcanic ash deposits	R	Short-range order; variable charge and highly sorptive
Sepiolite/ Palygorskite[c]	Phyllosilicates	Marine sediments, arid soils, high Si and Mg levels	R	Moderately high CEC, surface area, and sorptive properties
Halloysite	Phyllosilicates	Volcanic ash; granitic (feldspathic) saprolite	R	Ephemeral in intensely weathered soils
Vermiculites (dioct.)	Phyllosilicates	Mica alteration in well-drained soils	R	Very high CEC, fixation of K, sink for solution Al
Smectites	Phyllosilicates	Mica and/or vermiculite alteration	C	High CEC; high surface area; high shrink-swell capacity
HIV[d]	Phyllosilicates	Acid, highly weathered soil surface horizons	U	Variable CEC (degree of Al interfilling); high anion adsorption
Kaolinite	Phyllosilicates	Desilication of 2:1 clays/feldspathic	U	Low charge but highly pH-dependent; high anion adsorption
Hematite and Goethite	Oxides	Well-drained, near-surface soil	U	Variable charge; high anion adsorption
Gibbsite	Oxides	Old, stable soils or feldspar pseudomorphs	C	Variable charge; high anion adsorption
Anatase	Oxides	Dissolution of Ti-bearing parent minerals	R	Essentially chemically inert

[a] U = ubiquitous or dominant, C = common, R = rare or minor.
[b] Formed in soils as a secondary (authigenic) mineral, and also found as a primary mineral in geologic environments.
[c] Found as a primary mineral in rocks and sediments, and also formed as a secondary mineral in soils.
[d] Hydroxy-interlayered vermiculite.

on the nature of the parent material, the age and stability of the geomorphic surface, vegetative type and the intensity of pedochemical weathering (Allen and Hajek, 1989). Soil clay fractions in particular tend to be highly complex polymineralic mixtures, often composed of more than 10 or 15 different species (Figure S50), each with considerable variability. Many clay minerals exhibit characteristics of a solid-solution series, with continuous variation in properties such as degree of crystallinity, chemical composition, and magnitude of surface charge, even within a single mineral species (Newman, 1987). This variability is not surprising when one considers the diverse possibility of chemical conditions controlling dissolution and reprecipitation reactions at the microscopic level within a soil.

Unique minerals

The *pseudomorphic* (solid-state) replacement of one mineral by another is a poorly understood weathering mechanism responsible for considerable mineralogical variability in soils and influenced by many factors like temperature, moisture, and organic matter contents (Jolicoeur et al., 2000). Harris et al. (1985), for example, showed that the dominant alteration product of *biotite* in mesic (MAST = 8 to 15 °C) and warmer soils is *kaolinite*. This pseudomorph retains the optical properties of biotite, but even within single grains, it displays a 7.2 Å X-ray diffraction spacing characteristic of kaolinite. Conversely, vermiculitization was found to be the dominant weathering mechanism in the frigid (MAST < 8 °C) soils (Ghabru et al., 1989; Feldman et al., 1991). Pseudomorphic replacement of both *plagioclase* and *K-feldspars* has also been shown to occur widely in soils.

Interstratified minerals, such as mica-vermiculite, chlorite-vermiculite, or mica-smectite, contain sequences of different kinds of layers stacked along the c-dimension, and commonly occur in both soils and geologic environments (Brindley and Brown, 1980; Sawhney, 1989; Moore and Reynolds, 1997). They form in geologic environments primarily by hydrothermal alteration of micas, but in soils they form from weathering processes involving the partial removal of interlayer K from alternating layers within micas, or by removal of hydroxide interlayers from chlorite (Sawhney, 1989; Thompson and Urkainczyk, 2002). Accompanying these transformations are structural changes that result in greater surface area and the reduction of overall surface charge. Long-term weathering of interstratified species eventually results in the formation of individual phases of their respective components.

Soil *illite* (also hydrous mica, clay mica or sericite) occurs mainly in the clay fraction and is structurally similar to *muscovite* (*dioctahedral mica*) but has a lower layer charge (0.6–0.8 mole per molecular formula), poorer crystallinity, lower K_2O content, and higher H_2O content than muscovite (Środoń and Eberl, 1984; Fanning et al., 1989). The mineral often interstratifies regularly with smectites in geologic deposits, but the *interstratification* in soil is believed to be more random (Sawhney, 1989; Altaner and Ylagan, 1997; Moore and Reynolds, 1997). The soil illite phase is interpreted to be either a product of the

Table S15 Charge properties, specific area and particle size of common soil minerals

Minerals	Chemical formula[a]	Permanent charge[b]		Variable charge[c]		Specific area[d] ($m^2\ g^{-1}$)	Size fraction[e]
		Charge/formula	CEC ($cmol_c\ kg^{-1}$)	PZC	AEC ($cmol_c\ kg^{-1}$)		
Pyrophyllite	$M_{0.01}(Si_{3.88}Al_{0.12})[Al_{2.01}Fe(II)_{0.01}Mg_{0.02}]O_{10}(OH)_2$	0	<1			2–45	Sand-silt-clay
Talc	$M_{0.02}(Si_{3.97}Al_{0.03})[Mg_{2.89}M(III)_{0.03}M(II)_{0.10}]O_{10}(OH)_2$	0	<1			2–25	Silt-clay-sand
Mica			5–15			70–120	Sand-silt-clay
Biotite	$K(AlSi_3)[Mg_{0.6-1.8}Fe(II)_{2.4-1.2}]O_{10}(OH)_2$	1		7.5			
Muscovite	$K(AlSi_3)\ Al_2O_{10}(OH)_2$	1					
Illite	$K_{0.75}(Si_{3.5}Al_{0.50})[Al_{1.75}M(II)_{0.25}]O_{10}(OH)_2$	0.6–0.8	10–40			~150	Clay-silt
Feldspars			0–2	2–2.4		0–2	Sand-silt
Ca-plagioclase	$CaAl_2Si_2O_8$	0					
Na-plagioclase	$NaAlSi_3O_8$	0					
K-feldspar	$KAlSi_3O_8$	0					
Kaolinite	$Si_2Al_2O_5(OH)_4$	Uncertain	3 –15	4–5	0.75–4.0(3)	5–30	Clay
Halloysite, 0.7/1.0 nm	$Si_2Al_2O_5(OH)_4/2H_2O{\cdot}Si_2Al_2O_5(OH)_4$	Uncertain	40–50			5–10/10–40	Clay
Chlorites, Mg-interlayer	$[Mg_3(OH)_6]{\cdot}(Si_{4\text{-}x}Al_x)[M(II),\ M(III)]_3O_{10}(OH)_2$	Variable	1–2.5			25–45	Clay-silt
Vermiculite (di)	$M_{(x-y)}{\cdot}(Al_xSi_{4\text{-}x})[Al_{3-y}\ M(II)_y]O_{10}(OH)_2\ (x–y) = 0.6–0.9$	0.6–0.9	100–210			300–800	Clay
Montmorillonite	$M_{0.33}Si_4(Al_{1.67}Mg_{0.33})O_{10}(OH)_2$	0.2–0.6	80–150			800	Clay
HIV/HIS	Hydroxy interlayered vermiculite/smectites	0.2–0.9	Variable			Variable	Clay
Quartz	SiO_2		0.6–5.3	2–3		1–3.6	Sand-silt-clay
Calcite	$CaCO_3$			9.5			Variable
Goethite	α-FeOOH		0–6	7–8	4(6)–19(3.5)	14–177	Clay-silt-sand
Hematite	α-Fe_2O_3		0–6	8–8.5		30–50	Clay-silt-sand
Gibbsite	$Al(OH)_3$		0.2–3	8–9	7.2(6)	~50	Clay-silt-sand
Allophane	$xSiO_2{\cdot}Al_2O_3{\cdot}yH_2O\ (x = 0.8–2,\ y \geq 2.5)$	Variable	10–40	7–8.5	5–30(4)	900–1100	Clay
Imogolite	$SiO_2{\cdot}Al_2O_3{\cdot}2.5H_2O$	Variable	10–20	8.4	37(4)	700–900	Clay

[a] *M* = metal cations; e.g., M(II) = Fe^{2+}. The octahedral cations in soil vermiculites are not balanced because of the varying amounts of other metal cations present.

[b] There is uncertainty on the degree of isomorphous substitution in kaolinite and halloysites. A higher CEC for kaolinite is generally believed from other phyllosilicates as impurities. Chlorites are in a complete solid-solution series, and the substitution is variable. Smectites and vermiculites are usually classified by their charge values. Montmorillonite has a CEC of 80–110 $cmol_c\ kg^{-1}$ and some other high-charge smectites are also present in nature. There is evidence that Al substitution for Si occurs in allophanes and imogolite, but the chemical composition of both minerals varies so much that a general substitution number is not available. The CEC values for allophanes and imogolite are measured at pH 7.

[c] *PZC* = point of zero net proton charge or point of zero net charge reported by numerous authors. Quartz and calcite have the point-of–zero-salt-effect values. Values in parentheses are the pH values at which AEC is measured.

[d] For non-expandable minerals, the specific surface varies with particle size, and the N_2-gas surface in general agrees with the polar-liquid surface (e.g., EGME) within the same magnitude. The exceptions are allophanes and imogolite, whose N_2-surfaces (145–170 $m^2\ g^{-1}$) are much lower than the EGME values given (The EGME area of 435–534 $m^2\ g^{-1}$ is also reported for the two minerals).

[e] The size sequence given in the table roughly represents the abundance sequence in soils. Primary calcite appears in more coarse fractions, while secondary calcite is more concentrated in the clay fraction. Metal oxides are also present as coatings and nodules in highly weathered soils. Mica minerals can be abundant in all size fractions, but illites concentrate in clay fraction.

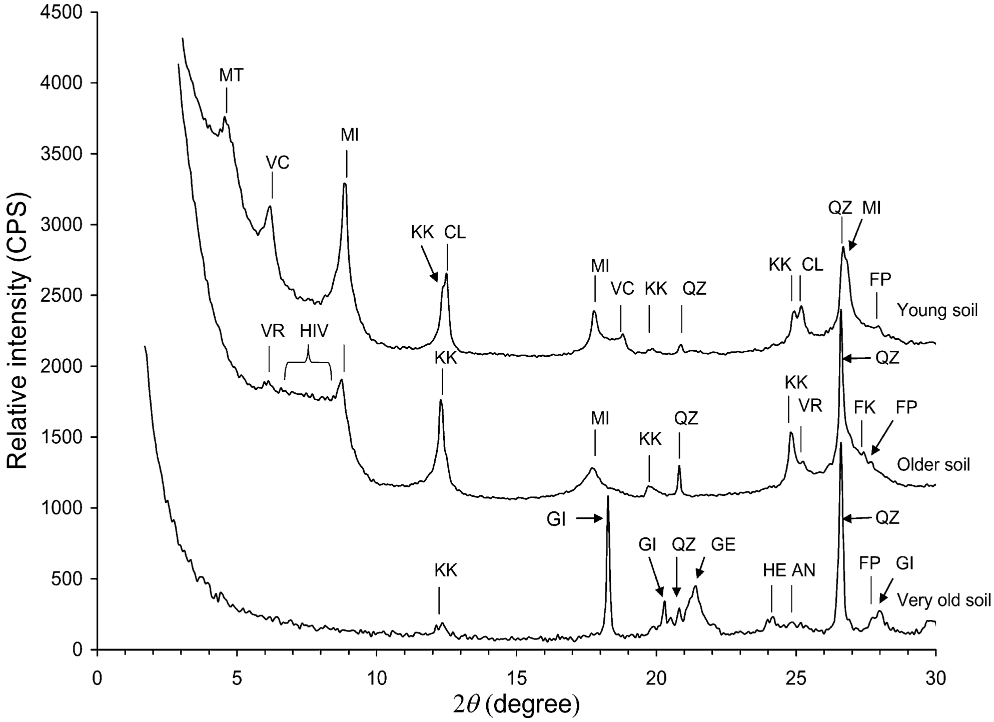


Figure S50 The mineralogical compositions of an Acadia soil from Nova Scotia, Canada (a young soil), a Frederick soil from Virginia, USA (an older soil), and a Nipe soil from Puerto Rico (a very old soil). The diffracted X-ray intensity was rescaled for clarity. *AN* = anatase, *CL* = chlorite, *FK* = potassium-feldspar, *FP* = plagioclase feldspar, *GE* = goethite, *GI* = gibbsite, *HE* = hematite, *HIV* = hydroxy-interlayered vermiculite, *KK* = kaolinite, *MI* = mica or illite, *MT* = smectite, *VC* = vermiculite/chlorite, *VR* = vermiculite, *QZ* = quartz.

weathering of mica originally present in the parent materials or the results of collapse of high-charge smectite layers around K ions (Thompson and Urkainczyk, 2002). However, both illite formation and illite/smectite interstratification in soils are not well understood.

Although *vermiculites* are common in both geologic and pedologic environments, only the dioctahedral (Al) varieties of this mineral are stable and persist in soils. *Trioctahedral* (Mg) varieties of vermiculite are found only in the least weathered environments. Dioctahedral (Al) vermiculites form as alteration products of *muscovite*, *biotite*, or *chlorite* and are very stable even in severe weathering environments (Douglas, 1989). Under acid weathering conditions, soil vermiculites act as sinks for Al released to solution by weathering becoming *hydroxy-interlayered dioctahedral vermiculites* (*HIV*). The hydroxy-Al interlayer that imparts a great deal of stability to the structure (Rich, 1958) makes HIV the most abundant clay mineral in surface horizons of soils containing mica in the parent material (Carlisle and Zelazny, 1973). The degree of interlayer filling (by hydroxy-Al polymers) in this mineral reflects the intensity of the weathering environment, and the age and acidity of the soil. There is a continuum between pedogenic chlorite (fully interlayered) and the non-hydroxy-interlayed vermiculitic end-members (Barnhisel and Bertsch, 1989).

In soils the authigenic formation of secondary minerals by *recrystallization* from solution often involves uniform incorporation of a trace element within a host mineral if the size and valence of the substituting element are comparable to those of the element replaced (Righi and Meunier, 1995). *Coprecipitation* of Al with *Fe-oxides* such as goethite and hematite is a nearly ubiquitous phenomenon in soils (Cornell and Schwertmann, 1996). In goethite, Al substitution ranges from 0 to 33 mole-%, reaching a maximum in highly weathered soils of subtropical and tropical areas (Fitzpatrick and Schwertmann, 1982). Higher levels of Al within Fe-oxide structures result in disorder and a decrease in crystallinity, changes in crystal growth and morphology, and a greater degree of thermodynamic and kinetic stability than their unsubstituted counterparts (Fitzpatrick and Schwertmann, 1982; Bryant and Macedo, 1990; Fontes and Weed, 1991). Whereas Al substitution in soil Fe-oxides is quite common, it is interesting to note that there are no reports of similar Fe for Al substitution in gibbsite and other Al-oxides in soils.

In addition to the coprecipitation, solid-state substitutions of ions commonly occur within the lattice positions of many soil phyllosilicates. This '*isomorphous*' *substitution* of lower valence for higher valence ions, such as Fe^{3+} or Al^{3+} for Si^{4+} in tetrahedral layers, and Mg^{2+}, Fe^{2+}, or Li^{+} for Al^{3+} or Fe^{3+} in octahedral layers, results in considerable compositional variability and inconsistent degree of surface charge even within a single mineral species (Newman, 1987).

Pyrophyllite and *talc*, the unsubstituted or zero-permanent-charge end-members of a solid-solution series of the 2 : 1 phyllosilicates, are found in ultramafic rocks and hydrothermal deposits, but they are not commonly found in near-surface environments (Zelazny et al., 2002). These minerals occur only in some young soils experiencing minimum weathering or in highly weathered soils if they are protected from intense weathering by encapsulation by Fe oxides (Harris et al., 1984).

Finally, additional soil components that are not abundant or not commonly found elsewhere include the amorphous and *paracrystalline* phases of Fe and Al oxides and oxyhydroxides and *aluminosilicates* (e.g., *allophane* and *imogolite*), which form in volcanic ash deposits (Harsh et al., 2002). These materials range continuously from *noncrystalline* to paracrystalline in nature, with little enhancement of observed X-ray diffraction peaks due to preferred orientation effects. These minerals and mineral materials as well as crystalline Fe and Al oxides and oxyhydroxides develop their surface charges (pH-dependent charge or *variable charge*) by the same mechanism: proton adsorption and desorption, which is dependent on solution pH and ionic strength. Crystalline compounds in this group are sometime called "variable-charge" minerals (see *Iron oxides*; *Mangan*).

Problems in mineral analysis (see Mineral analysis in Geochemistry volume)

Detailed characterization of the constituent minerals is essential for accurately understanding pedological and geochemical processes occurring in soils. However, because of the great complexity in weathering environments, one or more complementary analytical techniques is usually required to accurately identify clay mineral phases and noncrystalline aluminosilicates in soils. Quantifying the amounts of individual clay species in complex polymineralic mixtures poses quite another problem. Suitable reference standards with which to compare instrumental peak areas, or other analytical parameters, are often simply unavailable. The mined, geologic materials, which are used as reference standards for quantitative analysis, are often chemically or crystallographically dissimilar to the highly variable mineral phases in soils. Extraction of an identical mineral reference standard directly from the soil being analyzed is either impossible or prohibitively time-consuming for routine analysis. If X-ray diffraction is used for quantification, peak area (integrated intensity) instead of peak height must be used because the poor crystallinity and small particle size of secondary minerals cause significant line broadening. Despite many technological advances in analytical instrument electronics and data handling capabilities, quantitative clay mineral analysis remains a formidable obstacle.

Relevance to soil properties

Cation exchange capacity

Isomorphous substitution accounts for the majority of permanent surface charge from phyllosilicates, and consequently, much of the cation exchange capacity (CEC) of minerals soils. The permanent charge of soil minerals ranges from near zero in minerals possessing little or no isomorphous substitution to more than 200 $\mathrm{cmol_c\ kg^{-1}}$ in highly substituted minerals such as vermiculite (Table S15). A very small amount of cation substitution can have dramatic effects on the charge properties and cation exchange capacities of soil clays and thus of the whole soil. A simple sensitivity analysis shows that substitution of only one Al atom for every 400 Si atoms in kaolinite (or just 0.191% substitution) can result in the development of a permanent surface charge density of 1.94 $\mathrm{cmol_c\ kg^{-1}}$ on an otherwise theoretically uncharged mineral (Table S16).

A reduction in permanent CEC can occur in soils where nonexchangeable, positively-charged hydroxy-Al polymers either precipitate or are adsorbed within the interlayer spaces of vermiculite (HIV) or smectite minerals (HIS). Structural charges remain unchanged by this mechanism; however, these polymers satisfy the overall surface charges and block exchange sites resulting in a net decrease in CEC (Figure S51).

Soils in advanced stages of weathering are generally enriched in variable-charge minerals and mineral materials. They can have either cation or anion exchange capacities (AEC) depending upon soil pH and the ionic strength of the soil solution. Variable charges are also present on the edge sites of phyllosilicates like kaolinite (Ma and Eggleton, 1999). Chemisorption of metals on oxyhydroxides can also increase positive charge, while adsorption of anions such as phosphate can increase negative surface charge (Sposito, 1984; Bolan et al., 1999).

Cation exchange selectivity

Hydroxy-Al interlayering in 2:1 soil clay minerals dramatically affects the specific cation exchange behavior of K^+, NH_4^+, Cs^+, and Rb^+. These small, minimally-hydrated ions are ordinarily fixed in a nonexchangeable form within the collapsed interlayers of high-charge clay minerals such as vermiculite or beidellite. However, hydroxy-Al polymers present in interlayer areas prevent fixation by propping up clay layers thus stabilizing the structure. This results in the creation of 'wedge' zones whose size is sterically favorable for K^+ exchange. The pedogenic formation of Al interlayers in vermiculite reduces fixation while

Table S16 The effect of <0.2% Al substitution for Si in an ideal kaolinite on the surface charges (excluding edge sites)

	Unsubstituted	Substituted	Difference
Composition	$Al_{400}Si_{400}O_{1000}(OH)_{800}$	$KAl_{401}Si_{399}O_{1000}(OH)_{800}$	-1^{a}
Al, %	20.90	20.94	+0.191%
Si, %	21.76	21.69	
O, %	55.78	55.74	
H, %	1.56	1.56	
K, %[b]	0.00	0.07	+1
Charge ($\mathrm{cmol_c\ kg^{-1}}$[c])	0.00	1.94	+1.94

[a] One surface charge deficit associated with each Al^{3+} substitution for Si^{4+}.

[b] Interlayer cation ion used to maintain electrical neutrality at the surface.

[c] Charge calculated as: $\frac{1\ \text{mole e}}{51{,}670\ \text{g}} \times \frac{1000\ \text{g}}{\text{Kg}} \times \frac{100\ \text{cmol}_c}{1\ \text{mole}} = 1.94\ \mathrm{cmol_c\ Kg^{-1}}$, the formula weight is calculated from $KAl_{401}Si_{399}O_{1000}(OH)_{800}$. A much lower charge value was given by Ma and Eggleton (1999).

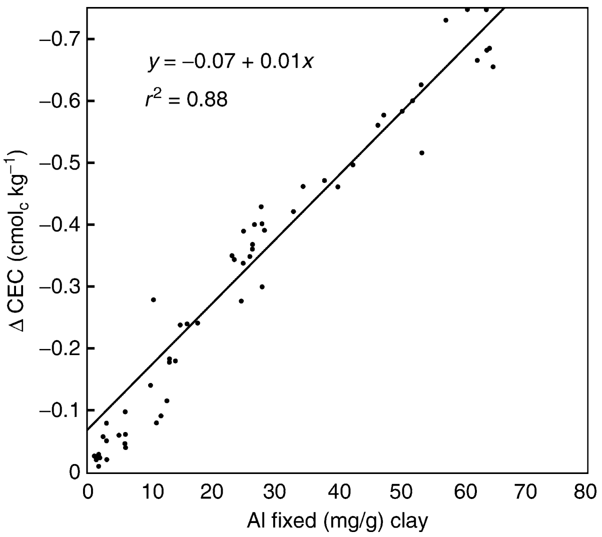


Figure S51 Decrease in cation-exchange capacity resulting from Al fixation by clays (from Barnhisel and Bertsch, 1989).

Table S17 Experimentally-determined values of the Gapon selectivity coefficient for several soil and geologic materials in the K-Ca exchange system

Material	Characteristics/Dominant clay minerals	K_G[a]
Oktibbeha fsl[b] – Bt2 horizon	Well-drained soil/smectite	5.0
Calais sil – Ap horizon	Acid soil/mica, chlorite	10.2
Berks sil – BA horizon	Acid, residual soil from shale/mica, kaolinite	17.0
Cecil sl – BA horizon	Acid, residual soil/kaolinite, HIV	47.9
Nason sil – BA horizon	Acid, residual soil/HIV, kaolinite	131.1
Wyoming Bentonite	Mined/geologic smectite (Ca-saturated)	2.6
Wyoming Bentonite	Mined/geologic smectite (Al-saturated)	19.7
Libby Vermiculite	Mined/geologic vermiculite (Al-saturated)	68.3

[a] Gapon selectivity coefficient measured at 20 °C (after Zelazny, 1970). Higher values denote increasing selectivity of K^+ over Ca^{2+} resulting from the formation of hydroxy-Al interlayers in vermiculite (HIV) and/or smectite.
[b] fsl = fine sandy loam, sil = silt loam, and sl = sandy loam.

increasing the ion exchange *selectivity* for K^+, relative to larger, highly hydrated ions such as Ca^{2+}. This preference for K is illustrated by considerably higher values of the Gapon selectivity coefficient (K_G) for acid soil systems, soils high in HIV (or its micaceous precursors), and Al-saturated clays than for the similar geologic materials shown in Table S17.

Adsorption

In contrast to the electrostatic attraction of ion exchange mechanisms, specific adsorption involves partial covalent bonding (chemisorption) of ions with surface metal-O or -OH groups on oxides and aluminosilicates in soils (Sposito, 1984). Specific adsorption occurs predominantly on variable-charge minerals and noncrystalline oxides and hydroxides of Al, Fe, and Mn (Ford et al., 2001). It is an important mechanism of both cation and anion retention in soils, and therefore, chemisorption is a significant means of controlling the movement of phosphorus or toxic elements in soils and their bioaccumulation in plants (Parker and Rae, 1998).

Stabilization of organic matter

It is known for a long time that clay minerals react with organics and humus (Oades, 1989; Yariv and Cross, 2002). With the aid of physical fractionation methods (particle-size, density, magnetic etc.), the interrelationship between mineral species and organic matter enrichment in soil matrix has been experimentally examined (Turchenek and Odaes, 1979; Christensen, 1992). As expected, organic matter abundance has a strong tie with noncrystalline Fe- and Al-oxides and expandable phyllosilicates (smectites, vermiculites etc.), whereas the correlation with kaolinite is weak. Primary minerals are always concentrated in organic matter-deficient soil fractions.

Soil structure

The most striking effect that clay minerals impose on soil structure is their swelling upon water uptake, which is determined by the exchangeable cation, particle size, surface area and charge properties of minerals (Emerson et al., 1978). Illite and kaolinite have basal spacings which are fixed at all water content, whereas a domain of Ca^{2+}-smectite layers can double its volume by swelling (to a less degree for vermiculites) (Quirk, 1996). A 15% or even less of Na^+ on the surface exchange sites may induce dispersion of smectite particles. Swelling degrades soil structure resulting in the decrease in soil permeability. Layer silicates tend to align parallel to each other and stack along c-axis forming crystals or quasi-crystals (Quirk and Aylmore, 1971). The pore sizes and distribution in an assemblage of such crystals would be different from those in a structure formed from non-lamellae particles. Iron and Al oxides, particularly the non-crystalline forms, are believed to play a role in soil structure formation and stabilization as cementing agents although the mechanism is difficult to be isolated for examination.

Conclusions

Much of the science of soil mineralogy focuses on the formation and properties of the secondary minerals or clay minerals. Clay minerals are not only the most reactive inorganic components of soils, largely governing soil behaviors and properties, but they exhibit an extreme degree of both compositional and structural variability that result from intensive pedogenic weathering. This variability makes identification and quantification of mineral suites, especially clay mineral suites, exceedingly difficult. In spite of this complexity, the need for accurate quantitative information regarding the performance and dynamics of the solid phase of the terrestrial system has never been greater. The traditional role played in understanding soil physical and chemical processes and properties and the implications to agricultural management practices is still important. However, soil mineralogy is increasingly shifting its focus to environmental problems, and computer modeling of interfacial reactions and colloidal behavior at atomic and molecular levels. Experimental verification of modeling results with newly-developed instrumentation tools, and scaling molecular-level data to management parameters will become future challenges for soil mineralogists.

S. B. Feldman, C. Shang, and L. W. Zelazny

Bibliography

Allen, B.L., and Hajek, B.F., 1989. Mineral occurrence in soil environments. In Dixon, J.B., and Weed, S.B., eds., *Minerals in Soil Environments.* Madison, WI: Soil Science Society of America, pp. 199–278.

Altaner, S.P., and Ylagan, R., 1997. Comparison of structural models of mixed-layer illite/smectite and reaction mechanisms of smectite illitization. *Clays Clay Miner.*, **45**: 517–533.

Appelo, C.A.J., and Postma, D., 1996. *Geochemistry, Groundwater and Pollution.* Rotterdam, The Netherlands: A.A. Balkema, 536 pp.

Barnhisel, R.M., and Bertsch, P.M., 1989. Chlorites and hydroxy-interlayed vermiculite and smectite. In Dixon, J.B., and Weed, S.B., eds., *Minerals in Soil Environments.* Madison, WI: Soil Science Society of America, pp. 729–788.

Blanc-Valleron, M., and Thiry, M., 1997. Clays minerals, paleoweathering, paleolandscapes and climatic sequences: the paleogene continental deposits in France. In Paquet, H., and Clauer, N., eds., *Soil and Sediments Mineralogy and Geochemistry.* Berlin Heidelberg: Springer, pp. 233–247.

Bolan, N.S., Naidu, R., Syers, J.K., and Tillman, R.W., 1999. Surface charge and solute interactions in soils. *Adv. Agron.*, **67**: 87–140.

Borchardt, G., 2002. Mineralogy and soil tectonics. In Dixon, J.B., and Schulze, D.G., eds., *Soil Mineralogy with Environmental Applications.* Madison, WI: Soil Science Society of America, pp. 711–736.

Brindley, G.W., and Brown, G., eds., 1980. *Crystal Structures of Clay Minerals and Their X-ray Identification.* London: Mineralogical Society, 495 pp.

Bryant, R.B., and Macedo, J., 1990. Differential chemoreductive dissolution of iron oxides in a Brazilian Oxisol. *Soil Sci. Soc. Am. J.*, **54**: 819–821.

Carlisle, V.W., and Zelazny, L.W., 1973. Mineralogy of selected Florida paleudults. *Soil Sci. Soc. Fla. Proc.*, **33**: 136–139.

Carroll, D., 1953. Weatherability of zircon. *J. Sed. Petrol.*, **23**: 106–116.

Christensen, B.T., 1992. Physical fractionation of soil and organic matter in primary particle size and density separates. *Adv. Soil Sci.*, **20**: 2–90.

Cornell, R.M., and Schwertmann, U., 1996. *The Iron Oxides.* Weinheim: VCH, 573 pp.

Dixon, J.B., and Schulze, D.G., eds., 2002. *Soil Mineralogy with Environmental Applications.* Madison, WI: Soil Science Society of America, 866 pp.

Douglas, L.A., 1989. Vermiculites. In Dixon, J.B., and Weed, S.B., eds., *Minerals in Soil Environments.* Madison, WI: Soil Science Society of America, pp. 635–674.

Ellis, S., and Mellor, A., 1995. *Soils and Environment.* London: Routledge, 364 pp.

Emerson, W.W., Bond, R.D., and Dexer, A.R., eds., 1978. *Modification of Soil Structure.* Chichester: Wiley, 438 pp.

Fanning, D.S., Keramidas, V.Z., and El-desoky, M.A., 1989. Micas. In Dixon, J.B., and Weed, S.B., eds., *Minerals in Soil Environments.* Madison, WI: Soil Science Society of America, pp. 551–634.

Feldman, S.B., and Zelazny, L.W., 1998. The chemistry of soil minerals. In Huang, P.M., ed., *Future Prospects for Soil Chemistry.* Madison, WI: Soil Science Society of America, pp. 139–152.

Feldman, S.B., Zelazny, L.W., and Baker, J.C., 1991. High-elevation forest soils of the southern Appalachians: II. Geomorphology, pedogenesis, and clay mineralogy. *Soil Sci. Soc. Am. J.*, **55**: 1782–1791.

Fisher, R.F., and Binkley, D., 2000. *Ecology and Management of Forest Soils*, 3rd edn. New York: Wiley, 489 pp.

Fitzpatrick, R.W., and Schwertmann, U., 1982. Al-substituted goethite: an indicator of pedogenic and other weathering environments in South Africa. *Geoderma*, **27**: 335–347.

Ford, R.G., Scheinost, A.C., and Sparks, D.L., 2001. Frontiers in metal sorption/precipitation mechanisms on soil mineral surfaces. *Adv. Agron.*, **74**: 41–62.

Fontes, M.P.F., and Weed, S.B., 1991. Iron oxides in selected Brazilian oxisols: I. Mineralogy. *Soil Sci. Soc. Am. J.*, **55**: 1143–1149.

Ghabru, S.K., Mermut, A.R., and St. Arnaud, R.J., 1989. Layer-charge and cation exchange characteristics of vermiculite (weathered biotite) isolated from a Gray Luvisol in northwestern Saskatchewan. *Clays Clay Miner.*, **37**: 164–172.

Giese, R.F., and van Oss, C.J., 2002. *Colloid and Surface Properties of Clays and Related Minerals.* Surface Science Series Vol. 105. New York: Marcel Dekker, 295 pp.

Grimshaw, R.W., 1971. *The Chemistry and Physics of Clays.* New York: Wiley, 1024 pp.

Harris, W.G., Zelazny, L.W., and Baker, J.C., 1984. Depth and particle size distributions of talc in a Virginia Piedmont Ultisol. *Clays Clay Miner.*, **32**: 227–230.

Harris, W.G., Zelazny, L.W., Baker, J.C., and Martens, D.C., 1985. Biotite kaolinization in Virginia Piedmont soils: II. Zonation in single grains. *Soil Sci. Soc. Am. J.*, **49**: 1290–1302.

Harsh, J., Chorover, J., and Nizeyimana, E., 2002. Allophane and imogolite. In Dixon, J.B., and Schulze, D.G., eds., *Soil Mineralogy with Environmental Applications.* Madison, WI: Soil Science Society of America, pp. 291–322.

Haygarth, P.M., and Jarvis, S.C., 2002. *Agriculture, Hydrology and Water Quality.* Wallingford, UK: CABI Publishing, 502 pp.

Johnston, C.T., and Tombácz, E., 2002. Surface chemistry of minerals. In Dixon, J.B., and Schulze, D.G., eds., *Soil Mineralogy with Environmental Applications.* Madison, WI: Soil Science Society of America, pp. 37–68.

Jolicoeur, S., Ildefonse, P., and Bouchard, M., 2000. Kaolinite and gibbsite weathering of biotite within saprolites and soils of central Virginia. *Soil Sci. Soc. Am. J.*, **64**: 1118–1129.

Loughnan, F.C., 1969. *Chemical Weathering of Silicate Minerals.* New York: Elsevier, 154 pp.

Ma, C., and Eggleton, R., 1999. Cation exchange capacity of kaolinite. *Clays Clay Miner.*, **47**: 174–180.

Moore, D.M., and Reynolds, R.C., 1997. *X-ray Diffraction and the Identification and Analysis of Clay Minerals*, 2nd edn. New York: Oxford University Press, 378 pp.

Newman, A.C.D., ed., 1987. *Chemistry of Clays and Clay Minerals.* New York: Wiley, 480 pp.

Oades, J.M., 1989. An introduction to organic matter in mineral soils. In Dixon, J.B., and Weed, S.B., eds., *Minerals in Soil Environments.* Madison, WI: Soil Science Society of America, pp. 89–159.

Quirk, J.P., 1996. Interparticle forces: a basis for the interpretation of soil physical behavior. *Adv. Agron.*, **53**: 121–183.

Quirk, J.P., and Aylmore, L.A., 1971. Domain and quasicrystalline regions in clay systems. *Soil Sci. Soc. Am. Proc.*, **35**: 6252–6254.

Parker, A., and Rae, J.E., eds., 1998. *Environmental Interactions of Clays.* Berlin: Springer, 271 pp.

Pavich, M.J., ed., 1991. Weathering and Soils. *Geoderma*, **51**: 1–299.

Rich, C.I., 1958. Muscovite weathering in a soil developed in the Virginia Piedmont. *Clays Clay Miner.*, **5**: 203–212.

Righi, D., and Meunier, A., 1995. Origin of clays by rock weathering and soil formation. In Velde, B., ed., *Origin and Mineralogy of Clays.* Berlin: Springer, pp. 43–161.

Rowe, R.K., Quigley, R.M., and Booker, J.R., 1995. *Clayey Barrier Systems for Water Disposal Facilities.* London: E & FN Spon (an imprint of Chapman & Hall), 390 pp.

Sawhney, B.L., 1989. Interstratification in layer silicates. In Dixon, J.B., and Weed, S.B., eds., *Minerals in Soil Environments.* Madison, WI: Soil Science Society of America, pp. 789–828.

Scudder, S.J., Foss, J.E., and Collins, M.E., 1996. Soil science and archaeology. *Adv. Agron.*, **57**: 1–76.

Sposito, G., 1984. *The Surface Chemistry of Soils.* New York: Oxford University Press, 234 pp.

Środoń, J., and Eberl, D.D., 1984. Illite. *Rev. Mineral.*, **13**: 495–544.

Thompson, M.L., and Urkainczyk, L., 2002. Micas. In Dixon, J.B., and Schulze, D.G., eds., *Soil Mineralogy with Environmental Applications.* Madison, WI: Soil Science Society of America, pp. 431–466.

Turchenek, L.W., and Oades, J.M., 1979. Fractionation of organo-mineral complexes by sedimentation and density techniques. *Geoderma*, **21**: 311–343.

Velbel, M.A., 1986. Influence of surface area, surface characteristics, and solution composition on feldspar weathering rates. In Davis, J.A., and Hayes, K. F., eds., *Geochemical Processes at Mineral Surfaces.* ACS Symposium Series 323, Washington, DC: American Chemical Society, pp. 615–634.

Velde, B., 1992. *Introduction to Clay Minerals: Chemistry, Origins, Uses and Environmental Significance.* London: Chapman & Hall, 198 pp.

Weaver, C.E., 1989. *Clays, muds, and shales. Developments in Sedimentology No. 44.* New York: Elsevier, 891 pp.

White, A.F., 1995. Chemical weathering rates of silicate minerals in soils. *Rev. Mineral.*, **31**: 407–462.

Yariv, S., and Cross, H., eds., 2002. *Organo-Clay Complexes and Interactions.* New York: Marcel Dekker, 688 pp.

Zelazny, L.W., 1970. Temperature effects on potassium calcium exchange and selectivity in selected soils, clay minerals, and cation exchange resins. Ph.D. Diss. Blacksburg, Virginia: Virginia Polytechnic Institute and State University (Diss. Abstr. 7 1-00520).

Zelazny, L.W., Thomas, P.J., and Lawrence, C.L., 2002. Pyrophyllite-talc minerals. In Dixon, J.B., and Schulze, D.G., eds., *Soil Mineralogy with Environmental Applications*. Madison, WI: Soil Science Society of America, pp. 415–466.

Cross-references

Iron Oxides
Mangan

SOIL ORGANIC MATTER

See *Humic Substances*; *Carbon Sequestration in Soil*.

SOIL PHYSICS

Soil physics is the body of knowledge dealing with the physical properties of soil and the physical processes occurring within soils. It seeks to describe and predict quantitatively the physical behavior of soils, their mechanical, thermal and electrical characteristics, and the transport of energy and materials through the soil, using the appropriate empirically determined properties and environmental variables.

Soil physics uses the primitive quantities, laws, methods and results of classical physics, especially fluid mechanics, together with the insights provided by physical chemistry to understand and characterize physical phenomena occurring in the soil. This understanding is best expressed in the language of applied mathematics. Mathematical descriptions have economy and precision, and mathematics offers the tools necessary to tease out the essential physical conceptual basis of the physical phenomena.

Progress in soil physics relies on the fruitful conjunction of testable theoretical results, laboratory investigations of new phenomena and the experimental testing of predictions, and field observations. Careful field experiments provide a further test of theoretical predictions and indicate new, and as yet unexplained, observations, and departures from theory. Together with soil chemistry and soil biology, soil physics forms the core of modern soil science. Many of the other entries in this deal with specific soil physical concepts in greater depth than here.

Soils are naturally heterogeneous materials and this heterogeneity is manifested on a variety of scales (see later). Soil physics operates principally on a macroscopic scale, large relative to the individual pores or the particles which surround them, but sufficiently small for the soil's physical characteristics to be treated as constant or varying slowly in a well-characterized way. The effective integration and estimation of transient soil physical behavior on the large scale, such as of an aquifer or a landscape, is a continuing issue in soil physics and hydrology.

Soils are porous media *par excellence* and, as such, share many physical characteristics with porous, fibrous and granular materials used in a gamut of other industries and technologies, such as mineral processing, oil production, catalytic processes, paper making, and the materials industries generally. All draw upon a common body of information about the general behavior of such media, as well as elements peculiar to each specific industry. There are good opportunities for intellectual borrowing and mutual aid between these various industries once the barriers of technological jargon unique to each industry are overcome. All too often in the past, the same basic physical phenomenon has occurred in different industries, but the common underlying physical basis has not been perceived. Soil physics thus shares a common ground with much of chemical engineering and material science and there is considerable scope for cross fertilization.

Prehistory

The rise of irrigated agriculture in the fertile triangle of the Middle East between the Tigris and Euphrates, in Egypt, and in China, stimulated the growth of empirical understanding of soil physical properties basic to successful agriculture. These early agriculturalists understood the importance of the soil pores for plant growth. The underpinning conceptual understanding could not emerge, however, until physics had itself emerged and developed millennia later in the middle of the 17th century.

The Sumerian farmer was enjoined more than 4 000 years ago "*to keep trampling oxen and other prowlers off nearby irrigated soil*" (Kramer, 1958). The *Georgics* by the Roman poet Virgil (70–19 B.C.), although intended as a bucolic idyll to "*delight readers rather than instruct farmers*", is full of practical advice about ploughing, animal husbandry and agriculture. Virgil notes (book 1, lines 89–90) that "*on some soils burning stubble opens up fresh ducts and hidden pores through which the juices of the soil may move to the growing plants*". Chinese agriculturalists had a similar practice; Needham (1984) records that "*tilling with fire and weeding with water*" was used to describe the agricultural practices in southern China in 90 B.C. He asserts that it is a technique for fertilizing and pest and weed control, rather than a well-founded attempt to manipulate the soil porosity to the agriculturalists' advantage. The conceptual understanding of the physical mechanisms – enhanced aeration and water transport – to the plant roots had to wait until the end of the last century. Soil physics emerged as a separate discipline within soil science only at about this time. Until then, attention had focused on soil chemistry as the explanation for most aspects of plant production. This was compounded by the mistaken concentration upon the dimensions of soil particles, rather than the dimensions and interconnectedness of the soil pores – one of the few counter examples to the adage of "watch the donut, not the hole."

Important steps in understanding the dynamics of the flow of liquids in porous media had been made by the French engineer, Henry Darcy, in the 1850s, but this work, absolutely central to understanding and quantifying soil water flow, only came to be recognized slowly towards the end of the 19th century. These twin strands of mistaken direction and protracted neglect of important extant knowledge have been recurring themes in the development of soil physics. In the next section we explore some of the major ideas, which have contributed to the advances in soil physical understanding. Readers should remember, however, that the growth of knowledge in soil physics has been fitful, rather than a smooth and inexorable progression to a more complete understanding of the physical behavior of soil.

History

A thoroughgoing critical intellectual history of soil physics does not exist. A recent and accessible first foray into soil physics' history is given by Gardner (1986). Interesting vignettes of the development of soil physics are given in lively accounts of the life and work (and the oversight and neglect) of the two seminal figures in soil physics, Edgar Buckingham and Henry Darcy (see later), by Philip (1974a, 1994). Philip's (1974) article offers a succinct and penetrating account of both the prehistory of soil physics and the development of soil water. The various editions of one of the leading textbooks, Soil Physics (Baver, 1940, 1948, 1956; Baver et al., 1972; Jury et al., 1991), give a sequential picture of the changes in soil physical knowledge over the last 50 years. Other texts such as Kirkham and Powers (1984), Marshall and Holmes (1979), and Hillel (1980, 2002), give occasional accounts of specific developments in historic context.

The following account is primarily concerned with the development of concepts now used in soil physics. The application and, indeed, the development of these analyses depend on the experimental measurement of soil physical properties. Methods and practical details are well described in Klute (1986), in Topp et al. (1992), Dirksen (1999), Dane and Topp (2002) and in other sections of the Encyclopaedia.

Heat flow through the soil

The fundamental physical law governing the conduction of heat through the soil (or any other medium) is Fourier's Law of Conduction (Fourier, 1822). This asserts that the flux of heat (J) (the quantity of heat passing through unit surface area in unit time) is proportional to the temperature (T) gradient. For the case of heat flow in one-dimensions along the z-axis we write Equation (1):

$$J = -\lambda \frac{\mathrm{d}T}{dz} \tag{1}$$

where K is effective thermal conductivity. Application of the principal of conservation of energy to an elementary volume allows us to derive Equation (2):

$$K = \frac{\lambda}{c} \tag{2}$$

where

$$\frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial z^2}$$

is the soil thermal diffusivity, and c is the volumetric heat capacity.

Fourier solved Equation (2) for various constant and time-varying boundary conditions, giving formulae and diagrams for predicting the temperature at specific points in a conductor. Fourier's work was not explicitly directed to the problems of soil temperature. Before long, however, these results were used to analyze the very extensive long-term (13 years) observations of soil temperature collected in Edinburgh (Forbes, 1849; Thomson, 1861), and to deduce the thermal diffusivity of the soil. Thus, by the middle of the last century, we had a good first order description of the propagation of the daily and annual temperature waves into the soil, and adequate methods for gathering and analyzing observations of soil temperature to provide reliable estimates of the thermal properties of the soil. The advanced state of heat flux knowledge was in marked contrast to the prevailing low level of understanding of flow of water through soil at that time. This gap started to close only with Darcy's singular contribution, which we discuss in the next section.

Further investigations showed that a soil's thermal conductivity was not a single unique parameter, but depended on particle size, degree of compaction and moisture content. Compaction raised the conductivity by increasing inter-particle contact and decreasing the proportion of the space occupied by poorly conducting air. Increasing moisture content increases the soil thermal conductivity also, with the greatest proportionate rise occurring at low moisture contents.

Detailed examination showed that the transport of heat through a soil involved two physical processes: conduction (the dominant process), and transfer of latent heat by evaporation and condensation of water within the soil pores. Fortuitously, the equations describing both the conduction and transfer of water in the vapor phase have identical mathematical form to Equation (1), with X, the thermal conductivity of the soil replaced by X_e an effective thermal conductivity (de Vries, 1958). Conversely, in a column of soil with an initially uniform water content, water will redistribute when a steady state temperature gradient is imposed (Jury and Miller, 1974).

Evaporation and condensation are involved in the greater transport of water vapor in soils (up to factor of 10) relative to the flow of non-condensing gases. This effect was elucidated by Philip and de Vries (1957), who explicitly took account of the possibility of condensation and evaporation occurring on opposite sides of the water meniscus separating particles and thus "short circuiting" flow relative to passage through the air-filled spaces alone. The second important element of their theory takes account of the quite dissimilar thermal conductivities of minerals, water and air, which had lead other investigators to underestimate the mean temperature gradient for transport of the water vapor, using sensors which average effectively over all three phases.

Soil-water flow

The first major advance in quantitative understanding of soil water flow was made in 1855 by the French engineer, Henry Darcy (Darcy, 1856). He made the first series of systematic measurements of the flow of water through sand beds. Figure S52 shows a schematic view of Darcy's apparatus with the original mercury monometers replaced by water manometers.

Hubbert (1987) gives an extensive account of Darcy's experiments, including plotting out the results, as well as dealing with later mis-statements and misapplications of Darcy's Law. Darcy concluded that the discharge rate of water (Q) is:

i. directly proportional to the cross-sectional area A;
ii. directly proportional to the pressure difference across the sand bed;
iii. inversely proportional to the length (l) of the sand bed.

Darcy combined his conclusions using the notation of Figure S52 in Equation (3):

$$Q = K \frac{A}{l}(h_2 - h_1) \tag{3}$$

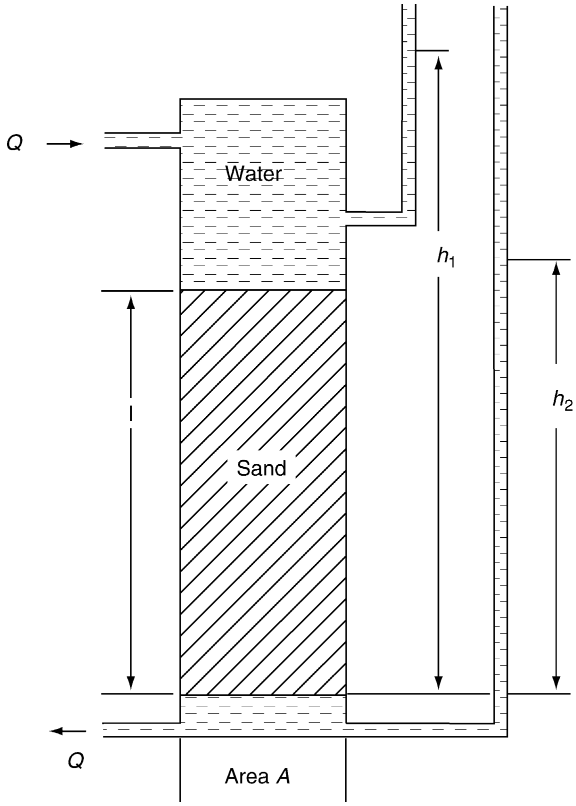


Figure S52 Schematic of Darcy's apparatus showing the quantities measured.

Noting that the flux (q) (flow per unit area per unit time) is Q/A and that the hydraulic gradient $\mathrm{d}h/\mathrm{d}l$ is $-(h_1 - h_2)/l$ where l is the length, Equation (3) reduces to Equation (4):

$$\frac{Q}{A} = q = -K\frac{\mathrm{d}h}{\mathrm{d}l} \tag{4}$$

Darcy described the proportionality factor K as "*a coefficient depending upon the permeability of the sand*". Equation (4) is known as *Darcy's Law*. The dimensions of K (now known as the hydraulic conductivity and a material property of the medium and the fluid) are LT^{-1}. The intrinsic permeability

$$k = \frac{K}{\mu}$$

where μ is dynamic viscosity and is a property of the medium only and has dimensions L^2.

Darcy's Law was regarded originally as an empirical relationship. Subsequently, it has been shown, both experimentally by Rose (1945), and theoretically by (Philip (1973), to be consistent with the Navier Stokes Equation in the limit of small Reynolds number, provided the medium has the appropriate statistical regularity. Practically, the linear relationship between flux and pressure gradient is valid only for flows where the Reynolds number (calculated on the basis of the mean particle diameter is less than 10.

Since its formulation almost 140 years ago, Darcy's Law has been modified to take account of anisotropy (permeability not the same in all directions). More importantly, the pressure gradient is now recognized as the spatial gradient of total potential energy/unit volume with the potential energy (Φ) of the elementary volume of fluid defined relative to a common reference state. The general form of Darcy's Law is thus (Equation (5)):

$$q = -K_{ij}\nabla\Phi \tag{5}$$

where K_{ij} is a symmetrical second-order tensor (expressed in standard summation notation).

Combining Equation (5) with the continuity equation yields the foundations for the theoretical analysis and prediction of flows in saturated media (see Bear, 1972; Freeze and Cherry, 1979; Raats et al., 2002).

By the beginning of the 20th century an adequate understanding of groundwater flow and flow in saturated soils had developed. Water flow in unsaturated soils (all soil pores not completely filled) was unknown territory. Attention focused on the classification of soil water into categories of differing accessibility: gravitation water, capillary water, hydroscopic water (Briggs, 1897; Warrington, 1900) and various empirical "soil constants" (wilting coefficient, moisture equivalent) which corresponded to specific points in the various classes of soil water. The physical meaning of these various points was obscure. This descriptive and qualitative approach inhibited the development of a quantitative and predictive analysis. Even after Buckingham (1904) had made the first sure and extraordinarily fruitful steps in establishing a convincing intellectual basis of soil-water physics, these qualitative ideas remained the dominant paradigm for almost another 30 years. Buckingham's ideas were neglected and soil physics remained in a dead end.

Edgar Buckingham (1867–1940) was an American physicist best remembered for the Buckingham II Theorem of dimensional analysis, Buckingham plastic flow in rheology, and his early work (and textbook) in thermodynamics (Hershey, 1980). Having graduated in physics from Harvard he received a doctorate from Leipzig and taught physics for 10 years at three prestigious U.S. universities before joining the U.S. Bureau of Soils as an "assistant physicist". Philip (1974a) characterized this as a "*strangely lowly situation … one can only guess at the reasons for the great gap between Buckingham's evident intellectual distinction and the subordinate place he occupied, not only in Brigg's laboratory, but throughout his subsequent career.*" At the Bureau of Soils, Buckingham (1904) rapidly completed an outstanding investigation of diffusion and gas flow in soils. This was, however, merely a prelude to his great and enduring work establishing the conceptual physical basis of water in unsaturated soils.

Buckingham's earlier thermodynamic investigations obviously shaped his approach of working at the phenomenological scale and eschewing the then common models of packed spheres or bundles of capillaries. He defined a "*capillary potential $\Psi(\theta)$, at a given moisture content (θ), temperature and bulk density, equal to the reversible work required to transfer water from the soil to a pore water reservoir.*" This is the mechanical component of the Gibbs free energy or chemical activity and corresponds to what is now designated "moisture potential" or "matric potential". The total potential (Φ) is the sum of the gravitational potential and the moisture potential (Ψ), and it determines the equilibrium and movement of soil water. These potentials are usually defined relative to a reference state of water (of the same chemical composition as the soil solution) at atmospheric pressure and at the datum elevation $z = 0$. z is the depth usually treated as positive downward. Thus for non-swelling unsaturated systems (Equation (6)):

$$\Phi = \Psi - z \tag{6}$$

By considering the infinitesimal change in vertical position of a soil water profile at equilibrium and the concordant change in water content, Buckingham established a method for measuring $\Psi(\theta)$ in vertical columns of soil with one end in water. He then determined the $\Psi(\theta)$ relationship for a variety of soils. Drawing on the formal analogy of Fourier's and Ohm's Laws he postulated a constitutive relationship between the vector flux of water (q) and the moisture potential of the form of Equation (7)

$$q = -k(\theta)\frac{\partial \Psi}{\partial z} \tag{7}$$

where k was the hydraulic conductivity. He recognized that $k(\theta)$ was strongly dependent upon the moisture content (θ) and went on to measure experimentally what is now known as the moisture diffusivity

$$D = k(\theta)\frac{d\Psi}{d\theta}$$

Buckingham showed that the form of the $\Psi(\theta)$ and $D(\theta)$ curves was consistent with his speculations on the form of $k(\theta)$ – highly dependent on θ – a result which has since been repeatedly verified. Figure S53 shows $\Psi(\theta)$, $k(\theta)$ and $D(\theta)$ for Yolo light clay.

Buckingham saw that knowing the functional dependence of $\Psi(\theta)$ and $k(\theta)$ made possible a complete mathematical treatment of the subject. Buckingham left the Bureau of Soils in 1905 and his epoch-making paper appeared, after a protracted, and still unexplained, hiatus of two years (Buckingham, 1907). A deafening silence greeted Buckingham's paper. There were only two low-key efforts to build on specific elements of Buckingham's insights in the following 25 years.

The Australians, Green and Ampt (1911), developed a model of one-dimensional unsaturated flow based on the assumption of a sharp boundary between the wetted and unwetted parts of the soil column. The capillary forces act at this interface and the diffusivity is considered to be concentrated at the moisture content of the dry side of the interface ("delta function" model). The Green and Ampt model has proved to be of enduring usefulness. It works best when the actual conditions depart least from the model assumptions: steep wetting fronts and one-dimensional infiltration with constant surface moisture potential into a coarse textured soil at a small and uniform initial water content.

Gardner (1919) proposed specific forms for the $\Psi(\theta)$ and $k(\theta)$ relationships and was the first to apply the continuity requirement and thus arrive at a diffusion type partial differential equation describing one-dimensional horizontal unsaturated flow. Unfortunately, while the $\Psi(\theta)$ and $k(\theta)$ relations were mathematically tractable, they were physically unrealistic. Gardner et al. (1922) made a fruitful practical contribution in devising better direct methods for measuring $\Psi(\theta)$ manometrically. The manometer was connected to the soil sample by means of a fine-pored ceramic disk saturated with water. This device, now known as the tensiometer, was a considerable advance over Buckingham's tedious method.

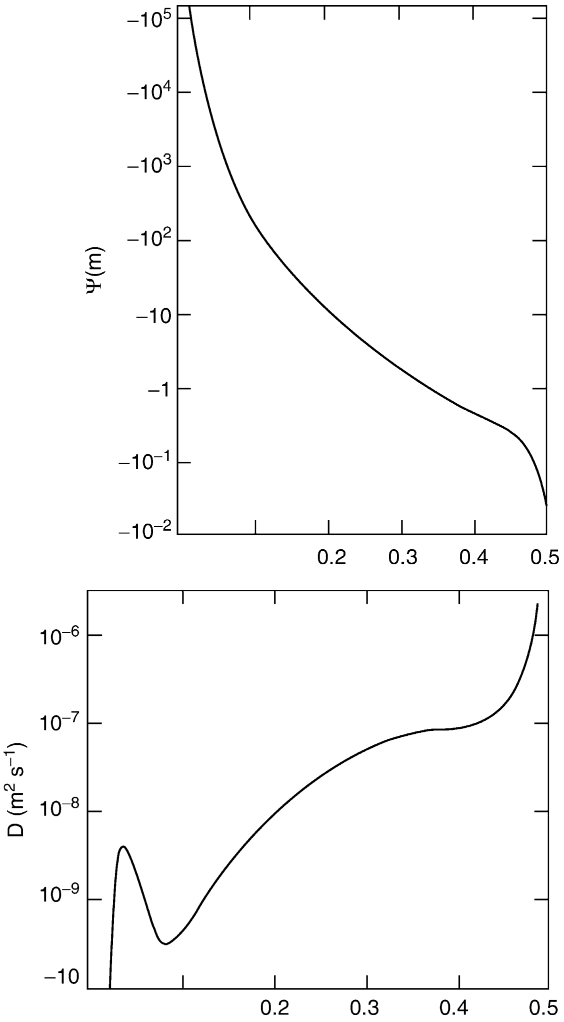


Figure S53 $K(\theta)$,$\Psi(\theta)$, and $D(\theta)$ curves for Yolo light clay. Note the logarithmic scale for $\Psi(\theta)$ and $D(\theta)$ (redrawn from Philip after Moore, 1939).

L. A. Richards, then a student in Willard Gardner's Department at Utah State University, made the next significant advance (Richards, 1928). In a debut paper surprising for its scope, maturity and sure grasp of theoretical and experimental issues, Richards discussed the design principles of tensiometers and the tension plate apparatus. He presented the first data since Buckingham of the soil water potential of four different soils. Richards went on to dissect the term "availability", showing how it involved both transfer of water within the soil to the plant roots, as well as movement of water in the plant. Possible new techniques for measuring capillary potential beyond the tensiometer range were adumbrated.

Richards followed up many of his own suggestions in what Gardner (1972) described as the "*best known PhD thesis in all of soil physics*", and Richards' whole career may be justifiably considered a working through of the ideas, both explicit and implicit, in his first paper. For the first time Richards (1931) combined Buckingham's extension of Darcy's Law with the continuity equation to produce a general partial differential equation describing water movement in unsaturated nonswelling soils, Equation (8):

$$\frac{d\theta}{d\Psi}\frac{\partial\Psi}{\partial\theta} = \nabla(k\nabla\Psi) - \frac{dk}{d\Psi}\frac{\partial\Psi}{\partial z} \tag{8}$$

Richards recognized that when Ψ and k are single-valued functions of the θ, this equation could be written with either θ or Ψ as the dependent variable. He opted for Ψ as the dependent variable yielding a more mathematically intractable equation with the diffusion form hidden.

Richards exerted a continuing influence on the development of the physics of soil water until his retirement in the early 1970s. He focused on the central problem of the energy status of soil water and experimental techniques for its measurement, producing a continuous stream of innovations in tensiometers. This work, summarized in Richards (1941), repays reading today. Richards created the pressure membrane apparatus for measuring capillary potential in semi-arid and arid zone soils where the tensiometer failed. This technique and Richards' constructive encouragement were instrumental to the development of the outflow method for measuring unsaturated permeability (Gardner, 1956).

Paradoxically, Richards' work in measuring soil water potential reinvigorated the old Briggsian concepts of "wilting point" and "field capacity" by giving them a spurious exactitude. They were now defined in terms of precise values of the soil water potential (15 bars and %bar respectively) rather than being recognized more realistically as spanning a range of potential. There was a common belief that, between these two limits, soil water content also had no impact on plant growth. This view was dissected and demolished by Richards and Wadleigh (1952). A generous and thorough account of the work and personality of Richards is given by Gardner (1972). The companion pieces in this Richards' valedictory volume offer diverse perspectives on the state of soil water physics at that time.

Modern soil water physics

The mathematical complexity of Richards' Equation inhibited further progress, though Richards did solve one problem – the steady state capillary rise from a water table. He was able to take advantage of the linear decrease of hydraulic conductivity with capillary potential and thus effect a considerable simplification of Equation (8). It was a further 17 years (though the Depression and World War II intervened) before Childs and George (1948) recognized the diffusion form for the steady state one-dimensional flow equation. This work combined some theoretical analysis with the experimental measurement of $D(\theta)$ in a sand, more than 40 years after the only prior estimates made by Buckingham.

It remained for Klute (1952) to rewrite Richards' Equation with θ as the dependent variable yielding Equation (9):

$$\frac{\partial\theta}{\partial t} = \nabla(D\nabla\theta) - \frac{dk}{d\theta}\frac{\partial\theta}{\partial z} \tag{9}$$

(see Figure S53). The physical concepts of soil water movement are now embedded in this mathematical formulation. Quantitative prediction requires the solution of Equation (8), subject to the boundary conditions appropriate to the specific physical circumstances. Klute (1952) considered the case of one-dimensional horizontal adsorption, which reduces Equation (8) to the nonlinear diffusion equation (Equation (10)):

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial\theta}{\partial x}\right) \tag{10}$$

Shortly after, Philip (1954) solved the full Equation (8) and derived an infiltration equation with physical significance, based on the leading terms of his full solution (Equation (11)):

$$i = S\sqrt{t} + At \tag{11}$$

Here i is the cumulative infiltration and t time. The constants (S and A) are explicitly related to the physical properties of the soil. Philip (1957) went on to show how a large number of different infiltration phenomena could be given a unified understanding based on solution of Equation (8) with various boundary conditions. Recognition of the non-linear diffusion form of Richards' Equation made it possible for soil water investigators to seek solutions in a vast array of situations. A telling example of the economy and efficiency of an approach at a sufficiently general level!

An enormous number of different physical situations involving infiltration were rapidly investigated. These results are brought together in Philip's encyclopaedic review (1969a), and in a thorough overview of subsequent developments in the solution of the nonlinear diffusion equation (Philip, 1974b). Clearly, divergent trends have now emerged in the treatment of Richards' Equation to predict soil water movement. One strand has involved the development of various algebraic expressions for the diffusivity and conductivity as a function of soil moisture (θ), leading to mathematical simplification of Richards' Equation amenable to analytic solutions. A related approach uses integral formulations for $K(\theta)$.

The second strand is based on the inexorable rise of the computer and its burgeoning calculating power. This has led to the industrial scale production of numerical solutions to Equation (8), subject to initial and boundary conditions reflecting the specific physical circumstances of the problem under consideration. There is some danger that blind calculation is displacing physical insight.

Heterogeneity

Soils are intrinsically heterogeneous. This heterogeneity undermines efforts to make quantitative predictions *on the field scale* about the equilibrium and movement of soil water and dissolved substances. Over and above the heterogeneity of the soil pores Dagan (1986) identified three scales of heterogeneity:

- laboratory: length scale of the order 10^{-1}–10^{0} m
- local: length scale of the order 10^{1}–10^{2} m
- regional/aquifer: length scale of the order 10^{4}–10^{5} m

These were additional to the molecular and pore scales, which serve as the bases for the formulation of the macroscopic theories such as Darcy's Law. The heterogeneity on each of these scales may be either deterministic or stochastic. In *deterministic heterogeneity* the soil properties vary spatially in a known way. In general, heterogeneity of this class may be dealt with using the standard methods of soil physics, although the juxtaposition of differing soil materials may give rise to new phenomena such as unstable flows or perched water tables.

Stochastic heterogeneity involves essentially random variations in soil properties on all the scales above, plus possible random variation in boundary conditions such as initial soil moisture, or precipitation rates. The physical parameters of the system are assumed to be independent of time, i.e., stationary in a statistical sense.

Effective methods of attacking the problem of statistical heterogeneity are problematic. One approach involves sampling the system and using measured parameters to deduce parameters for a uniform surrogate system with the same equivalent gross behavior. This is the "equivalent homogeneous medium" approach. It did not work well in saturated systems (Freeze, 1975) and similar pessimistic conclusions emerged from the analysis of unsaturated flow in a highly simplified one-dimensional heterogeneous system (Philip, 1980).

An alternative approach, pioneered by Dagan, explicitly treats the medium properties and related flow variables as random space variables, which are assumed stationary and have expected correlation scales much less than the scale of investigation. The mathematical equations describing the flow become stochastic partial differential equations, which can be solved in some cases, given knowledge of the statistical properties of the physical parameters – such as treating the hydraulic conductivity, say, as a normal distribution. It is assumed that these statistical quantities inferred by measurements on the appropriate scale are drawn from all possible realizations of the random variable. As Dagan notes "*this poses a conceptual difficulty, since only one realisation of a porous sample or formation is available, and it is not always possible to infer the statistical structure from a single realisation*." It is feasible, however, if the random function exhibits some kind of stationarity.

The growing recognition of the spread (and amelioration) of buried pollutants by groundwater flows (both saturated and unsaturated) has led to the development of a number of different stochastic approaches to what was formally a problem in convection-dispersion, in addition to the initial forays by Dagan and Freeze. They are reviewed in Dagan (1987) and in Jury (1988). Dagan considered that the lack of high quality field data "*analysed with the aid of the theoretical tools already developed or under development*" was the limiting step. One of the rare experiments of this category is reported in Sudicky (1986).

The general issues of the statistical characterization of the variation of soil physical properties is given by Warrick and Neilsen (1980). Jury and Horton (2004) gives an introduction to many of the concepts such as variogram, auto correlation etc., in a soils context. The geostatistical, fractal, fuzzy set and wavelet approaches are well displayed in Warrick et al. (1986), and Dane and Topp (2002).

Hysteresis

The characteristic curve relating the equilibrium moisture content to the applied moisture potential is not a smooth single curve, but has at least two branches (known as scanning curves), corresponding to the entry of water into the soil and its release from the soil. This phenomenon is termed hysteresis and most readers would be aware of the analogous phenomenon in magnetization of ferro-magnetic materials where the magnetic induction lags the magnetizing force. The physical cause for these two different scanning curves are the differences in radii between the channels connecting soil pores (r_a and the diameter of the pores themselves (r_b) (Figure S54).

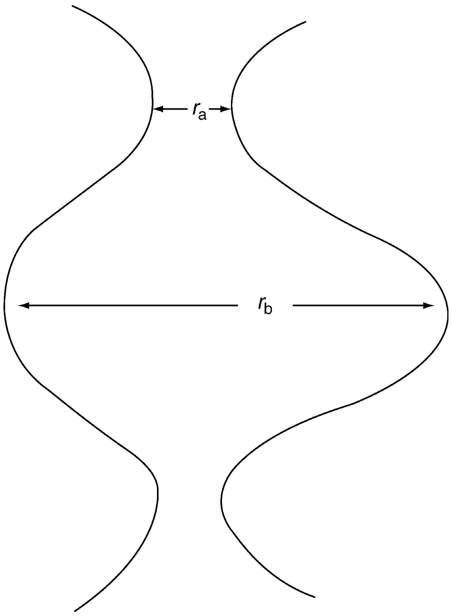


Figure S54 Cross-section of an idealized soil pore showing the different radii.

The initially dry pore will fill at a suction corresponding to $2\gamma / r_b$ when presented with water (γ is the surface tension). Emptying the pore requires, however, suction corresponding to $2\gamma/r_a$. Since $r_a < r_b$, the suction at which the pore fills is less than that of which it empties. Often on the first cycle of wetting and drying the curves do not close at the dry end due to entrapment of air. Subsequent cycles should close. Two additional points are noteworthy. Since in swelling soils (see later) the inter-particle spaces and pores are always filled with water, these materials do not display hysteretic behavior. Secondly, since straight capillaries do not vary in diameter they cannot display hysteresis. This is a further reason why the so-called "capillary bundle" approach represents an inappropriate model for real soils. We note also that the behavior of hysteretic soils clearly depends on their past history and the direction of change in moisture content or suction. Thus, they do not conform to the assumptions of ergodicity and stationarity, which underpin many of the stochastic approaches insofar as they are applied to unsaturated flows and redistribution.

Swelling soils

The foregoing discussion has been concerned with soils, which do not change their volume as their water content changes. They are regarded essentially as rigid matrices of inter-connected pores, which may contain water, the amount depending on the potential of the water supply. There is a second class of soils, predominantly clays or soils containing significant amounts of clay, which change their volume as their water content changes, and maintain all inter-particle spaces filled with water at all times. The physical mechanism by which these volume changes occur involves adjustment of inter-particle spaces between the charged platelets of clay to achieve a state of minimum free energy in response to changes in either water content or external loading. It is energetically advantageous to reduce the spacing between all particles to allow for the removal of a small quantity of water rather than to remove water totally from one inter-particle space and bring the two positively charged platelets into close (and highly energetic) proximity.

Swelling soils occur widely and are of considerable agricultural significance. An early and interesting attempt to describe their behavior (Terzaghi, 1923) recognized that part of the mechanical load was carried by the inter-particle water rather than by the rigid soil particle matrix as in non-swelling soils. However, it lacked a proper appreciation of the capillary potential and was more oriented towards the large loads characteristic of civil engineering and soil mechanics.

Almost 50 years later Philip (1969b) was able to develop a much improved conceptual basis for the physical and mathematical understanding of swelling soils. This work extended the precepts of the classical analysis of soil water movement in several important directions:

1. recognition that Darcy's Law refers to water movement *relative* to the soil particles (in a swelling soil both water and particles are moving relative to an absolute reference). The mass flow may be comparable to the Darcy flow relative to the particles. Thus Equation (12):

$$v_r = -K(\theta)\nabla\Phi \tag{12}$$

   where v_r is the flow relative to the particles.
2. the void ratio (e) changes during swelling/consolidation and must be included in the specification of soil properties;
3. inclusion of the overburden potential Ω, in the total potential. Thus, for one-dimensional systems (Equation (13)):

$$\Phi = \Psi + \Omega - Z \tag{13}$$

When these additional elements are incorporated into the classical analyses of two component horizontal systems, it is possible to derive expressions for swelling soils which are identical in form to those for non-swelling soils, provided we adopt a Lagrangian (material) coordinate formulation i.e., Equation (14):

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial m}\left(D^* \frac{\partial\theta}{\partial m}\right) \tag{14}$$

where

$$D^* = (1+e)^{-1} K \frac{d\Psi}{d\theta}$$

Here a material coordinate (m) is used such that (Equation (15)):

$$\nabla m = (1+e)^{-1} \tag{15}$$

where e is the void ratio. The use of the alternative Eulerian (physical space) coordinates greatly complicates the mathematics.

We must take account of the overburden potential in the analysis of vertical and loaded systems. The simplest case of a vertical column at equilibrium corresponds to Ω being a constant. Using realistic approximations for the dependence of the rate of change of void ratio with volumetric moisture content, it may be shown that there are three quite distinct types of equilibrium profiles: the soil moisture may increase, decrease, or remain constant with depth. Equilibrium moisture distributions in swelling soil are thus quite different from those of non-swelling soils.

The situation for vertical flows (both steady and unsteady) is complicated. The simplest generalization is that relative to non-swelling soils, gravity has a quite different effect on equilibrium and flow, varying by a function ($1 - ay$), which may range between +1 and −1 depending on the soil and moisture content (θ). Here y is the specific gravity of the soil minerals and a is the ratio of change of void ratio with moisture content at zero stress. Steady upward flows are possible, and flow *direction* depends on the surface and deep moisture contents, the external load, and the physical properties of the soil.

Epilog

This short overview of the history and development of soil physics reflects those issues and ideas, which appeal to me. The many other articles elsewhere in this encyclopedia dealing with more specific aspects of soil physics augment the discussion here and treat additional areas. The material presented here does permit, however, some general conclusions. The clear message in the history of development of soil physics so far is that it has been most rapid and fruitful when it has made use of the basic concepts of physics and physical chemistry, and when it has been prepared to explore their relations mathematically. This new understanding has been coupled with a willingness to pursue the associated mathematics to the level required, and to produce quantitative and predictive theories capable of being tested in the laboratory and the well-controlled field situation. This is the positive achievement. On the negative side there remains many difficult and unresolved issues in applying our knowledge and theory, which works well on the field scale, onto the larger scales of a landscape or catchment subject to all the intrinsic heterogeneities and natural stochastic variation (Scott, 2000). Hysteresis further complicates these issues. It may come about that some of these may be recognized ultimately as "trans-scientific" (Weinberg, 1972) and that although they may be posed as scientific questions, the answer is beyond the reach of the exact sciences. Much remains to be done.

P. W. Ford

Bibliography

Baver, L.D., 1940. *Soil Physics.* New York: Wiley.

Baver, L.D., 1948. *Soil Physics*, 2nd edn. New York: Wiley.

Baver, L.D., 1956. Soil Physics, 3rd edn. New York: Wiley.

Baver, L.D., Gardner, W.H., and Gardner, W.R., 1972. *Soil Physics*, 4th edn. New York: Wiley.

Bear, J., 1972. *Dynamics of Fluids in Porous Media.* New York: American Elsevier (See especially Chapters 4, 5, and 6.).

Briggs, L., 1897. The mechanics of soil moisture. *USDA Div. Soils Bull., 10. Washington, DC: USDA.*

Buckingham, E., 1904. Contributions to our knowledge of the aeration of soils. *USDA Bur. Soils Bull., 25.* Washington, DC: USDA.

Buckingham, E., 1907. Studies on the movement of soil moisture. *USDA. Bur. Soils Bull., 38. Washington, DC: USDA.*

Childs, E.C., and George, N.C., 1948. Soil geometry and soil–water equilibrium. Disc. *Faraday Soc.*, **3**: 78–85.

Dagan, G., 1986. Statistical theory of groundwater flow and transport: pore to laboratory, laboratory to formation, and formation to regional scale. *Water Resour. Res.*, **22**: 1205–1345.

Dagan G., 1987. Theory of solute transport by groundwater. *Ann. Rev. Fluid Mech.*, **19**: 183–215.

Dane, J.H., and Topp, G.C., eds., 2002. *Methods of Soil Analysis. Part 4, Physical methods.* Madison, WI: Soil Science Society of America, 1692 pp.

Darcy, H.P.G., 1856. *Les Fontaines Publiques de la Ville de Dijon*, Valmont, Paris.

Dirksen, C., 1999. *Soil Physics Measurements.* Reiskirchen, Germany: Catena, 154 pp.

Forbes, J.D., 1849. An account of some experiments on the temperature of the Earth at different depths and in different soils, near Edinburgh. *Trans. R. Soc. Edin.*, **16**: 189–236.

Fourier, J.B.J., 1822. *Theorie Analytique de la Chaleur*, Paris. English translation by Freeman, Cambridge, 1878, reprinted, New York, 1988.

Freeze, R.A., 1975. A stochastic-conceptual analysis of one-dimensional groundwater flow in non-uniform homogeneous media. *Water Resour. Res.*, **11**: 725–741.

Freeze, R.A., and Cherry, J.A., 1979. *Groundwater.* Englewood Cliffs, NJ: Prentice-Hall.

Gardner, W., 1919. The movement of moisture in soil by capillarity. *Soil Sci.*, **7**: 313–317.

Gardner, W.R., 1956. Calculation of capillary conductivity from pressure plate outflow data. *Soil Sci. Soc. Am. Proc.*, **20**: 317–320.

Gardner, W.R., 1972. The impact of L.A. Richards upon the field of soil water physics. *Soil Sci.*, **113**: 232–237.

Gardner, W.H., 1986. Early soil physics in the mid 20th century. In Stewart, B.A., ed., *Advances in Soil Science,* Vol. 4. New York: Springer, pp. 1–101.

Gardner, W., Israelson, O.W., Edlefsen, N.E., and Clyde, H.S., 1922. The capillary potential function and its relation to irrigation practice. *Phys. Rev. Ser. 2*, **20**: 196.

Green, W., and Ampt, G.A., 1911. Studies in soil physics I. The flow of air and water through soils. *Agric. Sci.*, **4**: 1–24.

Hershey, M.D., 1980. Edgar Buckingham. In Gillespie, C.C., ed. in chief, *Dictionary of Scientific Biography,* Vol. 1. New York: Charles Scribner's Sons, pp. 565–566.

Hillel, D., 1980. *Fundamentals of Soil Physics.* New York: Academic Press.

Hillel, D., 2004. *Introduction to Environmental Soil Physics*. Amsterdam: Elsevier, 494 pp.

Hubbert, M.K., 1987. Darcy's Law; its physical theory and application to entrapment of oil and gas. In Lander, E.R., and Ince, S., eds., *History of Geophysics,* Vol 3, *The History of Hydrology.* Washington, DC: American Geophysics Union.

Jury, W.A., 1988. Solute transport and dispersion. In Steffen, W.L., and Denmead, O.T., eds., *Flow and Transport in the Natural Environment Advances and Applications.* Berlin: Springer, pp 1–16. (The following "Commentary" (pp. 17–29) by Knight, J.H. draws out *inter alia* the strong linkages between the soil physical and chemical engineering approaches to essentially the same problem.)

Jury, W.A., and Miller, E.E., 1974. Measurement of the transport coefficients for coupled flow of heat and moisture in a medium sand. *Soil Sci. Soc. Am. Proc.*, **38**: 551–557.

Jury, W.A., and Harton R., 2004. *Soil Physics*, 6th edn. New York: Wiley. 370 pp.

Kirkham, D., and Powers, W.L., 1984. *Advanced Soil Physics.* Malabar, FL: Krieger, 534 pp. New York: Wiley, 270 pp.

Klute, A., 1952. A numerical method for solving the flow equation for water in unsaturated materials. *Soil Sci.*, **73**: 105–116.

Klute, A. ed., 1986. *Methods of Soil Analysis. Part 1 – Physical and Mineralogical Methods. Monograph 9.* Madison, WI: American Society of Agronomy.

Kramer, S.N., 1958. *History Begins at Sumer.* London: Thames and Hudson.

Marshall, T.J., and Holmes, J.W., 1974. *Soil Physics.* Cambridge: Cambridge University Press.

Moore, R.E., 1939. Water conduction from shallow water tables. *Hilgardia*, **12**: 383–426.

Needham, J., 1984. *Science and civilisation in China. Volume 6, Biology and Biological Technology II Agriculture.* Bray F. (auth.). Cambridge: Cambridge University Press.

Philip, J.R., 1954. Some recent advances in hydrologic physics. *J. Inst. Eng. Aust.*, **26**: 255–259.

Philip, J.R., 1957. The theory of infiltration: 1. The infiltration equation and its solution. *Soil Sci.*, **83**: 345–357. (This is the first paper in a 7 paper series and all should be consulted.)

Philip, J.R., 1969a. Theory of infiltration. *Adv. Hydrosci*, **5**: 215–296.

Philip, J.R., 1969b. Hydrostatics and hydrodynamics in swelling soils. *Water Resour. Res.*, **5**: 1070–1077. (But see also the Comment by Young, E.G., and Towner, E.G., and the reply by Philip, *Water Resour. Res.* (1970), **6**: 1246–1247 and 1248–1251, respectively.)

Philip, J.R., 1973. Flow in porous media. In Becker, E., and Mikhailov, O.K., eds., *Proc. 13th Int. Congr. Theor. App. Mech., Moscow 1972.* Berlin: Springer, pp. 279–294.

Philip, J.R., 1974a. Fifty years progress in soil physics. *Geoderma*, **12**: 265–280.

Philip, J.R., 1974b. Recent progress in the solution of non-linear diffusion equations. *Soil Sci.*, **117**: 257–264.

Philip, J.R., 1980. Field heterogeneity: some basic issues. *Water Resour. Res.*, **16**: 443–448.

Philip, J.R., 1995. Desperately seeking Darcy in Dijon. In Proc. J. R. Philip Symp. *Soil Sci. Soc. Am. J.* **59**: 319–324.

Philip, J.R., and de Vries, D.A., 1957. Moisture movement in soils under temperature gradients. *Trans. Am. Geophys. Un.*, **38**: 222–228.

Raats, P.A., Smiles, D., and Warrick, A.W., 2002. *Environmental Mechanics: Water, Mass, and Energy Transfer in the Biosphere.* Washington, DC: American Geophysical Union, 345 pp.

Richards, L.A., 1928. The usefulness of capillary potential to soil moisture and plant investigations. *Agric. Res.*, **37**: 719–742.

Richards, L.A., 1931. Capillary conduction of liquids through porous mediums. *Physics*, **1**: 318–333.

Richards, L.A., 1941. A pressure-membrane extraction apparatus for soil solution. *Soil Sci.*, **51**: 318–333.

Richards, L.A., and Wadleigh, C.H., 1952. Soil water and plant growth. In Shaw, B.T., ed., *Soil Physical Conditions and Plant Growth,* Monograph Vol. 2, American Society of Agronomy. New York: Academic Press, pp. 73–251.

Rose, H.E., 1945. An investigation into the laws of flow of fluids though beds of granular material. *Proc. Inst. Mech. Eng.*, **153**: 141–148.

Scott, H.D., 2000. *Soil Physics: Agricultural and Environmental Applications*. Ames: Iowa State University Press, 421 pp.

Si, B.C., and Kachanoski, R.G., 2000. Unified solution for infiltration and drainage with hysteresis: Theory and field test. *Soil Sci. Soc. Am. J.*, **64**: 30–36.

Sudicky, E.A., 1986. A natural gradient experiment on solute transport in a sand aquifer: spatial variability of hydraulic conductivity and its role in the dispersion process. *Water Resour. Res.*, **22**: 2069–2082. (But see also the comment by White, I. and reply by Sudicky, *Water Resour. Res.* (1988) **24**:, 892–894 and 895–986, respectively.)

Terzaghi, K., 1923. Die Berechnung der durchlassigkeitsziffer des Tones aus der Verlauf der hydrodynamischer Spannungserscheinungen. *Sitzber. Akad. Wiss. (Wien)*, Abt **2a**: 132, 125–138.

Thomson, W., 1861. On the reduction of observations of underground temperature; with application to Professor Forbes' Edinburgh observations, and the continued Gallon Hill Series. *Trans. Roy. Soc. Edin.*, **22**: 405–427.

Topp, G.C., Reynolds, W.D., and Green, R.E., eds., 1992. *Advances in Measurement of Soil Physical Properties: Bringing Theory into Practice* (Proceedings of a Symposium, San Antonio, Texas). SSSA Spec. Pub. 30. Madison, WI: Soil Science Society of America. Vergil Georgics Book I, lines 89–90.

de Vries, D.A., 1958. Simultaneous transfer of heat and moisture in porous media. *Trans. Am. Geophys. Un.*, **39**: 909–916.

Warrick, A.W., and Neilsen, D.R., 1980. Spatial variability of soil physical properties in the field. In Hillel, D.I. ed., *Applications of Soil Physics.* New York: Academic Press, pp. 319–324.

Warrick, A.W., Myers, D.E., and Neilsen, D.R., 1986. Geostatistical methods applied to soil science. In Klute, A., ed., *Methods of Soil Analysis. Part 1 Physical and Mineralogical Methods, Monograph 9.* Madison, WI: American Society of Agronomy, pp. 53–82.

Warrington, R., 1900. *Lectures on Some of the Physical Properties of Soil.* Oxford: Clarendon Press.

Weinberg, A.M., 1972. Science and trans-science. *Minerva*, **10**: 209–222.

SOIL PORES

Pores are the *sine qua non* of soil. Soil without pores we call rock. Life enters the soil through the pores, and further it is sustained by them. Pores allow roots, plus other soil flora and fauna, to penetrate the soil. Pores act both as conduits for, and reservoirs of the necessities of life. Water infiltration and storage, gaseous entry and exhaust, plus chemical transport and exchange are all facilitated by the network of pores that in sum often accounts for about half of the soil's total volume.

Porosity

Soil is a three-phase medium, comprising solid, liquid and gaseous volume fractions,

$$V = V_s + V_l + V_g \tag{1}$$

where V is the total volume of some representative elementary volume of soil (m^3), and the right-hand side identifies the volumetric contributions of the solid, liquid and gaseous phases (m^3). If this element of soil has mass of solids m_s (kg), then the bulk density ρ_b is simply m_s/V. When this soil is dry, $V_l = 0$, so the mass m_s is entirely due to the solid particles which are themselves of particle density ρ_s. Hence $V_s = m_s/\rho_s$. Thus the total porosity of this dry soil, ϕ, is V_g/V(m^3 m^{-3}). So upon dividing through by V, Equation (1) becomes

$$1 = \frac{V_s}{V} + \frac{V_g}{V} \tag{2}$$

or

$$\phi = 1 - \frac{\rho_b}{\rho_s} \tag{3}$$

Commonly soil solids have a particle density of around 2.65 M gm^{-3}, whereas the bulk density of field soils is often about 1.3 Mg m^{-3}. Thus soils frequently have a total volumetric porosity of about one half. This total porosity is however distributed across a wide range of pore sizes and shapes, ranging from the microscopic interstices between clay platelets to the large inter-connected burrows made by soil fauna such as worms.

Pore size classes

Classification of soil pores according to their size has the advantage of avoiding ambiguous use of terms such as microporous, while at the same time eliminating redundant terminology. However any such scheme by overlooking pore continuity, tortuosity and connectivity, ignores the fact that there is not necessarily a simple correspondence between pore size and function. Which classification scheme to adopt (Bouma, 1981), or whether indeed to classify or not, has been the subject of recent debate (Luxmoore, 1981). At the broad scale we can functionally distinguish between macroporosity and matrix porosity (Skopp, 1981). The former refers to the interconnected pore space of larger voids, which engenders preferential transport of both water and chemical such that there is only limited exchange with the pores of the matrix. The latter refers to those pores in which the flow through the body of the soil is slow enough that there is extensive inter-pore mixing. The separation between macropore and matrix pore will be discussed later in greater detail.

As for classification on the other hand, one scheme that has withstood the test of time, is that proposed by Brewer (1964). This pore-size classification scheme is presented in Table S18, where following Bouma (1981), Brewer's (1964) use of the word "void" has been replaced by "pore".

Whereas such a scheme ensures clarity of communication, it is often more important to characterize soil pores in terms of their function, in particular with regard to their ability to store and conduct water. Water is the dominant liquid in soil, and furthermore not only is it the substrate of life within the soil; it is also the vehicle for the transport through soil of such chemicals as nutrients. We now proceed to discuss the role of soil pores in the storage and transport of water.

Table S18 The size classification scheme of pore size developed by Brewer (1964)

Class	Subclass	Class limits (μm)
Macropores	Coarse	>5 000
	Medium	2 000–5 000
	Fine	1 000–2 000
	Very fine	75–1 000
Mesopores		30–75
Micropores		5–30
Ultramicropores		0.1–5
Cryptopores		<0.1

Statics of water in soil pores

Water is attracted into soil pores predominantly because of the attraction of water to surfaces, and the capillary forces associated with the surface tension of water at an air-water interface, σ (N m^{-1}). The surface tension of pure water is 73 N m^{-1} at 20 °C. The water molecules at an air-water interface thus feel at net attraction into the liquid, lending to the water surface a membrane-like property such that in a tube or pore the air-water surface becomes concave. The contact angle where this meniscus meets the pore wall is for soil commonly considered to be zero. Such soil is thus readily wetted. Hydrophobic substances such as organic material can however create non-zero contact angles and so lead to a slower wetting of the soil.

The pressure difference ΔP across a curved air-water meniscus is

$$\Delta P = \frac{2\sigma}{r_c} \tag{4}$$

where r_c is the radius of meniscus curvature. Thus the height of rise of water into a clean, cylindrical capillary tube of radius R can be found to be

$$H = \frac{2\sigma}{\rho_w g R} \tag{5}$$

where ρ_w is the density of water (kg m^{-3}) and g the acceleration due to gravity (m s^{-2}). The smaller the pore then the greater the capillary rise. The pressure required to return this capillary water to a free-water state (i.e., "blow" it out of the capillary tube), namely the potential of the water ψ in terms of its energy per unit volume, is

$$\psi = -\frac{2\sigma}{R} \tag{6}$$

where ψ is in units of pressure (N m^{-2}). A ready-reckoner of this relationship is that ψ in terms of energy per unit weight (in cm of H_2O head) is $-3/d$ where d is the capillary diameter in mm.

Thus the larger the pores in soil, the easier it is to remove water from them. Hence drainage of large pores may occur rapidly under the action of gravity. Conversely the smaller the pores the more work required, and in such cases even the roots of plants may experience difficulty in extracting capillary water from these pores.

Further, there even exists some non-capillary association of a thin layer of water directly with the particle surfaces of the walls of soil pores.

So in soil, the higher the potential, that is the closer to the $\psi = 0$ of free water, the wetter the soil. The volumetric soil water content, θ, is V_l/V (Equation (1)) and has units of $m^3\ m^{-3}$. At $\psi = 0$, the soil is said to be saturated; $\theta = \theta_s$. Depending upon the manner of wetting, it is generally observed that $\theta_s < \phi$ by about 0.05–0.1. Thus when wet to equilibrium with a free-water surface, some 5–10% of the soil's volume still remains air-filled, albeit probably in isolated pockets.

At lower potentials, as more work is done, successively smaller pores drain and the soil water content drops. Thus there is a relationship between ψ, the so-called matric potential, and θ. This relationship is termed the soil water characteristic function, or the water retention curve. This curve is not unique for it has a different form during wetting, to that which results from drainage. Primarily this hysteresis is due to the aptly named "ink-bottle" effect, which relates to the differential filling and draining of irregularly-shaped pores.

A range of techniques is available to measure $\psi(\theta)$ both in the laboratory on undisturbed cores, or in situ in the field. A host of functional forms have been proposed to describe this $\psi(\theta)$ relationship. One that is both effective and useful was proposed by Brooks and Corey (1966). This can be simplified to

$$\psi = \psi_e \left(\frac{\theta}{\theta_s}\right)^{-b} \tag{7}$$

where for $\psi_e < \psi \leq 0$, $\theta = \theta_s$. The reciprocal of the exponent b is often referred to as the pore-size distribution index for it reflects the rate at which pores drain as ψ decreases. Indeed Campbell (1985) related b to the standard deviation of the particle size distribution.

It is generally observed that θ_s for clay ($\approx$0.5) is greater than that for sand ($\approx$0.3). However b for sand ($\approx$0.2) is less than that for clay ($\approx$2). The drop-off in θ is rapid in sands as ψ decreases for there are few small pores that can remain water-filled.

Not only do pores provide the means by which water can be stored in soil, they also act as conduits for the passage of water and air through the soil.

Pore classes and the unsaturated flow of water

Water is the vehicle by which most compounds are moved through soil. Networks of soil pores form the routes along which this convective and diffusive transport occurs. The larger the pore, the faster the transport and the greater the amount of material moved. Thus soil pores play a dominant role in the transport of water and nutrients across the soil surface and through the soil towards the roots. Furthermore these pores play a critical role in establishing the propensity of water and its passenger solutes to leach beyond the rootzone, and so possibly pollute the underlying groundwater.

If we consider the unit soil pore to be a cylinder of radius r, then the Hagen-Poiseuille Law of fluid flow in a pipe can be used to describe the flow,

$$q = -\left(\frac{r^2}{8\upsilon}\right)\frac{\Delta P}{\Delta x} \tag{8}$$

where q is the flux density ($m\ s^{-1}$), υ the viscosity of water ($kg\ m^{-1}\ s^{-1}$) and ΔP (Pa) is the pressure difference across this pipe "pore" of length Δx (m). Thus we can compare Hagen-Poiseuille's pipe-flow equation with the Darcy Law of Saturated Water Flow

$$J = -k_s \frac{d\Phi}{dz} \tag{9}$$

where J is the flux density of water through the soil ($m\ s^{-1}$), and k_s is the saturated hydraulic conductivity of the soil, with $d\Phi/dz$ being the gradient in the total potential which comprises the sum of the matric potential ψ and the potential due to gravity z. By inspection of Equations (8) and (9) we thus note that a cylindrical pore possesses a conductivity of $(\rho_w g)r^2/8\upsilon$.

Now if soil is considered to be a bundle of capillary pipes of various sizes (Childs and Collis-George, 1950; Marshall, 1957; Campbell, 1974, 1985), and a face is cut across a slab of this soil, then the flux density of soil water flow will be the sum of the flux densities of each of the capillary classes, each multiplied by the fractional area of the face occupied by capillaries belonging to that class. On the exposed face, the fractional area covered by pores in the size class from r to $r + dr$, is the same as the probability of finding a pore belonging to that class, namely $f(r)dr$ where $f(r)$ is the pore size distribution function. The soil's porosity is of course ϕ, the integral across all pore sizes

$$\phi = \int_0^R f(r)dr \tag{10}$$

where R is the radius of the largest pore. Further, if the cut-faces of the soil are randomly rejoined, then the probability of finding a continuous pore of a given size from one face to the other is the product of the probability of finding it on either face, namely $(f(r)dr)^2$. Thus the fractional contribution of a connected pore of this area to the hydraulic conductivity is $(\rho_w g)r^2/8\upsilon(f(r)dr)^2$. This connected pore's contribution to the conductivity can be integrated across all pore classes to find the hydraulic conductivity of the entire capillary bundle in which connected pores up to size r^* are water-filled. Thus

$$k(r^*) = \rho_w g \int_0^{r^*}\int_0^{r^*} \frac{r^2}{8\nu} f(r)dr f(r)dr \tag{11}$$

Other forms of this integral have been derived (Burdine, 1953; Mualem, 1976).

Now for such cylindrical pores, the fractional water-filled area $f(r)dr$ will correspond to the volumetric water content of that class $d\theta$. So use of the capillary rise equation (Equation (6)), in conjunction with the functional form of the retentivity curve given by Equation (7), allows integration of Equation (11) to

$$k(\theta) = \frac{\rho_w g \sigma^2 \theta_s^2}{2\nu\psi_e^2(2b+1)(2b+2)}\left(\frac{\theta}{\theta_s}\right)^{2b+2} \tag{12}$$

Campbell (1985) used this equation in a very empirical way to estimate the saturated hydraulic conductivity k_s from soil textural data. However since k_s is best measured in the field, whereas the retentivity curve can more easily be determined in the laboratory on undisturbed soil cores, it is common to rewrite Equation (12) as being matched at saturation,

$$k(\theta) = k_s\left(\frac{\theta}{\theta_s}\right)^m \tag{13}$$

where $m = 2b + 3$ if a so-called pore-interaction term is included (Campbell, 1985). Now k_s can be some measured value, and the value of $m = 2b + 3$ obtained by measurement of the shape of the soil water retentivity curve. Thus knowledge of the distribution of pore sizes in the soil, as deduced by the wetting or draining of pores, can subsequently be used to estimate the shape of the unsaturated hydraulic conductivity function.

Other parametric forms of Equation (13) have been derived by Brooks and Corey (1966) and van Genuchten (1980).

In all of these derivations, knowledge of the pore sizes in the soil has lead to a formulation for the soil's conductivity, the latter being the property that characterizes the unsaturated flow of water through the soil. In some instances such parameterizations have been found wanting (Scotter et al., 1988). Thankfully new measurement techniques have however improved our ability to measure the unsaturated hydraulic conductivity, even in the field. Indeed these observations can be used, in the opposite sense to that outlined above, to infer an effective "mean" pore size for the soil.

Unsaturated flow and pore size

In Miller and Miller's landmark paper of 1956 a theory of similar media was developed, and a microscopic length scale was associated with the characteristic size of the pores. This microscopic length scale describes some physical property of one pore system, such as its conductivity, relative to that possessed by another medium that is similar, but differs only in the spatial scale of its pore system.

However at the macroscopic scale, the value of the conductivity and its drop-off with decreasing ψ in some way reflects the actual internal geometry of that soil's pore system. Philip (1985) noted it is possible to use a single parameter to characterize the capillary properties of pores in unsaturated soil. This he considered to be the length,

$$\lambda_c = [k_0 - k_n]^{-1} \int_{\psi_n}^{\psi_0} k(\psi)\mathrm{d}\psi \tag{14}$$

where $k_0 = k(\psi_0)$, $k_n = k(\psi_n)$ and ψ_0 and ψ_n are the wetting potential and the antecedent potentials. Raats and Gardner (1971) had earlier termed this length a conductivity-weighted mean soil water potential, which can be thought of as being some average height of water rise that can be sustained by the capillary forces within this soil.

In the mathematical treatment of soil water flow, analytical advantage accrues if the functional form of the conductivity-pressure potential relationship is considered exponential,

$$k(\psi) = k_s \exp[\alpha(\psi - \psi_0)] \tag{15}$$

This quasi-linear form (Philip, 1968), so-called because it linearizes a form of the soil-water flow equation, frequently provides a good rendition of $k(\psi)$ observations. When Equation (15) is substituted into Equation (14), clearly

$$\lambda_c = \frac{1}{\alpha} \tag{16}$$

Philip (1985) called $2\alpha^{-1}$, or $2\lambda_c$, the sorptive length since it is a length, which represents the capillary, or sorptive attractiveness of the soil's pores. Typically α ranges from 20 mm^{-1} in coarse-textured soils, up to 200 mm^{-1} in loams and clays. Further, Philip (1985) introduced this $2\alpha^{-1}$ length into the capillary-rise formula, i.e., Equation (5), to obtain an equivalent pore radius,

$$r_m = \frac{\sigma\alpha}{\rho g} \tag{17}$$

or $r_m = 7.4 \times 10^{-6}\,\alpha$, if both are in m. Thus a soil whose conductivity function $k(\psi)$ is given by Equation (15) would appear to transmit water as if it were composed of a suite of pores each of radius r_m. White and Sully (1987) called r_m a flow-weighted mean pore size.

Thus from observations of water flow in the soil over some range of ψ, it is possible to deduce an equivalent pore size that accounts for the observed capillary and gravitational effects. For repacked laboratory soils, White and Sully (1987) found there was a 1 : 1 correspondence between r_m and the particle size range. However for undisturbed field soils there was no such relationship. Close to saturation r_m was unrelated to particle size, with larger-than-expected pores accounting for the nature of the observed flows.

The use of tension infiltrometers (Clothier and White, 1981) and disk permeameters (Perroux and White, 1988) has allowed undisturbed measurement in the field of $k(\psi)$ over the range of ψ from 0 down to about −150 mm. These devices, and the analyses presented above, have provided insight into the size of those pores involved in the transport of water and chemical through field soils. The impact of macropores will be discussed later, after some consideration of the fraction of the soil's porosity involved in chemical transport.

Chemical transport and mobile-immobile pore water

In the laboratory, using carefully repacked media, many studies have shown that all of the soil's wetted porosity takes part in the transport of chemical by the moving water. However in the field, and even in aggregated media in the laboratory, deeper-than-expected penetration of surface applied chemicals has been noted. This has led to a reassessment of the fraction of the soil's pores considered to be actively involved in transporting chemicals. Following the petroleum engineering work of Coats and Smith (1964), only some fraction of the soil's wetted porosity is considered mobile; the complement being deemed to be effectively immobile with regard to solute transport. Hence the solute flow equation can be written for the transport of chemical during water flow at flux q (m s^{-1}),

$$\theta_m \frac{\partial c_m}{\partial t} + \theta_{im} \frac{\partial c_{im}}{\partial t} = \theta_m D \frac{\partial^2 c_m}{\partial z^2} - q \frac{\partial c_m}{\partial z} \tag{18}$$

Both convection, and the dispersion characterized by D (m^2 s^{-1}) are considered limited to the pores of the mobile fraction θ_m (m^3 m^{-3}). The concentration c_{im} (mol m^{-3}) in the pores of the immobile fraction θ_{im} (m^3 m^{-3}) can be most simply related to that in the mobile fraction c_m (mol m^{-3}) by

$$\theta_{im} \frac{\partial c_{im}}{\partial t} = \beta(c_m - c_{im}) \tag{19}$$

where β is a rate constant (s^{-1}). This formulation allows for more rapid and deeper transmission of non-reactive solute as a result of the effective transport volume of pores θ_m being less than the total water-filled porosity θ_o, which comprises $\theta_m + \theta_{im}$.

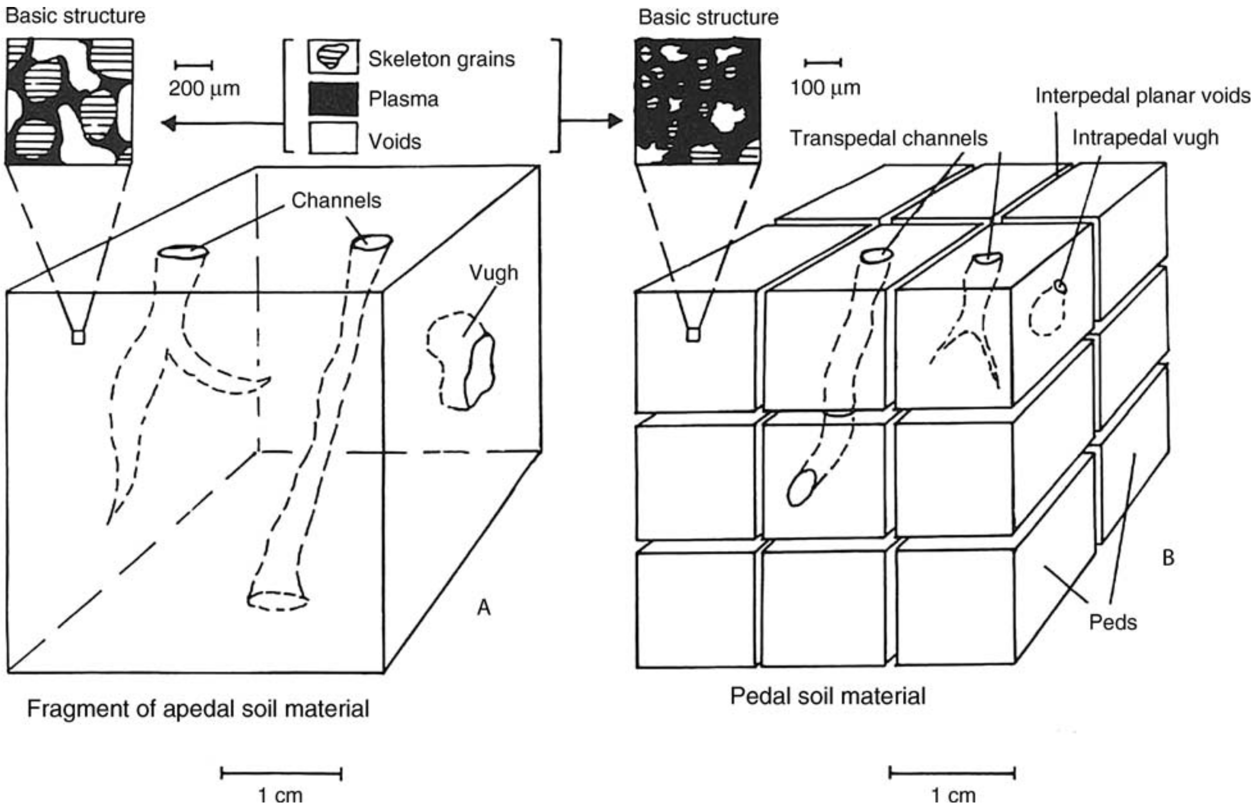


Figure S55 Simplified pore structure models for apedal and pedal soils (from Bouma and Anderson, 1973).

In a laboratory study with an artificially-aggregated soil, Nkedi-Kizza et al. (1983) showed the mobility ratio θ_m / θ_o to be dependent upon q and aggregate size. Clothier et al. (1992) developed a field technique for measuring the fraction of the soil's pores involved in chemical transport, θ_m / θ_o. They found in one soil during unsaturated flow engendered by $\psi_o = -20$ mm, $\theta_m/\theta_o = 0.5$. Only one half of this field soil's wetted porosity appeared to be actively involved in chemical transport.

Macropores

Traditionally soil physicists thought of soil as being the contradictory amalgam of a matrix of spheres enclosing a network of cylindrical pores. That soils can have pedal structure, and can be traversed by continuous macropores has however long fascinated pedologists, and especially micromorphologists (Brewer, 1964; Figure S55). These structural elements create interpedal voids, which along with channels can have a dramatic effect upon the transport of water, chemical and gas through soil. Recall that the conductivity of a cylindrical pore increases with the square of the radius. Thus these macropores, more so because they frequently form an interconnected network, can impact greatly on soil transport processes.

This realization has lead to the development of new field techniques and procedures such as the disk permeameter and capillary-length scale analysis (White and Sully, 1987).

In two forested watersheds, Wilson and Luxmoore (1988) found that macropore flow constituted 85% of the flux during infiltration from a free-water pond. Nonetheless there was sufficient capacity in the mesopores that the surface flux of most rainfall events, $q \approx 70$ mm hr^{-1}, could be accommodated without the need for the macropores to fill.

The macroporosity and structure depicted in Figure S55 can however be quite variable in space, especially with depth. Much of the biologically-engendered, or biologically-sustained macroporosity drops off with depth as the population density of soil flora and fauna declines. Also because of its fragility, macroporosity can also be temporally variable. Soil management, or even natural events, can substantially alter the macroporous structure, Using Equation (17), White and Perroux (1987) found that prior to drought-breaking rains, the soil at Murrumbateman, NSW, Australia had a "mean" flow-weighted pore size of $r_m = 240$ µm at $\psi_o = -22.5$ mm. High intensity rain (≈35 mm hr^{-1}), falling upon this soil that had been dry for 4.5 years, altered the pore size structure such that r_m dropped to just 99 µm.

Sauer et al. (1989) using the same analysis found that moldboard plowed soil had, near saturation, a "mean" pore dimension of $r_m \approx 150$ µm, as would have been expected from the soil's texture. However the same soil after 7 years of no-till management had, at saturation, an $r_m \approx 1.5$ mm reflecting the large amount of macroporosity that had developed. Transport through

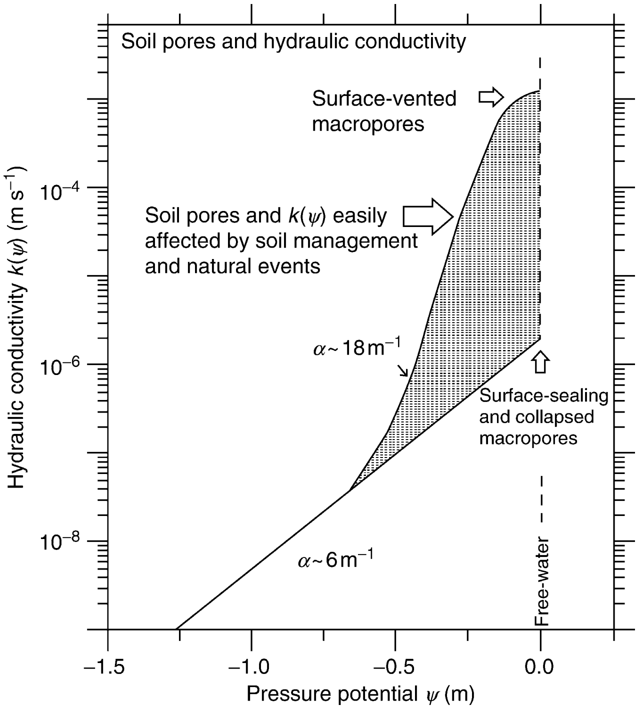


Figure S56 A conceptual view of the hydraulic conductivity function $k(\psi)$ that acknowledges both the role of matrix pores and the impact of macropores (after Clothier, 1989).

soil of water and its passenger chemicals, along with gaseous exchange, depends critically upon soil pores, and especially those larger and often-interconnected macropores. The latter are however very fragile, and these macropores can easily be disturbed or disrupted, especially at the surface where they can either be vented, or rendered ineffective by sealing. Thus we can postulate a hydraulic conductivity function that can vary dramatically, especially as a result of changes in the characteristics of those larger pores that only become filled at high potentials near saturation (Figure S56). For this hypothetical soil without macropores, the exponential representation in Figure S56 indicates $\alpha \approx 6\ \mathrm{m}^{-1}$ (Equation (15)), which suggests that a mean pore size of $r_m = 45\ \mu\mathrm{m}$ would best represent saturated flow through this soil (Equation (17)). However if macropores were to develop in this soil, then the $k(\psi)$ function could easily develop into that depicted by the upper curve in Figure S56. Over the region $-0.5 \leq \psi_o \leq 0$, α is now about $18.5\ \mathrm{m}^{-1}$, which suggests a mean pore dimension of about $135\ \mu\mathrm{m}$. This increase in pore size has a major affect on the transport processes operating in field soil. Furthermore the alteration of the distribution of pore sizes that leads to the change from one bound to the other in Figure S56 can be quite rapid and brought about either by soil management or natural events.

Soil is soil because it has pores. This goes beyond mere definition, it underpins soil functioning.

Brent E. Clothier

Bibliography

Bouma, J., 1981. Comment on micro-, meso- and macroporosity of soil. *Soil Sci. Soc. Am. J.*, **45**: 1244–1245.

Bouma, J., and Anderson, J.L., 1973. Relationships between soil structure characteristics and hydraulic conductivity. In Bruce, R.R., Chair, ed. comm., *Field Soil Water Regime.* Madison, WI: Soil Science Society of America, pp. 77–87.

Brewer, R., 1964. *Fabric and Mineral Analysis of Soils.* New York: Wiley, p. 470.

Brooks, R.H., and Corey, A.T., 1966. Properties of porous media affecting fluid flow. *J. Irrig. Drain. Div., Am. Soc. Civil Eng.*, **92**(IR2): 61–88.

Campbell, G.S., 1974. A simple method for determining unsaturated conductivity from moisture retention data. *Soil Sci.*, **117**: 311–314.

Campbell, G.S., 1985. *Soil Physics with BASIC: Transport Models for Soil Plant Systems.* Amsterdam, The Netherlands: Elsevier, p. 150.

Childs, E.C., and Collis-George, N., 1950. The permeability of porous materials. *Proc. R. Soc. Lond. A*, **201**: 392–405.

Clothier, B.E., 1989. Root zone processes and water quality: the effect of management. Proc. Symp. Water Quality Modeling of Agricultural Non-point Sources, Logan, Utah, USDA-ARS **81**(2): 659–683.

Clothier, B.E., and White, I., 1981. Measurement of sorptivity and soil water diffusivity in the field. *Soil Sci. Soc. Am. J.*, **45**: 241–245.

Clothier, B.E., Kirkham, M.B., and Mclean, J.E., 1992. In situ measurement of the effective transport volume for solute moving through soil. *Soil Sci. Soc. Am J.*, **56**: 733–736.

Coats, K.H., and Smith, B.D., 1964. Dead-end pore volume and dispersion in porous media. *Soc. Petrol. Eng. J.*, **4**: 73–84.

van Genuchten, M.Th., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.*, **44**: 892–898.

Luxmoore, R.J., 1981. Micro, meso- and macroporosity of soil. *Soil Sci. Soc. Am. J.*, **45**: 671–672.

Marshall, T.J., 1958. A relation between permeability and size distribution of pores. *J. Soil Sci.*, **9**: 1–8.

Mualem, Y., 1976. A new model for predicting the hydraulic conductivity of unsaturated media. *Water Resour. Res.*, **12**: 513–522.

Nkedi-Kizza, P., Biggar, J.W., Genuchten, van M.Th., Wierenga, P.J., Selim, H.M., Davidson, J.M., and Nielsen, D.R., 1983. Modeling tritium and chloride 36 transport through an aggregated oxisol. *Water Resour. Res.*, **19**: 691–700.

Perroux, K.M., and White, I., 1988. Designs for disc permeameters. *Soil Sci. Soc. Am. J.*, **52**: 1205–1215.

Philip, J.R., 1968. A linearization technique for the study of infiltration. In Rijtema, R.E., and Wassink, H., eds., *Water in the Unsaturated Zone.* IASH/UNESCO Symp., Vol. 1. Paris: UNESCO, pp. 471–478.

Philip, J.R., 1985. The quasilinear analysis, the scattering analog, and other aspects of infiltration and seepage. In Fok, Y.-S., ed., *Infiltration Development and Application.* Honolulu: Water Resources Research Center, pp. 1–27.

Raats, P.A.C., and Gardner, W.R., 1971. Comparison of empirical relationships between pressure head and hydraulic conductivity and some observations of radially symmetric flow. *Water Resour. Res.*, **7**: 921–928.

Sauer, T.J., Clothier, B.E., and Daniel, T.C., 1990. Surface measurements of the hydraulic properties of a tilled and untilled soil. *Soil Till. Res.*, **15**: 359–369.

Scotter, D.R., Clothier, B.E., and Sauer, T.J., 1988. A critical assessment of the role of measured hydraulic properties in the simulation of absorption, infiltration and redistribution. *Agric Water Manag.*, **15**: 73–86.

Skopp, J., 1981. Comment on micro-, meso- and macroporosity of soil. *Soil Sci. Soc. Am. J.*, **45**: 1246.

White, I., and Perroux, K.M., 1987. Use of sorptivity to determine field soil hydraulic properties. *Soil Sci. Soc. Am. J.*, **51**: 1093–1101.

White, I., and Sully, M.J., 1987. Macroscopic and microscopic capillary length and time scales from field infiltration. *Water Resour. Res.*, **23**: 1514–1522.

Wilson, G.V., and Luxmoore, R.J., 1988. Infiltration, macroporosity, and mesoporosity distributions on two forested watersheds. *Soil Sci. Soc. Am. J.*, **52**: 329–335.

Cross-references

Capillary Pressure
Diffusion Processes
Drainage
Field Water Cycle
Hydrophility, Hydrophobicity
Imbibition
Infiltration
Leaching
Particle Density
Particle-Size Distribution
Permeability
Pollution
Soil Drainage
Soil Water
Texture
Tillage
Transport Processes
Water Budget in Soil
Water Content and Retention
Water Movement
Wetting Front

SOIL PROBE

See *Auger*.

SOIL QUALITY

See *Health*; *Quality*.

SOIL REACTION

See *Acidity*.

SOIL SALINITY AND SALINIZATION

The term *salinization* refers to the process of accumulation of salts in soil. Salinization occurs when water, carrying dissolved salts, evaporates at the soil surface, frequently leaving a white salt crust at the soil surface. Salinization is generally more pronounced in arid and semi-arid, than in more humid regions, because of insufficient rainfall to flush accumulated salts from the crop root zone. Accumulation of salts occurs in irrigated areas where greater amounts are brought in by the irrigation water than are removed by the drainage. On a global basis, salt-affected soils occupy 954.8 million ha of land (Szablocs, 1989), constituting nearly 7% of total land area or nearly 33% of the area of potential arable lands of the world (Gupta and Abrol, 1990).

The original and, to some extent, the direct source of all the salt constituents are the primary minerals found in soils and in the exposed rocks of the Earth's crust such as Cretaceous shale or Devonian limestone. These salts were trapped (connate salts) during deposition of the sediment. In relatively rare cases salts may be added from a deep-seated source, for example along the East African rift system.

During the process of chemical weathering of minerals and rocks, which involves hydrolysis, hydration, solution, oxidation and carbonation, salt constituents are gradually released into solution. The soluble salts that accumulate in soils consist principally of cations of calcium, magnesium, and sodium and the chloride and sulfate anions. Potassium, bicarbonate, carbonate, and nitrate ions occur in small quantities. Borates occasionally occur in small amounts but receive considerable attention because of their exceptionally high toxicity to plants. The nature of the salts present obviously depends on the composition of the rock weathered, the nature of weathering process, and the subsequent reactions that occur during translocation of the compounds formed (Seatz and Peterson, 1965). The geochemistry of salts also depends on the sequence of precipitation of weathering products (Szablocs, 1989) and is affected by variations in temperature and moisture regime at the site of their deposition (Whittig et al., 1982).

Various theories have been proposed to account for the presence of soluble salts within glacial deposits of the Great Plains region of Northern America. These include brine squeezing (Cherry, 1972), oxidation of organic sulfur (Hendry et al., 1986) and oxidation of pyrite (Mermut and Arshad, 1987). Redistribution of the soluble salts occurred when ground water flow systems adjusted to the new ground-water regimes developed under crop fallow system. Up to 90 t ha^{-1} of salt was leached from glacial till surface soil in cultivated recharge areas (Ferguson and Bateridge, 1982).

Characterization of soil salinity

Soil salinity is described and characterized in terms of the concentration and type of soluble salts. The concentration of dissolved salts in water or soil extract is commonly determined by measuring the *electrical conductivity* (EC). EC is a measure of the conductance of the soil solution, which is dependent on the quantity of dissolved ions in soil water. EC is expressed in units of deci-Siemens (dS) m^{-1} at 25 °C (1 dS m^{-1} = 1 mmho cm^{-1}). For a more detailed discussion, see *Conductivity, electrical*.

There are direct and indirect methods of determining the EC of a soil solution. Direct methods involve sampling the soil and extracting the pore-water in the laboratory by suction-filtration and measuring EC of the extract (U.S. Salinity Laboratory Staff, 1954). The advantages of the saturated paste method are that it is often related to field soil water contents, it closely resembles the chemical composition of the soil solution and it is the standard upon which crop tolerance to salinity is appraised (Maas and Hoffman, 1977). Other extraction ratios, 1 : 1, 1 : 5, etc. have become popular because they are faster, less costly and usually more reproducible than saturated paste extracts. However, they are not so well related to field soil water contents. Errors from peptization, hydrolysis, cation exchange, and mineral dissolution also become greater for such extracts (Rhoades, 1982). As a compromise, a soil:water ratio of 1 : 2, as recommended by Sonnevelt and van der Ende (1971) is commonly used in many laboratories.

The major chemical parameters of interest that can be determined by direct sampling and soil solution extractions include pH, EC, soluble cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and anions (CO_3^{2-}, HCO_3^-, SO_4^-, Cl^-, NO_3^-, H_3BO_3). Analytical methods for determining these solutes are described by Rhoades (1982).

The most important single use of solute concentration and composition data is to estimate the osmotic potential of the solution so as to predict its influence on plant growth. The electrical conductivity and the osmotic potential of the soil-water extract are directly related as follows (U.S. Salinity Laboratory Staff, 1954):

$$\text{osmotic potential (MPa)} = -0.036 \times \text{EC (dS m}^{-1}) \qquad (1)$$

This relationship works well for soil solution extracts in the range 3–30 dS m^{-1} (Bresler et al., 1982).

The concentration of solutes in terms of their ionic strength (I) can also be estimated from EC according to the following expression developed by Griffin and Jurinak (1973):

$$I \text{ (mole l}^{-1}) = 0.0127 \times \text{EC (dS m}^{-1}) \qquad (2)$$

In addition to the total salinity (osmotic) hazard of soil solution, the tendency of the solution to produce exchangeable sodium must also be considered. Because of the adverse effects on soil structure, Na ions can have very important effects on the physical properties of soils, depending upon the nature of the colloids present and the abundance of other ions. A useful index for predicting this effect is the *sodium adsorption ratio* (SAR), defined by the relation.

$$\text{SAR} = \frac{[\text{Na}^+]}{\sqrt{0.5([\text{Ca}^{2+}] + [\text{Mg}^{2+}])}} \qquad (3)$$

where all concentrations are in meq l^{-1}. Unlike most theoretical ion "ratios", however, the SAR is expressed in terms of ion concentrations rather than in terms of ion activities. Furthermore, it does not take into account reductions in free ion concentrations and activities due to ion-pair or complex formation (Sposito and Mattigod, 1977). Justification for using concentration instead of activities in defining the SAR is discussed in detail by Bresler et al. (1982).

Although the *exchangeable sodium percentage* (ESP) has been commonly used as the main criterion for appraising soil alkalinity, emphasis has shifted more recently toward use of the SAR of the equilibrium soil solution for classification purposes. The SAR and ESP values are approximately numerically equivalent up to values of about 25. The SAR is readily determined from the saturation soil paste extract already required for the EC. An exchangeable sodium determination, on the other hand, requires extraction of all soluble and exchangeable sodium from the soil with an appropriate salt solution, and subsequent substraction of any soluble sodium present in the extract. In addition, a soil cation exchange capacity (CEC) determination is required. Because of the considerable experimental pitfalls involved in an accurate exchangeable sodium determination, deviations between measured ESP and ESP values as predicted from the SAR/ESP relationship generally are resolved in favor of the SAR-derived estimates (Bresler et al., 1982).

Periodic information on the status of soil salinity is essential to assess and evaluate the effectiveness of remedial and monitoring programs. However, monitoring of soil salinity is complicated by its spatial variability and its dynamic nature, due to the influence of management practices, water table depth, rainfall and salinity of the perched groundwater (Rhoades and Corwin, 1984). Numerous and frequent characterization of salt-affected areas by conventional measuring techniques is expensive. However, indirect and innovative methods have been developed. New instruments developed within the last two decades have the potential to meet the necessary requirements for salinity monitoring and mapping at the appropriate scales. Bulk soil electrical conductivity can be measured indirectly by using electrode probes or electromagnetic (EM) induction devices (Corwin and Rhoades, 1984). *Bulk or apparent soil electrical conductivity* is a measure of the overall conductivity of the solid, liquid and air phases. A number of EM devices developed by Geonics Limited, are available including EM-38, EM-31, and EM34-3 meters. The EM-38 is the most widely used instrument for soil salinity investigations.

The design of the EM-38 meter is such that when a conductivity reading is taken at the surface of a homogeneous medium the result reflects a cumulative relative contribution of soil conductivities from the various strata above some depth. Furthermore, the relative contribution of conductivity from the various depths depends upon the orientation (horizontal vs. vertical) of the transmitter coil with respect to the soil surface. The EM-38 meter measures apparent conductivity of the ground to a depth of 1.5 m in the vertical dipole mode, and 0.75 m in the horizontal dipole mode. The EM-31 meter measures conductivity to a depth of 6 m. The EM meter response is affected by such variables as soil temperature, soil moisture and soil mineralogical composition (see Corwin and Rhoades, 1984 for more detail). Consequently, the apparent electrical conductivity values should be interpreted with caution.

A relatively recent development in the application of EM meter technology has been the use of mobile, automated EM survey systems for producing contour maps of apparent electrical conductivity values. The system consists of an all terrain vehicle, a trailer for the EM-38 or EM-31 meter, a wheel and/or odometer mechanism for triggering EM readings, and a data storage system (datalogger or lap-top computer). This mobile system allows EC measurements to be taken while the operator drives across the field. A new cost effective airborne electromagnetic system, known as SALTMAP, specifically designed for soil and ground water salinity monitoring has recently been developed (Roberts et al., 1992; Duncan et al., 1992). By using these techniques, it is possible to define areas at risk of becoming saline. These surveys can be utilized to develop effective management strategies for combating soil salinity on a regional basis. The advantage of these systems compared to manual readings taken by walking is that a much larger area can be surveyed in a shorter period of time to produce high quality contour maps of the aerial distribution of salinity (see George and Woodgate, 2002).

Classification of salt-affected soils

The terminology applied to salt-affected soils varies from country to country and many colloquial terms are employed in certain areas (Abrol and Bhumbla, 1978; Szablocs, 1989). The designations proposed by the U.S. Salinity Laboratory (1954) are, however mostly used. Based on the composition of salts and their effects on soil properties and plant growth, salt-affected soils have been separated into saline and sodic (nonsaline-alkali) soils.

Saline soils

A soil is *saline* if the EC of saturation paste extract is >4 dS m^{-1}, ESP or SAR is <15 and the pH is usually <8.5. The limits set by the U.S. Salinity Laboratory (1954) are somewhat arbitrary.

According to Sposito (1989), salt-sensitive crops are affected even at EC of 1 dS m^{-1} that correspond to ionic strength of 14 mol m^{-3}. Thus in respect to crop salinity tolerance, a soil can be “saline” at any ionic strength >15 mol m^{-3} if the plants growing in it are stressed. The principal soluble salts are sulfate and chloride of sodium, calcium and magnesium. Small amounts of bicarbonates, and occasionally some nitrate are also present. Measurable quantities of soluble carbonates are usually absent.

Based on the hydrological, morphological and chemical properties of the soil profile, saline soils are also termed as *Solonchaks*. The basic morphological precondition for a saline or Solonchak is the lack of structural B horizon. For the purpose of reclamation they are categorized into several types such as active Solonchaks, puffy Solonchaks, crust Solonchaks, nitrate Solochaks, etc. (For a detailed discussion, see Szablocs, 1989).

Another type of soil salinization, which has been recognized relatively, recently is the seepage of salt-bearing leachate from areas of higher elevation and their concentration at lower elevation. Soils affected by this process are commonly confined to non-irrigated lands in the arid and semi-arid regions. During the last two decades, dryland salinity (commonly referred to as *saline seep* or *salting*) has become a major agricultural problem in many areas of Western Australia (Soil Conservation Authority, 1982), the Canadian Prairies (Vander Plyum, 1978) and the northern Great Plains of the United States (Brown et al., 1982). Increases in salinity from this kind of seepage is the result of long-term changes in climatic and hydrological conditions that influence salt retention, or changes in land use and management that increase the quantity of percolating water. The processes involved in the formation of various types of saline seeps are discussed by Brown et al. (1982). Briefly, a typical saline seep develops when water percolates through the soil profile beyond the root zone in the upland (recharge area) and transports soluble salts in the process. At some depth, the water is intercepted by a less permeable layer, which restricts further downward flow. The water then moves laterally to a position where the layer is truncated near the surface resulting in a saline seep (discharge area). The salts are accumulated at the soil surface by the upward capillary movement of water and its subsequent evaporation, thus depositing the salts on the surface (Figure S57).

Sodic (nonsaline-alkali) soils

These soils contain exchangeable sodium in a quantity sufficient to interfere with the growth of most plants. The ESP or SAR is >15, and the EC of the saturation extract is <4 dS m^{-1}. The pH usually ranges between 8.5 and 10. The soil colloids are usually deflocculated. The dispersive effect of exchangeable sodium, however, will be observed only if the electrolyte concentration in the soil solution is smaller than that required to flocculate clay particles, i.e., the critical coagulation concentration (Sposito, 1989). Thus increase in the EC tends to counteract the effect of exchangeable sodium on soil structure. Because of highly alkaline conditions, part of the soil organic matter is dissolved and deposited as a thin film on the surface of soil aggregates. The prevalence of such black stains in these soils has led to the common designation of *black alkali soils*.

When a saline-sodic soil is leached, the colloidal particles tend to disperse. The dispersed particles are gradually moved downward, and dense subsoil horizons are formed. Upon continued alternate wetting and drying, the dense subsoil develops a characteristic columnar structure. Soils having such subsoil structures are designated as *Solonetz*.

Soil salinity and plant growth

Plant growth on saline soils with pH < 8.5 is adversely affected primarily because of high concentration of soluble salts. Salts exert three major effects on plant growth. These are osmotic, specific ion effects and nutritional imbalances. The main effect of soluble salts on plants is osmotic. Relatively large amounts of dissolved salts in the root zone results in decreased ability of plants to obtain adequate water for growth. Therefore, plants growing on saline soils often appear to be suffering from drought. Osmotically stressed plants are generally stunted and their leaves are often darker green than leaves of normal plants. Plants that are stunted because of low fertility are generally yellowish green.

Plant species differ widely in their ability to tolerate salinity. Halophytes, those plants native to saline environments, are the most tolerant. Glycophytes, which include most crop species, are relatively less tolerant. Salt tolerance is a complex plant characteristic with physiological and biochemical functions controlled by numerous genes. Several factors, such as temperature, humidity, stage of plant growth, moisture, soil texture, compaction, type of salts and soil fertility, influence plant response to salinity. Because of these factors and their interactions affect plant response, it is difficult to establish a uniform scale of salt tolerance. Relative tolerance of crops to different levels of dissolved salts is useful, however, in providing crop selection guidelines for saline soils. An excellent review of relative tolerance of cereals, fibers, vegetable and fruits, grasses and

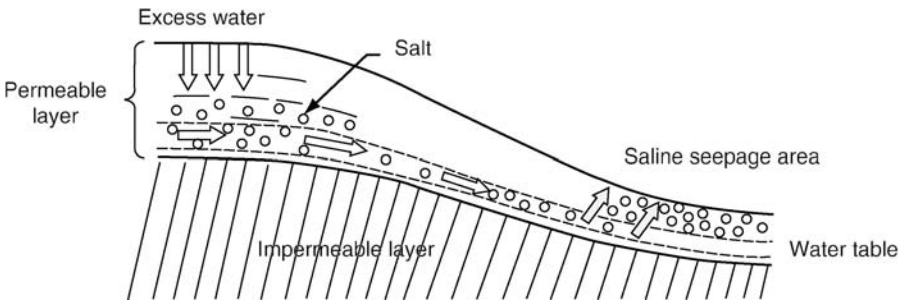


Figure S57 A generalized version of saline seep.

Table S19 Relative salt tolerance of plants

Crop type	Tolerance level	Electrical conductivity (dS m^{-1}) of saturated soil extract, EC_e	
		Threshold EC_e^a	50% Yield EC_e^a
Field crops:			
Barley	High	8	18
Cotton	High	8	17
Sugar beet	High	7	15
Sorghum	Moderate	5	12
Wheat	Moderate	9	12
Cow peas	Moderate	5	9
Peas	Low	3	5
Corn	Low	2	6
Rice	Low	3	4
Grasses and forages:			
Wheatgrass, tall	High	8	19
Bermuda grass	High	7	14
Trefoil, birdsfoot	Moderate	5	10
Vetch	Moderate	3	8
Alfalfa	Moderate	2	9
Clover, Alsike	Low	2	5
Vegetables and fruits:			
Broccoli	Moderate	3	8
Spinach	Moderate	2	9
Tomato	Moderate	2	8
Bean	Low	1	4
Strawberry	Low	1	3
Pineapple	Low	1	3

[a] Threshold is the salt level below which crop yields generally are not decreased significantly; 50% Yield EC_e refers to the salt concentration at which crop yield is only 50% of normal yield attainable at threshold ECe values.

forages, ornamental shrubs and trees have been published by Maas (1986). A brief listing of crops and their relative tolerance to dissolved salts in the root zone is given in Table S19. Crop yields generally are not decreased significantly until the electrical conductivity of the saturated soil extract (EC_e) exceeds a specific value, called *threshold* EC_e for that crop. Threshold EC_e values vary widely for different crops. According to Maas and Hoffman (1977), relative yield can be calculated by the following equation:

$$Y = 100 - B(EC_e - A) \tag{4}$$

in which A = the salinity threshold in dS m^{-1} and B = the percent yield decrease per unit salinity increase. For example, barley yields decrease approximately 5% per dS m^{-1} when EC_e exceeds 8 dS m^{-1} (see Table S19); therefore, at a soil salinity of 18 dS m^{-1} the relative yield, $Y = 100 - 5(18 - 8) = 50\%$. It may be pointed out that plants grown on gypsiferous soils will tolerate EC_e approximately 2 dS m^{-1} higher than those indicated in Table S19.

In addition to the contribution of total soluble salts on osmotic properties of soil solution, many plants are sensitive to specific ions. This is commonly referred to as *specific ion effect*. Toxicities to sodium, calcium, magnesium, potassium, chloride, sulfate, bicarbonate and boron have been reported (U.S. Salinity Laboratory, 1954). Some ions such as sodium can also affect soil physical properties. It is therefore difficult to differentiate toxic effects of sodium from its indirect effect on soil permeability, soil aeration and other structural properties thereby reducing plant growth. Plant tolerance to exchangeable sodium level varies with crop species. The relative tolerance of various crops to exchangeable sodium percentages in soils is given as follows: tall wheatgrass > barley > wheat > rice > tall fescue > oats (Pearson and Bernstein, 1958).

The nutritional effects of sodium depends on the concentrations of Na^+, Ca^{2+}, and Mg^{2+} in the soil solution. In sodic and non-saline sodic soils, total soluble salt concentrations are low and consequently, Ca^{2+} and/or Mg^{2+} concentrations are often nutritionally inadequate. The deficiencies rather than Na^+ toxicity are usually the primary influence on plant growth among non-woody species (Maas, 1986). In woody species, however, the direct effects due to the accumulation of toxic levels of Na^+ are pronounced. Na^+ injury in avocado, citrus and stone-fruit trees is rather widespread and can occur at Na^+ concentrations as low as 5 mol m^{-3} in soil water. When leaves of woody plants accumulate more than 0.2% Na^+ or 0.5% Cl^- on a dry weight basis, characteristic marginal or tip burn, or necrotic spots, generally develop (Bernstein, 1975). The most chloride-sensitive plants may be injured when Cl^- in soil saturation extracts exceeds 5 to 10 mmol l^{-1}, whereas the most chloride-tolerant plants are damaged only at concentrations above 30 mmol l^{-1}.

Boron is highly toxic to nearly all plants. Sensitive crop plants may be affected at concentration >0.50 g m^{-3} in soil saturation extract. Boron concentration exceeding the threshold value may cause leaf burn or loss of leaves. The boron tolerance limits for several plant species has been reviewed by Maas (1986).

In sodic soils when pH of soil solution exceeds 8.5, availability of some nutrients may be restricted resulting in nutrient imbalances. Bicarbonate toxicities occur primarily from reduced iron and other micronutrient availability at high pH while high Na^+ may lead to Ca^{2+} and Mg^{2+} deficiencies as discussed above.

Reclamation and management of salt-affected soils

Reclaiming saline soils, a question of managing the hydrologic regime (George et al., 1996), requires sufficient leaching with a good-quality water to remove excess soluble salts from the rooting zone. The first requirement for reclaiming salt-affected soils is adequate drainage. For sodic soils application of appropriate amendments may be required, in addition to leaching, to reduce exchangeable sodium. Once the soils are sufficiently salt-free, use of appropriate management practices are recommended. To prevent resalinization of irrigated lands, an increment of water over and above that required to meet the evapotranspiration demand of the crop must be passed through the root zone to keep the soil salinity within limits of crop tolerance. This is referred to as the *leaching requirement* (U.S. Salinity Laboratory, 1954). The amount of leaching required to reclaim saline soils is a function of the initial salt contents, acceptable salt level, the depth of soil to be reclaimed, and of certain soil and field properties and the method of water application, which influence leaching efficiency. Theoretically, the salt concentration of soil water passing a given depth in the soil profile should drop to the concentration of the applied water when the volume of applied water equals the pore space of the soil volume to be leached (1 pore volume, *PV*). However, soils seldom behave in such an ideal way. Considerable “bypass” may occur during leaching due to water moving through interpedal macropores relative to micropores within the peds. The various physical and chemical causes of this inefficiency of salt removal are described by Bresler et al. (1982).

Boron is more difficult to leach from soils than chloride and sulfate salts because it is adsorbed strongly onto soil particle surfaces. Thus, for soils high in boron, the amount of water required may be twice that required to remove soluble salts by continuous ponding. In addition, subsequent leaching may be required to remove additional boron released with time from soil constituents by mineral weathering (Sposito, 1989).

Frequent problems are encountered in reclaiming salt-affected soils, especially in non-irrigated areas. These include the availability and cost of leaching water and provision of adequate drainage systems. Possibilities of moderating the effects of climate and hydrological processes, which mainly contribute to dryland saline seepage, are also limited. Emphasis should therefore be laid on developing vegetative control methodologies to control salinization. Some of the recommended management practices for saline soils, especially to help control saline seep, include use of mulches and other surface management to enhance salt leaching, planting recharge areas with high moisture use crops and discharge areas with salt tolerant crops, and other cultural practices (Brown et al., 1982).

Reclamation of saline-sodic soils can also be achieved by simply leaching with water if they contain sufficient soluble salts. The deleterious effects of exchangeable sodium are not manifested in the presence of high salinity. In most cases, excessive exchangeable sodium in these soils is sufficiently reduced during leaching that no special reclamation procedures are required (Oster and Frenkel, 1980). However, reclamation of *non-saline* sodic soils by leaching without amendments is normally not recommended, unless the leaching water is sufficiently saline to promote infiltration into the soil. Incorporation of relatively soluble calcium salt or calcium containing amendment in the top-soil prior to leaching is generally required for reclamation of these soils. Gypsum ($CaSO_4 \cdot 2H_2O$) has been utilized for many years with varying success as a Ca^{2+} source to replace Na^+ from the soil exchange complex thereby increasing infiltration rates and reclaim sodic soils. Oster and Frenkel (1980) discussed the chemistry of sodic-soil reclamation with gypsum and lime, and suggested that gypsum requirements for sodic calcareous soils be increased by a factor of 1.1 to 1.3 depending upon the desired final exchangeable sodium percentage.

In addition to gypsum and lime, there are several other amendments, which can be used for reclamation of sodic soils. These include phosphogypsum (a by-product of the reaction of sulfuric acid and rock phosphate), $CaCl_2$, acid or acid formers such as sulfuric acid (H_2SO_4), sulfur (S), lime-sulfur (9% Ca + 25% S) ferric sulfate, aluminum sulfate and pyrite. Acid forming amendments requires special handling and should only be used on soils containing sufficient calcium source to effect reclamation.

M. A. Arshad

Bibliography

Abrol, I.P., and Bhumbla, D.R., 1978. Some comments on terminology relating to salt-affected soils. Proc. Dryland-Saline-Seep Control. Edmonton, Canada: Alberta Agriculture, pp. 6-19–6-27.

Bernstein, L., 1975. Effects of salinity and sodicity on plant growth. *Annu. Rev. Phytopatholo.*, **13**: 295–312.

Bresler, E., McNeal, B.L., and Carter, D.L., 1982. *Saline and Sodic Soils.* Berlin: Springer, 236 pp.

Brown, P.L., Halvorson, A.D., Siddoway, F.H., Mayland, H.F., and Miller, M.R., 1982. Saline-seep diagnosis, control, and reclamation. U.S. Dept. Agric. Cons. Res. Report No. 30. Washington, DC: U.S. Govt Printing Office, 22 pp.

Cherry, J.A., 1972. Geochemical processes in shallow groundwater flow systems in five areas in southern Manitoba, Canada. Proc. 24th Int. Geol. Congr., Sec. 11, Montreal, pp. 208–221.

Corwin, D.L., and Rhoades, J.D., 1984. Measurement of inverted electrical conductivity profiles using electromagnetic induction. *Soil Sci. Soc. Am. J.*, **48**: 288–291.

Duncan, A.C., Roberts, G.P., Buselli, G., Pik, J.P., Williamson, D.R., Roocke, P.A., Thorn, R.G., Anderson, A., 1992. SALTMAP – Airborne EM for the environment. *Explor. Geophys.*, **23**: 123–126.

Ferguson, H., and Bateridge, T., 1982. Salt status of glacial till soils of north central Montana as affected by the crops fallow system of dryland farming. *Soil Sci. Soc. Am. J.*, **46**: 807–818.

George, R.J., and Woodgate, P., 2002. Critical factors affecting the adoption of airborne geophysics for management of dryland salinity. *Explor. Geophys.*, **33**: 90–96.

George, R.J., Bennett, D.L., Wallace, K., and Cochrane, D., 1996. Hydrologic systems to manage salinity at the Toolibin and Towerrinning lakes. Proc. 4th National Workshop on the Productive Use and Rehabilitation of Saline Lands, Albany, March 1996, pp. 173–180.

Griffin, R.A., and Jurinak, J.J., 1973. Estimation of activity coefficients from electrical conductance of natural aquatic systems and soil extracts. *Soil Sci.*, **116**: 26–30.

Gupta, R.K., and Abrol, I.P., 1990. Salt-affected soils: their reclamation and management for crop production. In Lal, R., and Stewart, B.A., eds., *Advances in Soil Science.* New York: Springer, pp. 223–288.

Hendry, M.J., Cherry, J.A., and Wallick, E.I., 1986. Origin and distribution of sulfate in a fractured till in southern Alberta, Canada. *Water Resour. Res.*, **22**(1): 45–61.

Jury, W.A., Jarrell, W.W., and Devitt, D., 1979. Reclamation of saline-sodic soils by leaching. *Soil Sci. Soc. Am. J.*, **43**: 1100–1106.

Maas, E.V., 1986. Salt tolerance of plants. *Appl. Agric. Res.*, **1**: 12–26.

Maas, E.V., and Hoffman, G.H., 1977. Crop salt tolerance and current assessment. *J. Irrig. Drainage Div. ASCE.*, **103**: 115–134.

Mermut, A.R., and Arshad, M.A., 1987. Significance of sulfide oxidation in soil salinization in southeastern Saskatchewan, Canada. *Soil Sci. Soc. Am. J.*, **51**: 247–251.

Miller, M.R., Brown, P.L., Donovan, J.J., Bergantine, R.N., Sonderegger, J.L., and Schmidt, F.A., 1981. Saline seep development and control in the North American Great Plains: hydrogeological aspects. *Agric. Water Manag.*, **4**: 115–141.

Oster, J.D., and Frenkel, H., 1980. The chemistry of the reclamation of sodic soils with gypsum and lime. *Soil Sci. Soc. Am. J.*, **44**: 41–45.

Pearson, G.A., and Bernstein, L., 1958. Influence of exchangeable sodium on yield and chemical composition of plants: 11. Wheat, barley, oats, rice, tall fescue and tall wheatgrass. *Soil Sci.*, **86**: 254–261.

Rhoades, J.D., 1982. Soluble salts. In Page, A.L., ed., *Methods of Soil Analysis.* Madison, WI: American Society of Agronomy, pp. 167–179.

Rhoades, J.D., and Corwin, D.L., 1984. Monitoring soil salinity. *J. Soil and Water Conserv.*, **39**: 172–175.

Roberts, G.P., Duncan, A.C., Anderson, A., and Roocke, P.A., 1992. SALTMAP – a new airborne electromagnetic system for salinity studies. *Seventh International Soil Conservation Organization (ISCO) Conference Proceedings* Sydney, Australia, Vol. 2, pp. 745–750.

Seatz, L.F., and Peterson, H.B., 1965. Acid, alkaline, saline, and sodic soil. In Bear, F.E., ed., *Chemistry of the Soil.* New York: Reinhold, pp. 292–319.

Soil Conservation Authority, 1982. *Salting of Non-Irrigated Land in Australia.* Victoria: Soil Conservation Authority, 98 pp.

Sonnevelt, C., and Ende, van den J., 1971. Soil analysis by means of a 1:2 volume extract. *Plant Soil.*, **35**: 505–516.

Sposito, G., 1989. The *Chemistry of Soils.* New York: Oxford, 277 pp.

Sposito, G., and Mattigod, S.V., 1977. On the chemical foundation of the sodium adsorption ratio. *Soil Sci. Soc. Am. J.*, **41**: 323–329.

Szabolcs, I., 1989. *Salt-Affected Soils.* Boca Raton, FL: CRC Press, 274 pp.

U.S. Salinity Laboratory Staff, 1954. Diagnosis and improvement of saline and alkali soils. In Richards, L.A., ed., *U.S. Department of Agriculture Handbook No. 60.* Washington, DC: U.S. Government Printing Office, 160 pp.

Vander Pluym, H.S.A., 1978. Extent, causes and control of dryland saline seepage in the northern Great Plains regions of North America. In Proc.

Sub Commission on Salt-Affected Soils, *11th Int. Soil Sci. Soc. Congr.*, Edmonton, Canada, pp. 1-48–1-58.

Whittig, L.D., Deyo, A.E., and Tanji, K.K., 1982. Evaporite mineral species in mancos shale and salt efflorescence, upper Colorado River basin. *Soil Sci. Soc. Am. J.*, **46**: 645–651.

Cross-reference

Conductivity, Electrical

SOIL SCIENCE

See *Pedology and Pedogenesis*.

SOIL SEPERATES

The various classes of soil mineral particles ranked in terms of the effective diameter of the individual particles. The International Union of Soil Sciences uses the scheme in Table S20.

Table S20 Classes of soil mineral particles

Fraction	Range (mm)
Coarse sand	2.0–0.2
Fine sand	0.2–0.02
Silt	0.02–0.002
Clay	<0.002

SOIL SOLUTION

Soil is a three-phase system – solid, liquid, and gas – although the interface between colloid surfaces and solution is so important that the "surface phase" should probably be considered a fourth phase. The main component of the liquid phase is water, but it contains a number of dissolved materials: gases, soluble organic compounds, and simple inorganic salts. Larger amounts of some of these materials are adsorbed at surfaces and act as a reserve from which the solution can be replenished. When soil is saturated, some of the water is in wide pores that will eventually drain; this water is unlikely to be in equilibrium with the bulk of the soil. A number of definitions are possible, the simplest being "*the soil solution is the aqueous liquid phase associated with the soil*" (2000). Of more interest in a chemical context is Sposito's (1989) definition: "*the aqueous liquid phase in whose composition is influenced by flows of matter and energy between it and its surroundings and by the gravitational field of the Earth*". Finally, Wolt's (1994) definition recognizes that at a molecular level soil solution is part of a "*continuum of phases exhibiting indistinct interfaces at the molecular level. Solutes in the aqueous phase may be associated with bound water at the surfaces of soil colloids, free water percolating through soil macropores, water in the free space of plant roots, or immobile water in soil micropores*".

The main difficulty in the study of the soil solution is its separation, for some soils may contain as little as 10% by weight of water at field moisture capacity. The most reliable method is to displace the solution from a column of carefully packed soil by slowly percolating another liquid through it; the displacing liquid may be miscible with soil solution, for example alcohol, an electrolyte solution, or pure water, or it may be immiscible, carbon tetrachloride for example (Mubarak and Olsen, 1976). This was first done by Schloesing in 1866 (Russell, 1973), and the classical work by Burd and Martin (1923) showed that the composition and electrical conductivity of successive fractions of leachate remain constant until the displacing solution breaks through the column. The alternative is to use air pressure or suction to displace the solution from moist soil supported on a porous membrane or ceramic filter. This practice can remove only solution held at relatively low free energies, and it gives inaccurate results where the soil solution is very dilute. Furthermore, serious losses of components such as phosphate, present in low concentration (of the order of 10^{-5} mol l^{-1}), can occur by adsorption on the filter.

The concentration of the soil solution varies widely between soils, depending on the leaching regime of the soil (see *Leaching*), fertilizer addition, crop uptake, and processes that affect mineralization of organic matter. The range of figures shown in Table S21, from 5–50 meq l^{-1} of cations and anions, is probably typical for nonsaline soils, but 100 meq l^{-1} is commonplace for saline soils. As the moisture content is reduced, the concentration of soluble salts increases proportionately, particularly for Ca^{2+}, Na^{+}, NO_3^- and Cl^-, but concentrations of K^+, SO_4^{2-}, and phosphate vary less because they are governed by adsorption or solubility equilibria.

The soil solution is important because it is the immediate source of *plant nutrients* (*q.v.*). However, the gross composition with respect to the more abundant ions, as shown in Table S21, represents only one experimental approach. Apart from more detailed chemical analysis, a thorough investigation of the

Table S21 Solution composition of some nonsaline soils, from various sources

Soil Texture	Water (%)	pH	Cations (meq l^{-1})						Anions (meq l^{-1})			
			Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	*Sum*	No_3^-	Cl^-	HCO_3^-	SO_4^{2-}
Sandy loam	12	7.5	42.2	3.6	0.8	3.0	0.4	*50.0*	32.0	4.6	3.5	11.8
Loam	33	7.5	11.1	2.2	0.3	2.3	0.2	*16.1*	8.8	2.3	3.8	2.8
Loam[a]	20	3.9	1.0	1.4	0.4	0.4	0.1	*4.6*[a]	3.8	0.2	–	0.8
Clay	18	5.7	47.8[b]		1.7	5.6	–	*55.1*	30.4	3.8	1.8	17.0
	24	5.7	37.9[b]		1.5	4.3	–	*43.7*	22.1	2.6	1.6	14.4

[a] In addition to the cations listed here, this acid soil solution contained 0.7 meq Al^{3+} and 0.6 meq Mn^{2+} per litre.

[b] This figure is for calcium and magnesium.

amounts of each component present requires the use of activities rather than concentrations, and the consideration of ion pair formation, acid-base equilibria, hydrolysis equilibria, complex formation, and the interaction of gases (e.g., CO_2) with the species in solution. Adams (1971) lists the equilibrium constants of 53 such reactions. In addition, solubility product equilibria, cation exchange (see *Exchange phenomena*), and specific adsorption equilibria (see *Adsorption*) should be taken into account for a full understanding of the soil solution.

Bryon W. Bache

Bibliography

Adams, F., 1971. Ionic concentrations and activities in soil solutions. *Soil Sci. Soc. Am. Proc.*, **35**: 420–421.

Burd, J.S., and Martin, J.C., 1923. Water displacement of soils and the soil solution. *J. Agric. Sci.*, **13**: 265–295.

Mubarak, A., and Olsen, R.A., 1976. Immiscible displacement of the soil solution by centrifugation. *Soil. Sci. Soc. of Am.*, **40**: 329–331.

Russell, E.W., 1973. *Soil Conditions and Plant Growth.* London: Longmans, 849 pp.

Schwab, A.P., 2000. The soil solution. In Sumner, M.E., ed., *Handbook of Soil Science.* Boca Raton, FL: CRC Press, pp. B85–B122.

Sposito, G., 1981. *The Thermodynamics of Soil Solutions.* Oxford: Oxford University Press, 223 pp.

Wolt, J.D., 1994. *Soil Solution Chemistry: Applications to Environmental Science and Agriculture.* New York: Wiley, 345 pp.

Cross-references

Adsorption
Exchange Phenomena
Leaching
Plant Nutrients

SOIL STABILIZATION

See *Soil Engineering*.

SOIL SURVEY

A systematic examination in the field of the different kinds of soil present in a region or on a site, together with a report of the results so obtained with descriptions and details of the soils encountered, commonly augmented by laboratory analyses, and usually resulting in the production of a map. The term is also used for the body of people engaged in such work.

Cross-reference

Soil Mapping and Survey

SOIL VARIATION

The soil continuum or soil cover (Fridland, 1976) exhibits a spatial pattern that is characterized by more or less regular spatial succession of different soil bodies (Hole and Campbell, 1985). In effect, the whole concept of *Pedology* is considered in this context. According to McBratney (1992), there are several terms that may be used to describe inconstancy of soil or soil variation. However, the choice of which is the most appropriate in a particular context may be problematic. The terms are:

- *variation* (a change: continuous change; departure from the mean or usual character; the extent to which the soil varies);
- *heterogeneity* (state of being composed of different kinds);
- *variability* (the tendency or liability to change or vary; unsteadiness; quantitative indeterminacy);
- *variance* (variation; its statistical meaning connotes deviation or the average of the squares of deviations from the mean);
- *variety* (the quality of being various; diversity; difference; many sidedness; versatility);
- *diversity* (state of being multiform; unlikeness; variety).

The most commonly used are soil variation and *soil variability*. If a change in a mean value of an attribute is to be considered, then the term soil variation should be preferred to soil variability. The latter term is more vague. Soil variance is almost always used with its statistical meaning. Soil variety and diversity are hardly used. We are mainly concerned here with soil variation.

Models of soil variation

There are different models of soil variation depending on different perceptions of soil. A widely accepted concept of soil within the *soil science* community, especially among pedologists, considers soil as a natural body characterized by distinctive sequences of pedogenetic horizons produced by environmental forces (Simonson, 1968). The conceptual models of soil variation that emerged from this notion are described here.

Discontinuous model of soil variation. This model is based on the notion that soil forms discrete, internally uniform units, with sharp boundaries at their edges (Hole and Campbell, 1985). The model also implies that the predicted value of a given property of soil at any unobserved location within a mapable unit is the mean value for the unit. Conventional soil maps and soil classes are based on this notion of soil variation. However, this model has been found to be unrealistic because the within-unit variance is often unacceptably high for soil maps produced by conventional methods. In spite of incompatibility of this model with the landscape reality, most national soil surveys have adopted the model for routine use, most probably due to its convenient application to a complex system such as soil. Although it is possible to identify in nature extremely abrupt soil boundaries, seldom are the boundaries as distinct as the lines used to symbolize them on maps. There is an increasing requirement for an alternative model that describe the continuous nature of soil.

Continuous model of soil variation. This model is based upon the premise that soil properties change continuously over the land surface. This model is associated with scales of time and space. In this regard, soil is considered as a space-time continuum. As Hole and Campbell (1985) noted, a collection of soil profiles through time and space would constitute the soil universe in which adjacent and similar profiles would form the soil continuum. Two contiguous soil units on the continuum are connected by series of transitional soil entities. Thus "*no soil possesses a discrete existence but merges imperceptibly into the soil in juxtaposition with it*" (Jones, 1959).

A point of pedantry: the extent to which soil exhibits continuous variation is dependent on the scale at which a specific soil attribute is observed in the field. One would expect that at a

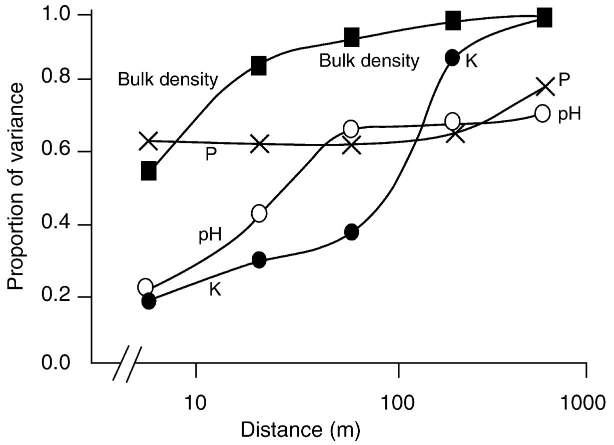


Figure S58 Graphs of variance (as a proportion of the total) of bulk density, pH, available phosphorus (P) and potassium (K), versus distance at Ginninderra, Australian Capital Territory (from Webster and Butler, 1976).

large scale, say at a few meters interval, measured attributes would exhibit more continuous variation than in a situation where observations are spaced at several hundred to thousand meters. Moreover, soil attributes measured at a given interval may exhibit different degree of continuousness of spatial variation within a given geographical area (Figure S58).

A simple model of continuous soil variation describes an attribute of soil as a realization of an intrinsic random function (McBratney, 1992). This is characterized by a variogram, which is a graph of the average variance of any two points within a finite area separated by a given distance and direction (Figure S59). Hole and Campbell (1985) likened the variogram of an attribute to a mixed type of soil variation in which the nugget observed in a variogram accounts for the discontinuities present within the observed place-to-place variation, while the difference between the sill and the nugget represents the nature and degree of continuous spatial variation. The variogram is somewhat similar to Figure S58 and could display how different soil properties exhibit different levels and rate of spatial variation.

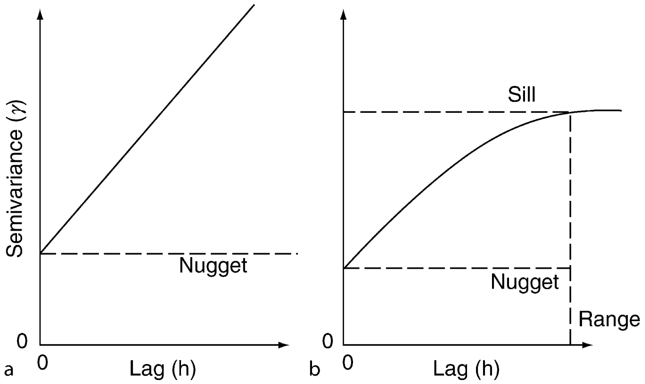


Figure S59 Principal features of one-dimensional variograms (after Webster, 1985); (a) no finite variance with nugget; (b) transitive variogram with nugget, sill (maximum variance) and range, the distance at which the sill is reached; the range indicates the limit of spatial dependence within which there is continuous variation.

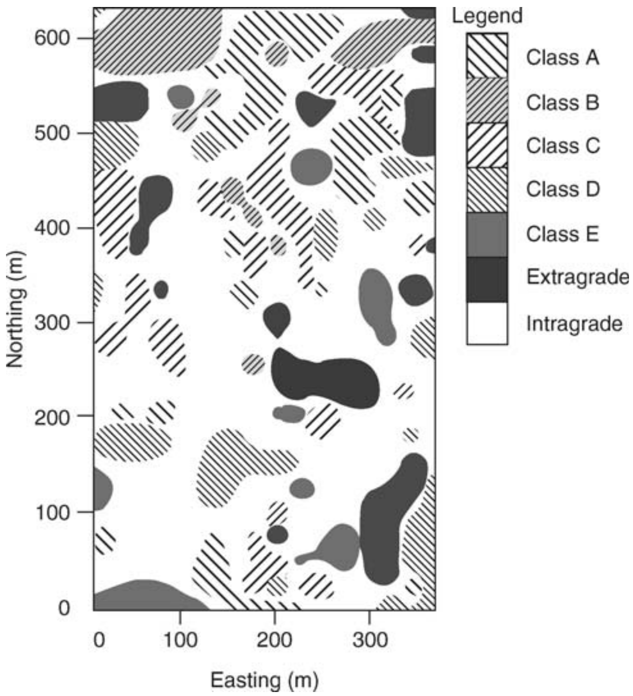


Figure S60 Map showing the core areas (membership >0.5) of continuous classes of textural profiles in a subcatchment in the Mt. Lofty Ranges of Southern Australia. The centroidal features are: *Class A* – sandy loam over clay loam; *Class B* – sandy loam over sandy clay loam; *Class C* – loam over heavy clay; *Class D* – slightly gravelly sandy loam over heavy clay; *Class E* – moderately gravelly sandy loam over sandy clay loam; the *extragrade* class constitutes profiles that do not have affinity towards the usual classes; the *intragrade* areas are the overlapping zones of some or all of the classes.

Continuous soil classification

Soil is multivariate and since different soil properties exhibit different levels and rates of spatial variation, traditional soil classification systems, which are based on the notion of discontinuous model of soil variation, are not always suitable. Inasmuch as the concept of the soil continuum is accepted, and it has been shown to be more realistic in the field (Odeh et al., 1992a), it is not axiomatic that a soil entity should fit perfectly into only one class. For the same reason, classification into mutually exclusive classes with rigidly defined boundaries is particularly unsuitable for the soil continuum. In response to these limitations of the traditional *soil survey and classification*, continuous class models that reflect both the geographic and taxonomic variations of soil have recently been developed (DeGruijter and McBratney, 1988; Odeh et al., 1990; McBratney and DeGruijter, 1992).

Continuous classification is based on fuzzy sets, although not in terms of vagueness of description (Burrough, 1989), but for the fact that the sets are multivariate (McBratney, 1992). The main key to classification is that an entity or object in a given data set (which constitutes a number of classes or subsets) has a varying similarity to some or all of the classes, i.e., the object has a membership function whose values are between zero and one, and which sum to unity over all the classes. The memberships are dependent on the multivariate distances of the measured attributes of the object to their class centroids termed *c*-means (Odeh et al., 1992b). Thus, in a situation where classes are not well separated with series of transitional entities between them, memberships are shared among some or all of the classes. And since soil attributes show different levels of variation within and between classes, the classes overlap (Figure S60). Several reports of the application of these techniques are now in the literature (e.g., Odeh et al., 1990, 1992b; Powell et al., 1991; McBratney and DeGruijter, 1992; McBratney et al., 1992). These techniques may well change the nature of soil classification.

Inakwu O. A. Odeh

Bibliography

Burrough, P.A., 1989. Fuzzy mathematical methods for soil survey and land evaluation. *J. Soil Sci.*, **40**: 477–492.

DeGruijter, J.J., and McBratney, A.B., 1988. A modified fuzzy k-means method for predictive classification. In Bock, H.H., ed., *Classification and Related Methods of Data Analysis.* Amsterdam, The NetherLands: Elsevier, pp. 97–104.

Fridland, V.M., 1976. *Pattern of Soil Cover.* Moscow: Geographical Institute of the Academy of Sciences of the USSR, 1972 (Israel Program for Scientific Translation).

Hole, D.F., and Campbell, J.B., 1985. *Soil Landscape Analysis.* Totowa, NJ: Rowman and Allanheld.

Jones, T.A., 1959. Soil classification, a destructive criticism. *J. Soil Sci.*, **10**: 196–200.

McBratney, A.B., 1992. On variation, uncertainty and informatics in environmental soil management. *Aust. J. Soil Res.*, **30**: 913–935.

McBratney, A.B., and DeGruijter, 1990. A continuum approach to soil classification and mapping: classification by modified fuzzy k-means with extragrades. *J. Soil Sci.*, **43**: 159–175.

McBratney, A.B., DeGruijter, and Brus, D.J., 1992. Spacial prediction and mapping of continuous soil classes. *Geoderma*, **54**: 39–64.

Odeh, I.O.A., McBratney, A.B., and Chittleborough, D.J., 1990. Design of optimal sampling spacings for mapping soil using fuzzy-k-means and regionalized variable theory. *Geoderma*, **47**: 93–122.

Odeh, I.O.A., McBratney, A.B., and Chittleborough, D.J., 1992a. Soil pattern recognition with fuzzy-c-means: classification and soil-landform interrelationships. *Soil Sci. Soc. Am. J.*, **56**: 506–516.

Odeh, I.O.A., McBratney, A.B., and Chittleborough, D.J., 1992b. Fuzzy classification and kriging for mapping soil as a continuous system. *Soil Sci. Soc. Am. J.*, **56**: 505–516.

Powell, B., McBratney, A.B., and MacLeod, D.A. 1991 The application of fuzzy classification to soil pH profiles in the Lockyer Valley, Queensland, Australia. *Catena*, **18**: 409–420.

Simonson, R.W., 1968. Concept of soil. *Adv. Agron.*, **12**: 1–47.

Webster, R., 1985. Quantitative spatial analysis of soil in the field. *Adv. Soil. Sci.*, **3**: 1–70.

Webster, R., and Butler, B.E., 1976. Soil survey and classification studies in Ginninderra. *Aust. J. Soil Res.*, **14**: 1–24.

SOIL WATER

The water present in a soil. Only about 2.5% of the hydrosphere is considered to be freshwater, and only 0.2% of this is contained in the soil at any one time. Despite this miniscule amount, it is what allows the soil to function as an ecological unit, sustaining life, and acting as a necessary agent of material transfers within the soil body, and performing a vital role in the geochemical cycling of nutrient and other elements. Soil moisture is commonly used as a synonym.

Cross-references

Hydrological Cycle
Thermodynamics of Soil Water

SOIL WATER AND ITS MANAGEMENT

Soil water is the chemically uncombined water contained in soil pores and adsorbed on soil particles. Even though some water is combined chemically with soil materials, this aspect will not be considered here. Water contained in soil is expressed as a percent of the dry soil weight (oven-dried at 105 °C) or of the bulk soil volume.

Importance of soil water

Soil water promotes innumerable chemical, physical, and biological activities and reactions. It also dissolves and carries plant nutrients and is a nutrient itself (Brady and Weil, 2004).

Water is arguably the single most important factor, with the possible exceptions of sunlight and air that influences the productivity of soil-grown plants. Soil water excesses may decrease or prevent plant growth through reduced soil aeration, while deficiencies may cause plant water stress and, if severe enough, plant wilting and death. For efficient production, a constant water supply is needed throughout the growing season to meet the plant's water needs and to aid in nutrient dissolution, transport, and absorption. Soil water also influences the timeliness and efficiency of tillage and harvest operations.

Soil water content influences soil compactability and load-bearing capacity and thus is of major concern for road, earthen-dam, and building construction. For optimum compaction, the water content must be within a rather narrow range, depending on the relative proportions of sand, silt, and clay particles in a soil (soil texture). Optimum compaction occurs at relatively high soil water contents, but not so high that water keeps the soil particles apart. Load-bearing capacity increases as soils become dry. Some soils shrink considerably when drying and swell when wetting, for example smectite-rich soils. These soils are undesirable foundation materials for roads and buildings. When present at construction sites, they may be removed, covered with stable materials, or stabilized with lime (calcium).

Soil water types and properties

Soil water is commonly classified as *gravitational*, *plant (readily) available*, and *plant unavailable water* (Gregorich et al., 2001). At saturation, all soil pores and voids are filled with water. However, under the influence of gravity much of that water freely drains from soil after water application ceases, provided drainage is not restricted by compacted or impermeable layers. Rapid drainage stops in one to three days in coarse-textured soils, whereas fine-textured soils drain more slowly. All soils may continue to drain slowly for a much longer time. Water freely draining from soil is called *gravitational water.* Plants may absorb some of this water before it leaves the soil.

The soil water content at which free drainage stops is called the *field capacity* of the soil. It is considered the upper limit of a soil's capacity to store water for plant use and is approximated under laboratory conditions by allowing a saturated sample to reach equilibrium with an applied pressure of 0.033 MPa (–0.033 MPa soil matric potential) in an appropriate membrane or ceramic plate apparatus. The lower limit of available water is at the *permanent wilting point*, which is the largest soil water content at which indicator plants growing in a particular soil wilt and then fail to recover turgidity when placed in a humid chamber. It is approximated in the laboratory by allowing a saturated sample to reach equilibrium with an applied pressure of 1.5 MPa (–1.5 MPa soil matric potential) in a pressure membrane or ceramic plate apparatus. Under field conditions, many plants extract soil water at matric potentials below –1.5 MPa. Water held in soil between the two limits, *field capacity* and *permanent wilting point*, is considered *plant available water*, and it is this water that is used by plants.

Unavailable water is held in soil by forces strong enough to prevent significant absorption by plant roots. This water is held in fine pores and as extremely thin layers on soil particles.

Factors influencing soil water retention

A soil's capability to retain water is influenced by soil texture, structure, organic matter content, and other factors. Coarse-textured (sandy) soils generally retain low amounts of water, often less than 10% by weight at field capacity. In contrast, some clay soils (over 40% clay by weight) retain over 40% water by weight. At the permanent wilting point, water retention ranges from about 3% for sandy soils to about 25% for some clay soils. Besides the amount of clay, the types of clay minerals present also influence soil water retention.

Soil structure, namely, the combination or arrangement of primary soil particles into secondary particles (aggregates), influences water retention through pore formation. Improved structural development promotes pore formation. Hence, the degree of structural development influences soil pore space, which in turn influences the amount of water a soil may retain. Organic matter has a high affinity for water. Therefore, soils high in organic matter retain more water than similar soils with less organic matter.

After precipitation or irrigation, gravitational water percolates through the soil profile. A coarse-textured layer in the profile or an impervious or slowly permeable layer or bedrock sufficiently near the surface may restrict percolation, thus increasing water retention in soil above the restricting layer.

The foregoing major factors, which influence the potential water-holding capacity of a soil, cannot be readily altered by management. However, soil water storage can be controlled to some extent by factors such as irrigation amount and frequency, infiltration and runoff, evaporation, weed control, and tillage method.

Techniques for controlling soil water

Soil water excesses

Excess soil water may be detrimental to timely performance of field operations for crop production, to plant growth and development, to soil compaction for construction purposes, and to traffic of off-road vehicles. To decrease the water content of soils plagued by excesses, open drainage ditches or subsurface drains may be installed. Drainage of agricultural lands has been thoroughly discussed in a book edited by Skaggs and van Schilfgaarde (1999).

Excess soil water at critical times may be reduced also by (*a*) allowing plants to grow, thus removing the water by transpiration; (*b*) removing surface residues to hasten evaporation; and (*c*) plowing, stirring, or mixing the soil to hasten evaporation by exposing moist soil to the atmosphere. Excess water contents can be avoided by reducing or preventing water entry into soils by (*a*) using surface covers or soil water-proofing materials; (*b*) smoothing the surface to enhance runoff and reduce infiltration; and (*c*) constructing dikes or diversions to hold or divert surface waters away from affected areas.

Soil water deficiencies

Water deficiencies at construction sites can be overcome by applying water to obtain the desired water content. Since the area or soil volume is generally limited and water content is critical for relatively short periods only, no major difficulties generally are encountered in raising the soil water content to optimum levels.

Of greater importance and concern is the water content of vast areas of croplands (field, range, orchard, forest, etc.). Where water is readily available and plentiful, water deficiencies can be overcome by irrigation if the land is suitable. Irrigation principles and practices for numerous crops have been reviewed and discussed in "*Irrigation of Agricultural Crops*" edited by Stewart and Nielsen (1990).

Although large land areas are irrigated, plants on the majority of land depend on precipitation for their water supply. Hence, an important crop production activity is the management of soils and crops to obtain maximum benefits from precipitation. While precipitation in some regions is adequate in amount and distribution to sustain favorable crop production, it is limited and erratic in others, which results in droughts of varying duration. Because plants depend on soil water in the interval between precipitation events, soils must retain sufficient water to sustain the plants. Major factors responsible for inadequate soil water storage for sustained plant growth and possible techniques for overcoming or avoiding the undesirable conditions are discussed in the following sections.

Inadequate soil water storage capacity. Water storage capacities are inherently low in sandy and shallow soils. Unless precipitation is frequent, production generally is low. Hence, these soils are best adapted for low-water-requirement crops or crops capable of withstanding droughts of varying duration without being severely affected. Mulches and reduced-tillage practices reduce evaporation, thus permitting greater water use by plants (Unger, 1984). Where a dense subsurface horizon restricts water storage and plant rooting, soil profile mixing increases storage, plant rooting, and crop yields.

Precipitation rates greater than infiltration rates. Water infiltration rates are relatively high for most soils when they are dry, but the rate decreases with time as a soil's water content approaches saturation. However, high-intensity precipitation may cause runoff long before a soil becomes saturated. This results from surface sealing due to the formation of a dense soil layer at the surface or from lower potential infiltration rates than precipitation rates. Practices for increasing infiltration include tillage to disrupt dense surface layers, create depressions at the surface for temporary water storage, and increase depth of loosened soil; contour plowing to hold water on the surface; land leveling and furrow diking to prevent runoff; and maintaining residues on the surface to dissipate raindrop energy, thus reducing soil dispersion and surface sealing. Surface residues also retard runoff, thereby permitting more time for infiltration. No-tillage cropping practices, for which residues of the previous crop are retained on the soil surface and the next crop is grown with no soil disturbance other than that necessary to place seeds in soil, often reduce runoff and evaporation and increase infiltration and thereby increase soil water storage (Unger, 1984).

Inadequate precipitation. In arid and semi-arid regions, precipitation that is erratic in amount and distribution limits production when crops depend mainly on growing-season precipitation. When soil water storage is adequate at the start of a crop's growing season, production often is good even if growing season precipitation is low because the plants extract sufficient soil water for development and reproduction. To maximize water storage during fallow periods (intervals between crops), runoff and evaporation should be minimized. In addition, weeds must be controlled to prevent them from using soil water. Some regions have distinct wet and dry seasons. However, because of other climatic conditions and for economical reasons, growing crops at times other than during the major wet season may be more desirable. Consequently, water must be stored in soil for use by a subsequent crop.

Summary

Most plants require a continuous supply of water for growth and reproduction. However, because water is supplied to plants intermittently by precipitation or irrigation, plants depend on water stored in soil between such events. Soil water content is important also for such crop production operations as tillage and harvesting, and for road, earthen-dam, and building construction. Water excesses as well as deficiencies may cause problems. Excesses can be reduced by drainage, allowing plants to grow, and enhancing evaporation by removing residues or plowing, stirring, or mixing to expose moist soil to the atmosphere. Excesses can be avoided by covering the soil, smoothing the surface to enhance runoff, or diverting runoff water from the affected areas.

On small areas such as construction sites, deficiencies can be overcome by applying water to achieve the optimum water content. On large fields, irrigation may be used to overcome the deficiency if water is available. On other water-deficient areas, practices such as mulching, soil-loosening tillage, plowing on the contour, land leveling, furrow diking, and retaining crop residues on the soil surface help to conserve water for subsequent use by plants.

Paul W. Unger

Bibliography

Brady, N.C., and Weil, R.R., 2004. *Elements of the Nature and Properties Of Soils.* Upper Saddle River, NJ: Prentice-Hall, 606 pp.

Gregorich, E.G., Turchenek, L.W., Carter, M.R., and Angews, D.A., 2001. *Soil and Environmental Science Dictionary.* Boca Raton, FL: CRC Press, 577 pp.

Skaggs, R.W., and van Schilfgaarde, J., eds., 1999. *Agricultural Drainage.* Madison, WI: American Society of Agronomy, Monograph 38, 1328 pp.

Stewart, B.A., and Nielsen, D.R. eds., 1990. *Irrigation of Agricultural Crops.* Madison, WI: American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, 1218 pp.

Unger, P.W., 1984. *Tillage Systems for Soil and Water Conservation.* Rome: FAO (Food and Agriculture Organization of the United Nations). Soils Bulletin 54, 278 pp.

SOIL-ROOT INTERFACE

During its life cycle the plant releases a wide variety of compounds from its roots. The composition of these compounds, known as root exudates, varies widely and includes, in addition to organic moieties of low molecular weight, inorganic ions, gases, protons and electrons, a mucilagenous substance mainly formed by uronic acid polymers and polysaccharides (Rovira et al., 1983; Uren and Reisenauer, 1988).

The mucilage mixed with material of microbiological origin envelopes the apical regions of the root in a gelatinous layer. Its distribution is somewhat variable depending on several factors such as plant species, age, environmental conditions etc. This gelatinous layer, which constitutes the soil-root interface, plays a fundamental role in plant nutrition (Jenny and Grossenbacher, 1963). Being highly hydrated, it ensures effective contact between the root system and the soil surfaces, facilitating exchange processes, transfer of water and nutrients, and the growth of the root. The mucilage binds heavy metals strongly, and acting as a selective filter, accumulates them, thus regulating the movement of ions and molecules from and to the roots. It may support nitrogen-fixing bacteria as well as microorganisms which produce substances that are antagonistic to root pathogens.

Origin and structure

The youngest parts of the root – root caps, epidermal cells, root hairs and proximal zones – are mainly responsible for the release of the mucilage and other substances.

The mucilage originates in the Golgi apparatus; its removal from the protoplast to the plasmalemma is performed by the Golgi vescicles and it is finally exuded through the cell wall. The ultrastructure of the root surfaces has been widely investigated by scanning (SEM) and transmission (TEM) electron microscopy. A TEM micrograph of a garlic root is shown in Figure S61.

The epidermal cell wall consists of two layers: the inner layer is compact whereas the outer is more tenuous and largely mucilaginous. The latter shows a network of electro-dense zones and is enclosed in an electro-dense "cuticle". The outer layer extends to the root mucilage (Figure S62), which, moreover, constitutes the discrete phase. It is continuously regenerated as its components are discharged into the rhizosphere.

The mucilaginous interface is a few Å thick and has been characterized as a fibrillar structure (Floyd and Ohlrogge, 1970; Leppard, 1974; Ramamoorthy and Leppard, 1977), which can be easily modified following the different analytical techniques. Due to difficulties in its isolation and study, attempts have been made to develop a model of the real system; using polygalacturonic acid (PGA), the main component of the mucilage, a gel characterized by a fibrillar arrangement has been obtained which closely resembles the naturally formed mucilage (Gessa and Deiana, 1991a).

From a molecular point of view the fibrillar arrangement seems to result from the dissociation of carboxyl groups, placed as distantly as possible from each other, so that galacturonic monomers would be positioned at an angle of 120° in the chain. Interchain interactions would be mainly assured by calcium bridges, each formed between two $-COO^-$ groups. The structure would be stabilized by H-bonds formed between the $-OH$ groups of the polymer and the first layer of the water molecules. Molecular Dynamics experiments confirm that the aggregation of the polygalacturonic chains is mainly due to the interchain ionic bridges (Manunza et al., 1999).

The fibrillar structure defines a porous system (the free space volume) where the water and all chemical species present in the liquid phase can diffuse (Figure S63).

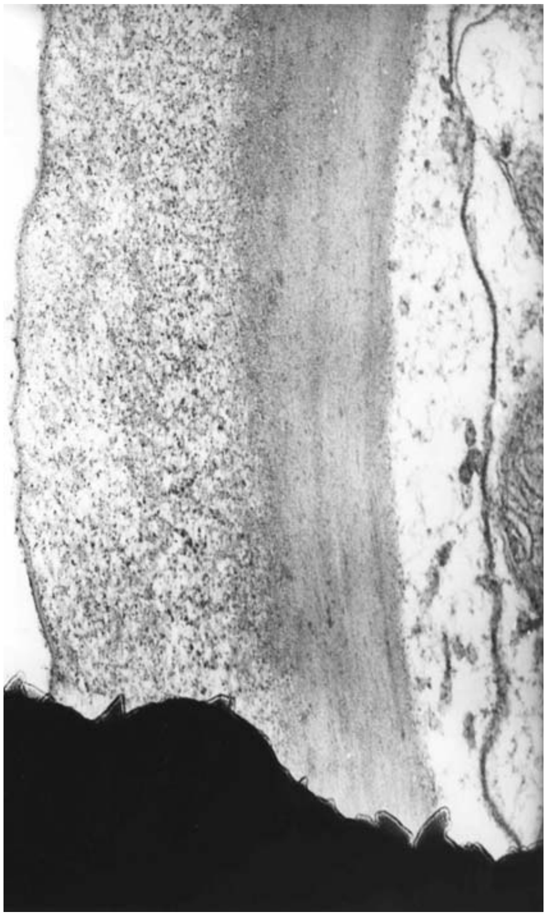


Figure S61 Transmission electron micrograph of an ultra-thin section of a garlic root showing the epidermal cell wall; ×55 000.

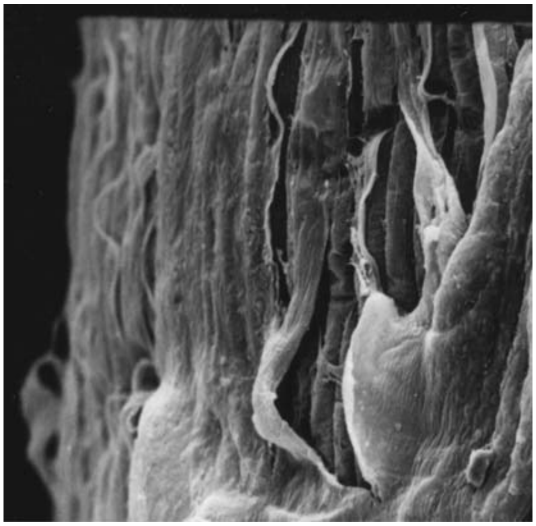


Figure S62 Scanning electron micrograph of garlic root: *M* = mucilage; × 500.

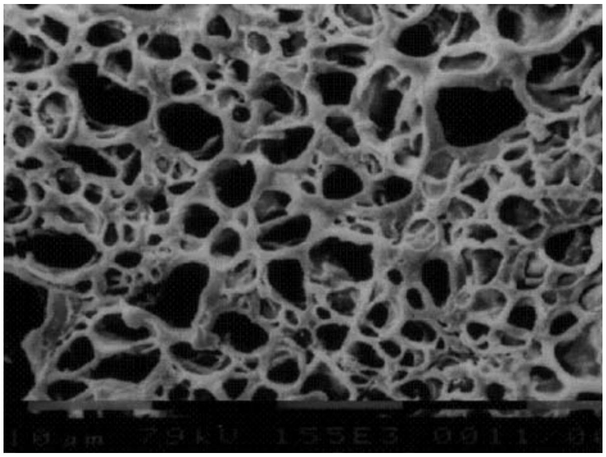


Figure S63 Scanning electron micrograph showing the porous structure of interface; ×50 000.

Free space volume as a result of the soil solution "activity"

The porous structure of the interface is due to the fibrillar arrangement of the mucilage. It is closely related to the stability of the fibrils, which – in turn – depends considerably on the ionic species involved in bridge formation among the polymer chains.

Therefore the functionality of the interface (and that of the apoplast) is strongly related to the soil liquid phase composition. Among the cations present in the soil solution, calcium is normally well represented whereas microelements and other heavy metals are present in very low amounts. Since the latter show a very high affinity for the mucilage, they accumulate in the reticulation sites even though their concentration in the soil solution is low.

Studies carried out on the PGA model have documented well the important role of calcium as stabilizing agent of the fibrillar structure; other ions which, as Ca^{II}, interact eletrostatically with acid groups of the polymers are: Mg^{II}, Mn^{II}, Zn^{II}, and Cd^{II}. Of course the electrostatic interaction is more or less strong depending on the involved ionic species; for example Cd^{II} forms a very weak electrostatic bond so that this ion can rapidly diffuse into the root cells. By contrast ions forming inner sphere complexes such as Cu^{II}, Fe^{III}, Ae^{III}, Cr^{III}, VO^{IV}, and reasonably Pb^{II}, have a destabilizing effects on the porous structure (Gessa et al., 1991b; Deiana et al., 1999). Recent studies on Al,Fe-PG systems also suggest that metal accumulation can occur in different sites of the polysaccharide in which –OH alcoholic groups and the oxygen of the glycosidic bond are involved (Deiana et al., 2003; Mimmo et al., 2003).

Among the metal ions having a strong affinity for the interface, iron shows a peculiar behavior, which appears to be associated with its oxidation state. Fe^{III} interacts with the mucilage destabilizing the porous structure; in the presence of reducing agents originating in the rhizosphere or released by plants, Fe^{III} is reduced to Fe^{II} in the reticulation sites (Gessa et al., 1997); following this redox reaction the metallic center modifies its coordination geometry and seems to interact as Ca^{II}.

Also the polysaccharidic matrix shows redox properties; Mössbauer and Electronic Spin Resonance (ESR) measurements evidenced the reduction of Fe^{III}, VO^{V}, Cr^{VI}, to Fe^{II}, VO^{IV}, Cr^{III} respectively, and the formation of formic acid as a decomposition product of the polymer (Gessa et al., 1983).

Role of soil-root interface in nutrient acquisition

Several chemical reactions can take place in the soil-root interface when ions and molecules flow in the free space system. As a consequence of such reactions the porosity of the interface can be modified so that the transit of nutrients can be promoted or hindered. Factors such as pH, redox potential, ionic strength and biological activity are very important in this regard. The transit of the nutrients through the interface, known as the passive phase of root uptake, can occur with different mechanisms, controlled by the affinity of ions and molecules for the mucilaginous matrix: chemical species which interact very weakly with the mucilage are quickly transferred to the plasmalemma by diffusion and mass flow; ions able to form outer sphere complexes in the reticulation sites can be involved in exchange processes so that they can be "adsorbed" or released from the interface and, at the same time, are useful in maintaining the porosity of the interface; ions strongly bound are accumulated in the interface and their transfer to, or exclusion from, the root cells, is controlled by organic molecules released either from the rhizosphere or from the plant roots, through complexation or redox reactions (Maschner et al., 1986; Uren and Reisenauer, 1988; Fusuo et al., 1989; Didier et al., 1995; Grayston et al., 1996; Gessa et al., 1997; Deiana et al., 2003a,b).

The mobilization of Fe is an important example: complexing agents, such as phytosiderophores, microbial siderophores and organic acids, can remove Fe^{III} from the interface or the rhizosphere and transfer it to the plant (Romheld, 1987; Crowley et al., 1991; Deiana et al., 2003), whereas reducing molecules, such as caffeic acid, can reduce it to Fe^{II} which is easily exchanged with Calcium ions (Gessa et al., 1997). The oxidation of caffeic acid gives rise to the formation of products of low and high molecular weight which again show reducing and complexing activities which allows them to promote the reactivity of the system – that is the mobilization of nutrients from the medium (Deiana et al., 2001).

The root mucilages, discharged into the rhizosphere, are degraded to uronic acid monomers, which constitute a pabulum for microorganisms or can be involved in redox and complexing reactions (Deiana et al., 1991).

The soil-root interface works as a selective filter, which is continuously regenerated by the biological activity of the roots. Its functionality is related to its structural arrangement, which allows optimal nutrient acquisition and, at the same time, controls the transit of toxic chemical species.

Carlo Gessa

Bibliography

Crowley, D.E.,Wang, Y.C., Reid, C.P.P., and Szaniszlo, P.J., 1991. Mechanisms of iron acquisition from siderophores by microorganisms and plants, *Plant and Soil* **130,** 179–198.

Deiana, S., Gessa, C., Piu, P., and Seeber, R., 1991. Iron(III) reduction by D-galacturonic acid. Part III. Influence of the presence of additional metal ions and of 2-amino-2-deoxy-D-gluconic acid. *J. Chem. Soc. Dalton Trans.*, 1237–1241.

Deiana, S., Gessa, C., Marchetti, M., and Usai, M., 1995. Phenolic acid redox properties: pH influence on iron(III) reduction by caffeic acid. *Soil Sci. Soc. Am. J.*, **59**: 1301–1307.

Deiana, S., Manunza, B., Palma, A., Premoli, A., and Gessa, C., 2001. Interaction and mobilization of metal ions at the soil–root interface. In Gobran, G.R., Wenzel, W., and Lombi, E., eds., *Trace Elements in the Rhizosphere.* Boca Raton, FL: CRC Press, pp. 127–148.

Deiana, S., Gessa, C., Palma, A., Premoli, A., and Senette, C., 2003a. Influence of organic acids exuded by plants on the interaction of copper with the polysaccharidic components of the root mucilages. *Org. Geochem.*, **34**: 651–660.

Deiana, S., Premoli, A., Senette, C., Gessa, C., and Marzadori, C., 2003b. Role of uronic acid polymers on the availability of iron to plants. *J. Plant Nutr.*, **26**: 1927–1941.

Didier, M., Pellet, M., Grunes, D.L., and Kochian, L.V., 1995. Organic acid exudation as an aluminum-tolerance mechanism in maize (*Zea mais*). *Planta*, **196**: 788–795.

Floyd, R.A., and Ohlrogge, A.J., 1970. Gel formation on nodal root surfaces of Zea mais. Investigation on the gel composition. *Plant Soil*, **33**: 341–343.

Fusuo, Z., Romheld, V., and Marschner, H., 1989. Effect of zinc deficiency in wheat on the release of zinc and iron mobilizing root exudates. *Z. Pflanzen. Bodenk.*, **152**: 205–210.

Gessa, C., and Deiana, S., 1991a. Ca-polygalacturonate as a model for soil–root interface II: fibrillar structure and comparison with natural root mucilages. *Plant Soil*, **140**: 1–13.

Gessa, C., and Deiana, S., 1991b. Role of soil–root interface in mobilization of nutrients and their absorption by plants. *Trends Soil Sci.*, **1**: 307–313.

Gessa, C., De Cherchi, M.L., Dessi, A., Deiana, S., and Micera, G., 1983. The reduction of Fe(III) to Fe(II) and V(V) to V(IV) by polygalacturonic acid: a reduction and complexation mechanism of biochemical significance. *Inorg. Chim. Acta*, **80**: L53–L55.

Gessa, C., Deiana, S., Premoli, A., and Ciurli, S., 1997. Redox activity of caffeic acid towars iron(III) complexed in a polygalacturonic networt. *Planta Soil*, **190**: 289–299.

Mimmo, T., Marzadori, C., Francioso, O., Deiana, S., and Gessa, C., 2003. Effects of aluminum sorption on a Ca-polygalacturonate network used as a soil–root interface model. *Biopolymers (Biospectroscopy)* **70**: 655–661.

Grayston, S.J., Vaughn, D., and Jones, D., 1996. Rhizosphere carbon flow in trees in comparison with annual plants: the importance of root exudation and its impact on microbial activity and nutrient availability. *Appl. Soil Ecol.*, **5**: 29–56.

Jenny, H., and Grossenbacher, K., 1963. Root–soil boundary zones as seen in the electron microscope. *Soil Sci. Am. Proc.*, **27**: 273–277.

Jones, D.L., 1998. Organic acids in the rhizosphere: a critical review. *Plant Soil*, **205**: 25–44.

Leppard, G.G., 1974. Rhizoplane fibrils in wheat: demonstration and derivation. *Science*, **185**: 1066–1067.

Manunza, B., Deiana, S., and Gessa, C., 1999. Molecular dynamics of pectic substances. In Balbuena, P.B., and Seminario, J.M., eds., *Molecular Dynamics: From Classical to Quantum Methods. Theor. Comput. Chem.*, **7:** 899–932.

Marschner, H., Romheld, V., Horst, W.J., and Martin, P., 1986. Root induced changes in the rhizosphere: importance for the mineral nutrition of plants. *Z. Pflanzen. Bodenk.*, **149**: 441–456.

Ramamoorthy, S., and Leppard, G.G., 1977. Fibrillar pectin and contact cation exchange at the root surfaces. *J. Theor. Biol.*, **66**: 527–540.

Romheld, V., 1987. Existence of two different strategies for the acquisition of iron in higher plants. In Winkelmann, G., Van der Helm, D., and Neilands, J.B., eds., *Iron Transport in Animals, Plants, and Microorganisms.* Weinheim: VCH Chemie, pp. 353–374.

Rovira, A.D., Bowen, G.D., and Foster, R.C., 1983. The significance of rhizosphere microflora and mycorrhizas in plant nutrition. In: Lauchli, A., and Bielesky, R.L., *Encyclopedia of Plant Physiology,* Vol. 15A. Berlin: Springer, pp. 61–93.

Uren, N.C., and Reisenauer, H.M., 1988. The role of root exudates on nutrient acquisition. *Adv. Plant Nutr.*, **3**: 79–114

SOILS OF THE COASTAL ZONE

Introduction

The occurrence of soil in coastal zones is not a simple matter to resolve. Summarized coastal zones form a global perspective that only briefly indicates potential occurrence of soil in relation to coastal landforms, maritime climates, drainage, vegetation, and time available for formation. Increased understanding of coastal soils is, however, only possible from the purview of specific examples that illustrate soil distribution patterns in terms of sequences based on soil-forming factors of topography (toposequences), time (chronosequences), climate change (climosequence), and biological factors (biosequence). The conceptual frameworks for the models were initially postulated by Jenny (1941) and subsequently enhanced by various other researchers (e.g., Butler, 1959, 1967; Runge, 1973; Huggett, 1975). The value of these sequential paradigms is that they provide visualization of complex interrelationships in a framework that clarifies and elucidates coastal soil transition inland from the shore.

The models are relatively uncomplicated in young (Holocene) more or less uniform parent materials such as may occur in small deltaic areas, mangrove swamps, coastal alluvium, and dunes. Complications arise along most coasts because coastal fringes reflect polygenetic development where exceedingly old parent materials and associated soils may occur juxtaposed to incipient pedogenesis. *Environmental complexity* in coastal areas where there is rise and fall of relative sea level, stillstands and diastems, increase and decrease of sediment supply, delta progradation and retrogradation, alluvial channel avulsion, development of deltaic superlobes, chenier formation, climatic change, and so forth, is manifested in weathering zones and soils that provide clues to evolutionary sequences as does the stratigraphy and nature of the included materials. Examples of depositional sequences are reported by Davis (1979), Milliman and Meade (1983), Liu and Walker (1989), Less and Lu (1992), Roberts and Coleman (1996), Saito et al. (2000), Yatsko (2000), and Fletcher et al. (2005) among others, for a variety of coastal settings. Dune systems, including large eolianites, which can be just as complicated as deltaic sequences, often provide stratigraphy with intercalated paleosols (e.g., Fairbirdge, 1950; Cooper, 1966; Denny and Owens, 1979; Hearty and Kindler, 1997; Fletcher et al., 2005). Pedogenic inertia and persistence (e.g., Huggett, 1975; Finkl, 1980) is another problem where older soils (which in turn may be initial parent material for soil forming under new environmental conditions) may occur in geomorphically young coastal landscapes or in coastal situations where regolith is eroded away leaving behind core stones (e.g., Johnson and Baarli, 2005).

Thus, coastal soils *sensu stricto* are often regarded as those soils that are derived form marine or estuarine parent materials that have recently been exposed subaerially to pedogenesis viz. acid sulfate soils, etc. Others might be related to coastal dunes, beach ridges, chenier plains, salt marsh or upland freshwater marsh. The soils mostly range in age from late Holocene to early Pleistocene, reflecting a chronosequence that is geologically very young. This restricted point of view excludes many coastal sectors where soils of great age may be found, especially in the intratropical zones where coastal erosion may expose intensely weathered deposits as coastal cliffs in laterite (e.g., Hays, 1967; Petit, 1985; Retallick, 1990; Wang, 2003). Coastal soils *sensu lato* include a very wide range of possibilities as almost any kind of soil may occur in coastal zones. Fortunately, the possibilities are not endless and there is some order to apparent chaos of haphazard occurrence. Some clues as to potentialities for soil distribution patterns, at myriametric scales, on coasts may be gleaned form the morphological classification of coasts on the basis of plate tectonics (e.g., Inman and Nordstrom, 1971) where tectono-physiographic settings limit the scope of pedogenesis. Trailing continental margins provide large expanses of coastal plain sediments, as occur along the eastern seaboard of the USA south of Washington, DC, where there are thick weathering sequences composed of residual oxidized materials and soils developed in alluvial, estuarine, and marine deposits (e.g., Markewich et al., 1986). In the vicinity of major rivers, especially on the southern coastal plain of the USA, major floodplains and deltas give rise to organic-rich soils. The coastal plains of southern Florida give rise to Holocene calcareous soils on slightly higher elevations whereas lower poorly drained sites contain a suite of organic and muck soils related to Everglades, sloughs, swales, and other karst depressional areas that became infilled with fine grained materials mixed with organic materials following the Holocene transgression (e.g., Gleason et al., 1978; Finkl, 1994, 1995; Lodge, 1994).

Leading continental margins, such as occur along the mountainous and (strike-slip) faulted North American west coast where an oceanic plate is subducted below an overriding continental plate, provide a completely different set of tectono-physiographic conditions for soil development. Uplifted marine terraces contain soils of different ages, depending on the rates of uplift and number of terraces along the coast. Tsunami deposits, which are preserved in protected areas, provide allochthonous arenaceous parent materials for soils (Clague et al., 1999) that date back to the penultimate great Cascadia earthquake 1 000 years ago. Coastal valleys in Oregon and Washington often retain interesting stratigraphy where earthquake-induced subsidence leads to the burial of alluvial and marsh soil profiles and the development of younger soils in the new parent materials above (e.g., Nelson and Kashima, 1993). Pedogenic environments along these kinds of tectonic coasts where there are active seismotectonic regimes, as in Greece (Maroukian et al., 2000) and throughout much of the Mediterranean region and elsewhere, are much more dynamic than the quiescent trailing margins.

Finally, there is the ultimately confounding situation where former coastlines are now stranded long distances from present shores. Many of these rocky shores (e.g., Johnson, 1992; Libbey and Johnson, 1997) provide parent materials for subsequent soil development (neopedogenesis of soil materials), but these occurrences can hardly be considered 'coastal' in that pedogenesis is now unrelated to coastal factors of soil formation, other than coastal-marine parent material. Coastal paleosols are, however, usually associated with modern as well as ancient shorelines whether at present sea level, emergent, or submerged. Emergent examples are best known and have been extensively studied along with Quaternary geomorphology and stratigraphy, for example, in Papua New Guinea (e.g., Bloom and Yonekura, 1985), Barbados (e.g., Radtke, 1989; Schellmann and Radtke, 2001), Bermuda (e.g., Hearty et al., 1992), Bahama Islands (e.g., Hearty and Kindler, 1997), Point Peron in Western Australia (Fairbridge, 1950), Chile and Argentina in South America (e.g., Rutter et al., 1989) and many other coastal areas too numerous to mention. Notable within the present purview of coastal soils, however, is the study by Schellmann and Radtke (2003) who employ morphologic, pedostratigraphic, and chronostratigraphic assessments of marine terraces along the Patagonian Atlantic coast. Many of these studies were used to for reconstruction of local sea-level history, including evidence in southwestern Western Australia for a higher relative MSL during the Holocene (Fairbridge, 1961; Playford and Leech, 1977), but as discussed by Searle and Woods (1986) evidence for the ±3 m oscillations proposed by Fairbridge can be elusive. Still other ancient shorelines, instead of experiencing terrestrial sequestration from the sea, are found as drowned relicts. Examples are reported form Hawaii (Fletcher and Sherman, 1995), but there is no mention of included drowned soils.

Deltaic plains, such as the Mississippi River delta deposits, provide similar examples where constructive (alluvial accumulation, buildup and soil formation) and destructive cycles (e.g., subsidence and drowning) present complex pedogenic environments that respond to fluvial-deltaic processes and longer-term base level changes (Roberts and Coleman, 1996). Callaway et al. (1997), studying sedimentary accretion rates on low tidal-amplitude sites along the Gulf of Mexico, found evidence that contravened previous hypotheses concerning the relationship between tidal range and marsh vertical accretion rates. They found that there was little correlation between mineral and organic matter accumulation rates, with average organic matter accumulation rates showing less variation compared to mineral matter accumulation. There thus may be limits to annual rates of organic matter accumulation. Sediment addition is, however, clearly required for maintenance of coastal marsh soils (e.g., DeLaune et al., 1987, 1990).

There are many different soil classifications in use today throughout the world (see discussions in Finkl, 1981), but none feature specific sections on coastal soils *per se*. Rather than being perceived as a disadvantage, this is situation is an advantageous because soils occurring in coastal environments are hierarchically related throughout comprehensive soil classification systems and placed within continental or international schemes that facilitate reference and comprehension. Prominent among the major soil classifications are efforts by American, Australian, Canadian, French, German, Brazilian, and Russian soil researchers but the system employed here is the one adopted by the Food and Agricultural Organization of UNESCO. The FAO system (FAO-UNESCO-ISRIC, 1988; FAO, 1991) is employed because it is specifically designed as an international system and because it provides a comprehensive inventory of world soil resources in the form of electronic databanks and maps. Although this is the primary organizing or categorical basis for discussing coastal soils, classes in other systems are sometimes equally valid (Spaargaren, 2000) and they are sometimes referred to for ease of reference and also to avoid unnecessary complications that would arise from correlation with other systems. Local soil classification schemes often reflect regional or cultural bias in their geography and therefore international efforts are encouraged (e.g., Finkl, 1982a,b). As already appreciated by many coastal researchers, they must be ambidextrous when dealing with coastal soil morphology, genesis, and classification. Unless otherwise stated, classificatory units referred to here belong to the international FAO system of soil classification, but similar and related terminology is also employed from the U.S. soil classification system as applied in Soil Taxonomy (Soil Survey Staff, 1975) and keys (Soil Survey Staff, 1992). The following descriptions are based on FAO major soil groups.

Histosols

The major soil groups of Histosols (from Gr. *histos*, tissue) include a wide variety of peat and muck soils that range from moss peats of the boreal tundra, moss peats, reeds/sedge peats, forest peats of the temperate zone, and mangrove and swamp forest peats of the humid tropics (Spaargaren, 1994; Inubushi et al., 2003). Histosols are unlike all other soils in that they are formed in and by 'organic soil material' with physical, chemical, and mechanical properties that differ strongly from those of mineral soil materials. They develop in conditions where organic materials are produced by an adapted (climax) vegetation, and where biochemical decomposition of plant debris is retarded by low temperatures, persistent waterlogging, extreme acidity, oligotrophy and/or the presence of high levels of electrolytes from organic toxins. Organic soil material contains more than 12% organic carbon by weight (20% OM). The diagnostic horizons for Histosols are the histic and folic horizons. Other diagnostic horizons used to separate soil units in Histosols are termed sulfuric, sulfidic, and salic. The combination of specific environmental conditions, composition of the organic soil material, and degree of decomposition produces six soil units that include: Gelic Histosols (permafrost occurs within 200 cm of the soil surface), Thionic Histosols (there is a sulfidic or sulfuric horizon starting within 125 cm of the surface), Salic Histosols (there is a salic horizon starting within 50 cm of the surface), Folic histosols (folic horizon present), Fibric Histosols (more than two-thirds of the organic soil material consists of recognizable plant material), and Haplic Histosols (other units).

Histosols form where the rate of accumulation of plant debris exceeds the rate of its decay (e.g., Nyman et al., 1993). In practice, Histosols occur where microbial decomposition of plant debris is impaired by: cold temperatures, excessive wetness, salts or other toxins, and severe aridity or oligotrophy. Histosols under the permanent influence of groundwater, unless artificially drained (e.g., 'low moor peats') occur in low-lying positions in fluvial, lacustrine, and marine landscapes, mainly in temperate regions but also to limited extents in the tropics. Other soils occurring in the same environment include Fluvisols, Gleysols and, in coastal regions, Solonchaks (e.g., adjacent to coastal mangrove peats). In lacustrine landforms and in coastal marsh embayments, histosols may be associated with Vertisols, such as occur on the Texas Gulf Coastal Plain (e.g., Stiles et al., 2003). Oligotrophy and prolonged wetness are primarily accountable for the low decay of organic debris. In the wet tropics (mainly the Indonesian region surrounding the Sunda Flat), their formation is conditioned by high rates of organic matter production from the climax forest vegetation. Change in use of tropical peatlands can affect the decay rates of organic matter and production of methane and nitrous oxide gases viz. conversion from secondary forest peatland to paddy fields, as reported for Kalimantan in Indonesia (Inubushi et al., 2003). In addition to land-use change as a forcing function for pedogenic succession, similar migration of soil properties are associated with tidal inundation along transgressive coastal areas such as around the Chesapeake Bay on the eastern U.S. coastal plain. Hussein and Rabenhorst (2001) report, for example, pedogenic transformation of ultisols to alfisols and eventually to Histosols in response to sea-level rise, based on changes in sodium adsorption ratios and exchangeable sodium percentages. Salinization and alkalization processes as a function of tidal inundation frequency across low-lying coastal landscapes produce lateral changes in pedogenic properties that ultimately relate to different profile characteristics and classification of soils. Lateral pedological linkages exist with a variety of other soil groups, including Podzols, Fluvisols, Gleysols, Cambisol, and Regosols.

The global extent of Histosols is about 275 million ha (FAO, 1991) (Table S22), roughly half of which are located in the Arctic zone, one-third in temperate lowlands, and one-sixth in tropical lowlands (Spaargaren, 1994). An example of the latter case is the subtropical Florida Everglades, which constitute the largest single body of Histosols in the world (Stephens, 1956,

Table S22 Main kinds of soils occurring in coastal areas, based on a world reference base for soil resources, indicating the different types of soil cover in relation to landscape features and associated linkages with related soils

Soil group (FAO)[a]	Area ($\times 10^6$ ha)[b]	Major subdivisions[c]	Associated soils[d]	Lateral linkages or intergrades[e]	Landscape position, climate, drainage, topography, or parent materials
Histosols	275	Gelic, thionic, salic, folic, fibric, haplic histosols	Fluvisols, gleysols, solonchaks, vertisols	Podzols, fluvisols, gleysols, cambisols, regosols	Low-lying positions in fluvial, lacustrine, and marine landscapes. Solonchaks often adjacent to coastal mangrove peats.
Anthrosols	NA	Hydragric, irragric, cumulic, hortic anthrosols	Border most of the major soil groups where soils have been strongly influenced by man.	Includes coastal archaeological sites	Old cultivates sites, excluding paddy soils, on coastal plains, river valleys, deltas, etc.
Leptosols	1655	Lithic, cryic, skletic, rendic, mollic, umbric, dystric, eutric leptosols	Regosol, cambisol, podzol, calcisol, luvisol, histosol, anthrosol	Wide range of intergrades	Tropics to polar tundra, coastal lowlands to mountains.
Cryosols	1800	Histic, thixotropic cryosols	Histosols, gleysols, stagnosols, cambisols	Gelic or cryic units of histosols, gleysols, podzols, planosols, glossisols, stagnosols, cambisols	Arctic coastal plains of NE Eurasia, Alaska, Yukon and NW Territories of Canada; islands of Siberian, Beringian, and North American sectors of the Arctic Ocean; coastal Greenland.
Fluvisols	350	Thionic, salic, vertic, mollic, calcaric, umbric, dystric, eutric	Cambisols, regosols, arenosols, leptosols, gleysols, solonchaks	Arenosols, cambisols, fluvic Gleysols, salic fluvisols (intergrade to solonchaks)	Large deltas and fans viz. Ganges, Mekong, Mississippi, Niger, Po, Rhine; major river floodplains; coastal barriers; tidal flats.
Solonchaks	260–340	Gleyic, stagnic, mollic, gypsic, calcic, sodic, haplic solonchaks	Chlorida and sulphate soils	Salic fluvisols, thionic fluvisol – solonchak intergrades	Coastal salt lakes, lagoons, pans; chloride facies – soils of marine origin under mangrove; neutral chlorido-sulphate soils – of marine origin but enriched by sedimentary gypsum deposited by rivers; acid sulphate soils – soils of marine origin under mangrove as in Gambia, Senegal, Guinee Bissau.
Gleysols	720	Cryic, thionic, plinthic, arenic, mollic, umbric, fluvic, calcic, haplic gleysols	Leptosols, vertisols, fluvisols, solonchaks, stagnosols, histosols, regosols	Histi-mollic, histi-umbric gleysols, fluvic gleysols (intergrades to fluvisols)	Sandy to loamy (sometimes clayey) textural classes of parent material on alluvial, fluvial, fluvioglacial deposits in riverine or coastal areas. Common in depressional and organic-rich coastal areas; for example, Arctic coastal plains, coastal Alaska; Florida Everglades.
Podzols	485	Gelic, gleyic, stagnic, humic, duric, umbric, cambric, haplic	Histosols, gleysols, cryosols, cambisols, ferralsols, planosols, glossisols	Podzol-histosol-gleysol sequences, cambisol-podzol sequence	Sandy deposits affected by illuviation & cheluviation, boreal climatic zone, coniferous vegetal cover, temperate and tropical wet climatic zreas. For example, NE & NW coastal Canada, Scandinavia, NW coastal Russia; coastal plain of Florida; southwestern Australia; coastal Indonesia.
Sesquisols	60	Petric, aeric, albic, stagnic, humic, eutric, haplic sesquisols	Ferralsols, alisols, acrisols, lixisols	Found in association with gleysols and stagnosols in areas conditioned by hydromorphy; with feralsols, alisols, acrisols, and lixisols in better drained positions in the landscape.	Usually ancient landsurfaces truncated by modern coastal erosion or in close proximity to the sea; older coastal plains; for example, western Africa, western India, Mekong catchment, northern and southwestern Australia, eastern Amazon region.
Ferralsols	750	Humic, geric, gibbsic, lixic, rhodic, eutric, plinthic, gleyic, haplic ferralsols	Cambisols, acrisols, nitisols, gleysols, planosols, arenosols, sesquisols	Intergrades to cambisols, acrisols, nitisols, gleysols, planosols, arenosols, sesquisols	Mid- to end-Tertiary peneplains; for example, Brazilian Shield, French Guyana, Senegal, Madagascar, northern and SW Australia; extreme tropical and subtropical weathering.
Planosols	130	Gelic, vertic, histic, mollic, umbric, dystric, eutric planosols	Vertisols, acrisols, luvisols	Stagnic solonetz, albic sesquisols, stagnic gleysols; related soils with abrupt textural change but insufficiently wet to show reduction by surface water would fall into luvisols, lixisols, alisols, acrisols.	Low-lying, nearly level fluvial or marine terraces, depressional lands on coastal plains, incl. wetland rice paddies; most extensive in climes with a strongly seasonal variation in rainfall that results in intermittent saturation and reduction of upper soil horizons.

Continued

Table S22 (Continued)

Soil group (FAO)[a]	Area ($\times 10^6$ ha)[b]	Major subdivisions[c]	Associated soils[d]	Lateral linkages or intergrades[e]	Landscape position, climate, drainage, topography, or parent materials
Solonetz	135	Gleyic, stagnic, salic, albic, mollic, gypsic, calcic, haplic solonetz	Linked through sodic units to vertisols, solonchaks, gleysols, calcisols	Salic Solonetz, sodic solonchaks; through sodic properties in vertisols, solonchaks, gleysols, and calcisols; with gleysols and stagnosols through the gleynic and stagnic solonetz soil unit.	Solonetz landscapes are governed by microrelief, waterlogging at the surface, and salinity in the profile; lake terraces, river deltas, depressions along liman coasts; Rio de la Plata deltaic plain in Argentiina; coastal South Australia and coastal southeastern Western Australia.
Calcisols	800	Petric, luvic, sodic, cambic, and haplic calcisols	Vertisols, solonchaks, gleysols, solonetz, luvisols	Calcic gleysols, calsic gypsicsols, calcic luvisol	Arid coastal regions viz. Baja, California; Patagonia and Argentine Pampa; coastal Atacama; Namibia; coastal northern Africa; Nullarbor Plain in Western Australia and coastal plain in South Australia
Alisols	>100	Plinthis, gleyic, humic, vertic, ferric, chromic, luvic, haplic alisols	Ferralsols, nitisols, acrisols, lixisols, vertisols, cambisols	Vertic alisols, alic nitisols, alic acrisols, facies of other highly weathered soil units in intertropical regions	Coastal plain in southern USA; parts of intertropical coastal India, Africa, and northern Australia.
Acrisols	>900	Plinthic, gleyic, humic, arenic, albic, ferric, haplic	Lixisols, luvisols, alisols, nitisols, glossisols	Planosols, lixic ferralsols, arenosols, regosols, cambisols	Ancient shield landscapes, in tropical regions, that are truncated by coastal plains or marine erosion; coastal plain is southeastern USA, Caribbean Central America coastal lowlands, Orinoco deltaic plain, western Africa, Southeastern Asia, Indonesia.
Luvisols	650	Gleyic, albic, vertic, calcic, ferric, chromic, dystric, and haplic	Alisols, lixisols, acrisols, nitisols, glossisols, solonetz	Luvic chernozems, luvic gypsicsols, luvic phaeozems, luvic calcisols, luvic arenosols	Humid to subhumid temperate regions of western Europe (Belgium, The Netherlands, coastal Germany), parts of the Mediterranean region, southern Australia (extreme southwestern Western Australia, central South Australia), eastern Indian coastal regions, Sri Lanka.
Lixisols	435	Plinthis, gleyic, humic, arenic, albic, ferric, haplic	Nitisols, alisols, acrisols, luvisols, glossisols	Ferralsols, regosols, cambisols, luvisols	On stable shield landscapes in tropical regions; in seasonally dry tropical, subtropical and warm temperate regions, on Pleistocene and older surfaces (incl. Alluvial fans); coastal savanna regions.
Cambisols	1 500	Gelic, gleyic, vertic, fluvic, mollic, calcaric, ferralic, dystric, chromic, eutric cambisols	Luvisols, alisols, acrisols, lixisols, nitisols, ferralsols	Regosols, leptosols, gleysols, fluvisols, acrisols, sesquisols	Islands (Puerto Rico, Madagascar, New Zealand, Papua-New Guinea); Atlantic Spain and Portugal; Mediterranean Spain, France, western Italy, Turkey; southeastern Australia.
Arenosols	900	Leptic, albic, protic, gypsiric, calcaric, luvic, ferralic, cambic, haplic	Regosols, leptosols, cambisols, gleysols, fluvisols	Acrisols, lixisols, ferralsol, planosols, histosols, anthrosols, solonchaks, regosols, leptosols, calcisols	Dry tropical and temperate interior regions, but some coastal areas in western Africa, western Madagascar, and northwestern Australia.
Regosols	260	Gelic, anthropic, tephric, gypsiric, calcaric, dystric, eutric	Arenosols, leptosols, gypsisols, ferralsols, cryosols	Found in all landscapes of the world; intergrades and extragrades may develop into many other soils, depending on the most important soil forming factor(s).	Shallow, weakly developed mineral soils in the initial stages of soil formation; all coastal landscapes.

Notes:
Compiled from Spaargaren (1994).

[a] Based on the FAO World Reference Base (WRB) major soil groups, compiled and revised from the FAO/UNESCO International Reference Base for Soil Classification and the Legend of the Soil Map of the World (FAO-UNESCO, 1974).

[b] Total area (in millions of hectares) is based on estimated WRB worldwide occurrence of the soil group; coastal occurrences are a smaller subset of unknown areal extent.

[c] Major subdivisions that are proposed to separate the soil groups on the basis of diagnostic properties. Not all of the soil units listed occur in coastal areas as major soils, but they are listed for completeness where they may be found in specialized environmental situations.

[d] Other soil groups that occur in the same general area or environment; soil groups were not differentiated on the basis of climate in order to keep the number of units manageable. Differences in topography, drainage, and other diagnostic properties and materials result in a range of different soil groups that occur in close geographic proximity to each other.

[e] Lateral linkages are commonly intergrades that merge soil units in time and space. These units also reflect the spatial integration of soil properties in the coastal landscape where differences in the factors of soil formation (i.e., topography or relief, time, drainage or hydrology, organics, parent or initial materials) may lead to rapid lateral changes in soil units. Relief, drainage (or lack thereof, salt spray, or influence of tidal waters), parent materials (terrestrial versus marine sediments), and time (especially in regard to young soils forming in marine sediments) are particularly relevant to coastal soil distribution patterns.

cited in Amador and Jones, 1995). A large area of cold region organic soils occurs on the southern and southwestern Subarctic margins of Hudson Bay (Manitoba, Ontario, Quebec) and around Great Bear Lake (Northwest Territories) in Canada. Here, cryic fibrisols (with frozen subsurface) occupy about 171 715 km^2 of coastal plain (Clayton et al., 1977).

In lower latitude coastal areas, continually rising sea level has caused brackish or saline waters to engulf drowned river valleys (rias) or to extend over formerly upland soils. This has led to the formation of coastal marsh Histosols in several geomorphic settings (Darmody and Foss, 1979). As sea levels continue to rise, marsh margins are pushed landward and the organic materials continue to thicken so that the older and deeper Histosols generally exist nearer the open water (e.g., Nyman et al., 1993; Rabenhorst, 1997). Although distant from high-latitude glacial activity, coastal Histosols at lower latitudes were impacted by glacio-eustatism (e.g., Rabenhorst and Swanson, 2000). During the glacial maximum (~20 000 yr B.P.) when large quantities of water were bound in glacial ice, eustatic sea level was at least 150 m below present MSL. Deglaciation cycles caused sea level to rise at such a rapid rate (~10–20 mm a^{-1}) that initially vegetation could not colonize tidal regions. Approximately 3 000–5 000 years ago, sea-level rise slowed so that marsh vegetation became established and organic parent materials began to accumulate (Bloom and Stuvier, 1963; Redfield, 1972). As sea level rose, organic materials accumulated in Histosols so that coastal marshes and mangroves generally accreted at about the same rate. Peat accretion in coastal areas presently ranges from 3–8 mm a^{-1}, which is much higher than in non-coastal regions. The highest rates of sea-level rise may, however, be too great for marsh systems to maintain and some areas suffer marsh loss and degradation (e.g., Huiskes, 1990; Nyman et al., 1993; Boesch et al., 1994) where Histosols are eroded, degraded (e.g., Mendelssohn and McKee, 1988) or drowned. Loss may also occur in response to subsidence (primarily as microbial mineralization of soil organic matter), such as in areas of the Florida Everglades where drainage of coastal wetlands (Everglades marsh) (Finkl, 1995) has exposed organic soils subaerially (Stevens et al., 1984) and their surface elevations may decrease by as much as –2.5 cm a^{-1}.

The Florida Everglades is the largest continuous sedge moor outside of the Pleistocene glaciated area of the United States (Gleason et al., 1984). The expansive coastal wetlands and freshwater marsh of southern Florida are a result of the very slow relative rise of sea level during the past 3 200 years (average rate of 4 cm per century) (Spackman et al., 1966; Wanless et al., 1994). A large number of coastal sediment bodies in southern Florida were initiated or stabilized between 3 300 and 3 000 yr B.P. and again approximately between 2 300 to 2 500 yr B.P. (Wanless et al., 1994). The origin and development of those coastal and shallow-marine carbonate and clastic sediment bodies is dependent on the interactive roles and timing of sea level changes, climatic fluctuations, storm influences, vegetative colonization, pre-existing topography, and provision of detrital (input or recycled) siliciclastic and carbonate sediment. Of these, the rate of sea-level rise was the primary control on the clastic, carbonate, and organic sediment bodies of southern Florida.

As one of the largest marshes in the world, the Everglades peat deposits are commonly differentiated into subtypes based on compositional variation, thickness, and degree of weathering. Water is required for the formation of peat soil because it restricts atmospheric oxygen from the soil; without oxygen, microorganisms cannot decompose dead marsh plants as fast as they accumulate. Ever-thicker deposits of peat are deposited until an elevation is reached where the surface dries enough that oxygen-dependent decay (the opposing aerobic process), or fire, prevents accumulation (Lodge, 1994). Freshwater peats of the Everglades merge southwards with mangrove peats on the tidal plain fronting Florida Bay. Occupying more than 400 ha of marshland, the Everglades Peat forms from degraded sawgrass in long-hydroperiod habits. It is most the most abundant peat occurring in the Everglades Basin. The Loxahatchee Peat, covering about 29 000 ha, occurs in deeper marsh areas and contains less sawgrass remains and more evidence of slough vegetation such as the roots, rhizomes, leaves, and seeds of water lilies. Very poorly drained organic soils of the Everglades usually have a surface layer of black muck (sapric material – organic material that is too finely divided for identification of plant remains) that overlies black or reddish brown muck subsoils that in turn rest on sand, limestone bedrock, or other materials (McCollum et al., 1978). The term *muck* refers to highly disintegrated peat soils that are composed of more mineral than organic matter (see discussion in Brown et al., 1990). *Marl* is the product of periphyton. During the dry season, the organic material (dead algae) in the periphyton mass oxidizes, leaving the calcium carbonate particles as a light-colored soil. Marl is descriptively called *calcitic mud* and is the main soil of the short-hydroperiod wet prairie habitats near the margins of the southern Everglades where bedrock lies close to the surface (Lodge, 1994). Marl and peat soils are opposites, requiring aerobic and anaerobic soil conditions, respectively. Peat cannot accumulate in shorter hydroperiod marshes where marl persists, and acid conditions within a peat soil dissolve marl and prevent its accumulation. However, there are large areas in the northern Everglades where a thick layer of marl underlies peat. This occurrence is evidence that the hydroperiod increased substantially in those areas as the Everglades ecosystem evolved. Much of the Everglades region is flooded during the summer rainy season, which is a natural process essential to the health of this wetland. Many areas of urban development, especially on the coastal plain of southeast Florida, occur on former Everglades (wetlands that were drained as part of reclamation programs) (Finkl, 1995) where Histosols have been stripped away and building sites 'demucked' and filled with dredged materials. The region is, however, prone to returning to its natural wetland condition during high rainfall events making localized sectors of the region susceptible to flooding (Finkl, 2000).

Acid sulfate soils

Acid sulfate soils occupy an area of some 24 million ha worldwide where the topsoil is severely acid or will become so if drained (Ritsema et al., 2000). An equal area of these soils may be thinly covered by peat and nonsulfidic alluvium (van Mensvoort and Dent, 1997). Acid sulfate soils are typically associated with mangrove forests that once covered 75% of the coastlines in tropic and subtropical countries (Quarto and Cissna, 1997). Estimates of the extent and distribution of acid sulfate soils suffer, however, from the lack of field surveys, few reliable laboratory data, and from variable definition. More significant than their areal extent is their location where they are concentrated in otherwise densely settled coastal and floodplains, mostly in the tropics, where development pressures are intense with few suitable alternatives for expansion of farming or urban or industrial development. Two-thirds of the known extent is in Vietnam (e.g., Mekong River Delta), Thailand, Indonesia, Malaysia, Western Africa (Senegal, Guinea Bissau), northern Australia, and on coastal plains in southern China (e.g., Pearl River Delta). By far the largest use of acid sulfate soils is for rice cultivation viz. the Balanta system in Western Africa (van Ghent and Ukkerman, 1993) where land is ridged annually to a height commensurate with the expected freshwater flood of the rainy season. The ridging and annual turning speed up removal of soluble toxins from the surface soil, but the system is declining because of the heavy labor demand and low financial returns.

Acid sulfate soils exhibit enormous spatial variability that is tied to the dynamic estuarine, deltaic, and flood plain environments in which they occur. Organic-rich muds will eventually develop and be accompanied by pedogenesis. Significant spatial variability occurs at myriametric scales from pyrite-plugged pores to the fine-grained soil matrix to in-field, local, and regional soil patterns (Dent, 1986). Remote sensing is widely used in tropical, tidal environments because surveys are arduous and difficult due to mosquitoes and crocodiles. Acid sulfate soils also exhibit significant temporal variability that is associated with their defining characteristics of acidity and related toxicities. Almost uniquely, acid sulfate soils export their problems in drainage and floodwaters.

Evident in acid sulfate soils are patterns related to sedimentary history viz. the common distinction between highly sulfidic, unripe clays or peat in backswamps and riper, coarser textured soils, or even calcareous soils on levees and creek fillings. Soil patterns are not always visible at the surface because present landforms and vegetation may be only partly and indirectly related to the environment of sulfide accumulation. The area may, for example, have been buried by peat or nonsulfidic alluvium, fresh waters may have succeeded brackish, and new plant communities have replaced prior ones.

Sulfidic soils that oxidize and generate H_2SO_4 when drained are referred to as *potential acid sulfate soils* (Wang and Luo, 2002). If they have been drained and are generating H_2SO_4, they are called *raw acid sulfate soils*, but if they have passed through the acid generating phase but remain severely acid, they are referred to as *ripe acid sulfate soils*. Sulfidic materials include marine and estuarine sands and clays, gytja in brackish lakes and lagoons, and peats that originally formed in freshwater but which have been inundated subsequently by brackish water. The common factors are: (1) supply of organic matter, (2) severely reducing conditions caused by continuous water logging, and (3) a supply of SO_4^{2-}, usually from tidewater that is reduced to sulfides by bacteria decomposing organic matter, and (4) a supply of Fe from the sediment for the accumulation of iron sulfides which make up the bulk of reduced S compounds. These conditions are fulfilled in tidal swamps and salt marshes where thick deposits of sulfidic clay have accumulated in concert with Holocene sea-level rise (e.g., Pons and van Breeman, 1982; Dent and Pons, 1995). As sedimentation raises the soil surface above mean sea level, topsoil accumulates under better drainage as a nearly ripe, mottled layer that contains little or no sulfide. Sulfidic clays may be buried by peat or nonsulfidic alluvium where freshwater conditions succeed brackish water.

Reclamation and drainage of sulfidic soils causes dramatic changes. When insufficient carbonate is present to neutralize the H_2SO_4 generated by oxidation of sulfides, extreme acidity develops within weeks or months. Raw acid sulfate soils, characterized by a pH < 3.5, contain jarosite but frequently display a black subsoil as some of the SO_4^{2-} generated by drainage is reduced to FeS deeper in the profile. Experiments on acid sulfate soils in the southern coastal regions of Guangdong, China, for example, show that the sulfur content of acid sulfate soils is 2 to 6 times higher than that of coastal Solonchaks and 3 to 9 times higher than that of paddy soil (Wang and Luo, 2002). The potential acidity is 2 to 3 times higher than the actual acidity and the amount of lime required to correct the potential acidranges from 143.5 t ha^{-1} to 2687.5 t ha^{-1}.

Acid sulfate soils cause on-site problems and also in adjacent areas with the latter attracting attention (Dent, 1986). On-site problems include Al toxicity in drained soils, Fe and H_2S toxicity in flooded soils, salinity, and nutrient deficiencies. Engineering problems include: (1) corrosion of steel and concrete, (2) uneven subsidence, low bearing strength, and fissuring leading to excessive permeability of unripe soils, (3) blockage of drains and filters by ocher, and (4) difficulties of establishing vegetation cover on earthworks and restored land. Off-site problems stem from drainage effluents, earthworks, excavations, and mines. The acid drainage waters carry Al released by acid weathering of soil minerals and heavy metals that are released by oxidation of sulfide minerals. Episodic release of toxic drainage waters may occur, for example, at the onset of the wet season after a period of low water table during which oxidation has taken place.

Gleysols

Gleysols (from Russian local name *gley*, mucky soil mass) or soils with gleyic properties are permanently wet and reduced in the subsoil (e.g., Schlichting, 1973), and periodically to permanently wet in the topsoil (Spaargaren, 1994). Mainly found in periodically poorly drained depressions, valleys, and low-lying coastal areas, the solum is either mottled (in case of temporary aeration) or has colors reflecting reduction. These redoximorphic features form under the influence of poorly to well-drained groundwater regimes. Typical gleyic soils are classified as Gleys or Groundwatergleys in many European systems of soil classification (e.g., Austria, Germany, France, Switzerland, UK), although in the German classification the periodically flooded soils of coastal regions are separated as *Marschböden* from normal Gleysols. Gleysols are found in nearly all climates, from perhumid to arid conditions, and cover an area of almost 720 million ha (FAO, 1991) (Table S22). In regions with permafrost (e.g., Arctic Canada, coastal plain of northern Siberia), Cryic Gleysols occur in association with Cryosols and Gelic Histosols. In the lowlands of the temperate latitudes, they are formed in alluvial sediments associated with Fluvisols near riverbeds in coastal areas, and with Histosols. In the humid tropics, they are found in valleys associated with Acrisols, Lixisols, Nitisols, Alisols, or Ferralsols.

Gleysols (Eutric Gleysols, FAO) are a dominant soil of Canada, with major areas occurring in the Subarctic and Hudson Bay Lowland (Clayton et al., 1977). Most Gleysols occur on nearly level to undulating topography, particularly where associated with lacustrine, alluvial, or marine deposits that are moderately calcareous and loamy in texture. Cryic Gleysols occur throughout the entire Arctic region of northern Canada, including the Arctic islands extending from the Labrador coast to the Yukon-Alaska border. About 37 698 km^2 or 0.4% of Canada is mapped as dominantly Cryic Gleysols; these areas occur in the Northwest Territories and Yukon. They are found within the Mackenzie Delta and the Arctic Coastal Plain. Gleysols are often spatially associated with Podzols and Luvisols.

Anthrosols

These soils result from human activities that produce profound modification or burial of the original soil horizons. In the 1988 Revised Legend of the Soil Map of the World (FAO-UNESCO-ISRIC, 1988), these are "… *soils in which human activities have resulted in profound modification or burial of the original soil horizons, through removal or disturbance of surface horizons, cuts and fills, secular additions of organic materials, long-continued irrigation, etc.*" Implicit in this general definition is the recognition of a distinct set of anthropedogenic processes that are associated with characteristic anthric diagnostic horizons. Anthropogenic soil materials that result from anthropogeomorphic processes are better considered as 'non-soil', unless they are subjected to a sustained period of pedogenesis (Spaargaren, 1994). Many different soil classification systems from around the world make provisions for these kinds of soils. Continuous cultivation of paddy soils often produces a hydragric horizon that also includes redoximorphic and illuviation features in the subsoil. Many Anthrosols occur in coastal deltaic environments, especially in Southeast Asia and Indonesia. The Mississippi Delta region in the USA contains extensive areas of Anthrosols that are now subject to drowning by relative sea-level rise and contribute to the land-loss problem in coastal Louisiana (Boesch et al., 1994).

Leptosols – entosols, Regosols, lithosols, etc.

The name Leptosols (from Gr. *leptos*, thin) is used in the FAO *World Reference Base for Soil Resources* (Spaargaren, 1994) for shallow soils overlying hard rock or highly calcareous material, and soils that have, by weight, less than 10% fine earth material. Leptosols occupy more than 1 655 million ha from the tropics to polar tundra (Table S22). Different names have been used in reference to these kinds of shallow, rocky soils. The term *lithosol* was applied by Thorp and Smith (1949) to denote azonal soils having an incomplete solum or no clearly expressed soil morphology and consisting of freshly or incompletely weathered mass of hard rock or hard rock fragments. *Rankers* were defined as soils that have a dark colored surface horizon, rich in organic matter with a low base status that is overlying unconsolidated siliceous material exclusive of alluvial deposits or hard rock. The name *rendzina*, as first used by Sibirtzev (1901), was originally assigned to intrazonal soil on calcareous rocks. *Regosols* were first defined by Thorp and Smith (1949) as an azonal group of soils consisting of deep unconsolidated rock (soft mineral deposits) in which few or no clearly expressed soil characteristics developed.

Leptosols represent the initial phases of soil formation and as such, they are of great significance because they are the forerunners of the young or weakly developed soils of other units. These soils occur in landscapes where deposition or erosion, resistant bedrock, inert parent material, saturation, or human activity was limited normal pedological development. These soils commonly form on mountains, sand dunes, flood plains, and riverine lunettes, and coastal plains. In northern Canada, for example, Cryic Orthic Regosols in Arctic Lowlands commonly occupy gently undulating coastal plains developed on stony or sandy glacial till and marine deposits and occupy upwards of 1 305 423 km^2 (Clayton et al., 1977), but not all of this area is coastal. Parent material lithology is a factor that may inhibit pedogenesis where resistant bedrock, for example, increases runoff and erosion, and thereby decreases weathering. These soils also form in sandy parent materials that have an abundance of rock fragments. When parent materials consist of quartzitic sands without coarse fragments, such as in many sand dunes, profile development is also retarded.

Coastal dunes are built of beach sand blown onshore. Calcareous sand may give rise to calcareous eolianite, as on the coast of western Victoria (Australia), southwestern Western Australia, Bermuda, and the Bahamas. Quartz sand dunes are common in eastern Australia and grew particularly large during the last ice age, when sea levels were low and wide sandy flats were exposed (Ollier and Pain, 1996; Short, 2003). The high dunes of Queensland such as Fraser Island are the highest dunes in the world. Leptosols are also associated with beach ridges (Tanner, 1995) that are formed as beaches with broad curved shapes and lengths often of many tens of kilometers, as seen in this aerial photograph of a pocket beach in the Bahama Islands where the beach ridges mirror successive storm deposit buildup. Cheniers on the Yangtze Delta (China) are also tens of kilometers in length (Yan et al., 1989), up to 500 m wide, and similar to bight coast cheniers (Otvos and Price, 1979) along the Louisiana – Texas coast. As wind blows sand from the beach to make ridges, these accumulations eventually become stabilized to support soil formation. Beach ridges often join together to make a chenier or beach ridge plain where the ridges usually consist of coarser materials than the intervening swales. The more inland ridges are older than nearshore ones and composition of the ridges may be quite variable. A recent study by Rink and Forrest (2003) regarding the accretion history of beach ridges on Cape Canaveral and Merritt Island, Florida, estimated ridges to be 4 000 to 150 years old on the peninsula and about 43 000 years old on the more landward Merritt Island. Average ridge spacing was 109 ± 20 m, giving an average ridge accumulation rate of 80 ± 8 years per ridge on the cuspate foreland. The ridge accumulation rate is related to storm frequency (tropical storms or hurricanes); soil formation proceeded on the ridges subsequent to deposition. On a coastal plain in southeastern Australia, for example, the inland beach ridges are quartzitic in composition and date back to the Miocene whereas the nearshore sets are calcareous and formed throughout the Quaternary to the late Holocene (Cook et al., 1977). Many Tertiary marine beaches are now found high and dry in Western Australia, at places like Eneabba, Yoganup, and Minninup (Lissman and Oxenford, 1975) that are now some distance inland from the present shore of the Indian Ocean. More recent beach ridge systems are described for the inner Rottnest Shelf coast near Perth in southwestern Australia by Searle et al. (1988) where the main geomorphic components in the area are shore-parallel Pleistocene eolianite ridges and their associated intervening depressions, and the Holocene units in basins, slopes, banks – nearshore platforms, beaches, and beach-dune complexes.

Anaerobiosis may slow pedogenesis where there are persistent high water tables that prevent leaching of soil constituents, inhibit redox cycles, or preclude subsurface horizon development. Poorly drained floodplains and coastal marshes host these kinds of soils.

Cryosols

Cryo-hydromorphic soils occur in Arctic, subarctic, and boreal regions under cold continental, (sub)humid, or semiarid climatic conditions. They support a characteristic vegetation cover of dominantly taiga, forest-tundra, or tundra with a ground cover of lichen moss. These soils have permanently frozen subsoil, often at a shallow depth of <1 m, and occupy enormous areas (1 800 million ha) typically on Arctic coastal plains

(Table S22). Some show a significant accumulation of organ matter (dominantly weakly decomposed tissues of oligotrophic plants) at the surface, others are mainly mineral (or organo-mineral) in nature. They are saturated with water during the entire period of thawing, but lack features associated with reduction or redistribution of iron. The more mineral soils often show the peculiar phenomenon of thixotropy. Thixotropic properties are defined as the ability of relatively compact fine-textured soil materials to transform under pressure into an apparent liquid and unstable state when saturated with loosely bound water (quicksand-like property). When pressure weakens, the material gradually regains its initial compactness. Cryosols have been previously described in Russia as peaty frozen, taiga frozen, gleyic frozen, and destructive taiga frozen soils and more recently as homogeneous (or peaty-duff) and thixotropic cryozems. In Canada they are known as organic and Turbic Cryosols. In Soil Taxonomy (Soil Survey Staff, 1975, 1992), they correspond with soils having a pergelic soil temperature regime.

Fluvisols

The central concept of this group relates to soil developed in fluvial (alluvial) sediments. Fluvisols were previously recognized by a variety of names including but not limited to swamp soils, lithomorphic soils, brown soils, groundwater gley soils, and vaaggronden (“vague soils”, Netherlands). Whatever the name, these soils are deposited in aqueous sedimentary environments viz. (1) inland fluvial and lacustrine environments, (2) marine environments, and (3) coastal saltings or brackish marsh environments, of which deltas are a special case (Driessen and Dudal, 1989). Fluvisols occupy significant areas on deltas and fans, coastal barriers, and tidal flats (350 million ha) (Table S22). On aggrading coastlines, combinations of sand or shingle spits and offshore bars allow dunes to accumulate, giving shelter to a nearshore zone where silts and organic muds accumulate in low-energy or quiescent environments. Tidal inundation brings additional supplies of new suspended sediment that flocculates in the water column but which eventually settles to the bottom to help accretion of marsh soils. Aggradation of marsh surfaces takes place relatively slowly and is often associated with strictly zoned vegetation according to the length of time the marsh is inundated. Creeks give tidal waters access to the marsh at flood tide and drain the marsh at ebb tide. Deltaic systems develop where rivers debouching in the sea bring significant amounts of material, providing coastal conditions are satisfactory for sediment accumulation, as seen here in Figure S64 along the Netherlands coast. In the intertropical regions, particularly, the conditions are such that reducing conditions may be developed in which the sulfates in the seawater are reduced to pyrites. Sediments containing pyrites may become parent materials for acid sulfate soils.

Fluvisols show clear sedimentary layering or stratification in a major part of the profile. Soil formation may have affected the upper part of the profile to produce dark colored surface horizons that are high in organic matter and which form in comparatively little time. Also, the material in the upper part of the profile below the surface horizon may have lost evidence of sedimentary layering due to weathering and have acquired the color and structure of stronger developed soils. These juvenile soils tend to show little evidence of weathering and soil formation below 25 cm depth, except possible gleying. Permanent or seasonal saturation with water, causing recurrent anaerobic conditions and low biological activity, tends to preserve the original stratified nature of the original deposits. Consequently, the more important linkages of Fluvisols are with other weakly developed soils viz. Cambisols, Regosols, Arenosols, Lleptosols, Gleysols, and Solonchaks.

Figure S64 Soil pit on the coastal plain in The Netherlands showing a polder profile. In these kinds of subsiding landscapes, parent materials are episodically deposited as alluvial and aeolian accumulations that produce a complicated stratigraphy. Hiatuses in the depositional cycles provide time for pedogenesis to take place. Pedogenic alteration is conditioned by the nature of the parent materials, drainage conditions (level of groundwater), and the intensity of biochemical processes over time. A complicated pedostratigraphy is shown in this profile that contains evidence (*from bottom to top*) of oxidation (*basal layer*), gleying, rubifaction, and bioturbation.

Solonchaks

Solonchaks (from Russian *sol*, salt, and *chak*) are widespread in arid and semiarid regions, occurring widely (covering 260–340 million ha) in many parts of Asia, Australia, South and North America, China, and the Middle East (Table S22). Salts responsible for salinity have many origins in parent materials that are related to marine deposition; volcanic, hydrothermal, and aeolian processes, and lithological properties of initial materials. Mangrove deforestation contributes to salinization of coastal soils, erosion, land subsidence and release of carbon dioxide to the atmosphere. The presence of these salts, the amount of osmotic pressure of the soil solution, or the toxicity of a given ion leads to special landscapes, either occupied by salt-tolerant (halophyte) vegetation or characterized by the complete absence of vegetation (salt lakes, salt lagoons, salt pans, etc.), depending on the degree of salinity.

Two chemical criteria are used to define these soils: (1) the solubility product of the accumulated salts or of salts that may form and (2) the ion concentration in the soil solution. To be considered salt-affected, the soils must contain an important quantity of salts that are more soluble than gypsum ($CaSO_4 \cdot 2H_2O$: $\log K_s$ is –4.85 at 25 °C), thus also more soluble than calcium carbonate, jarosite and iron sulfide. For this reason, gypsiferous soils, calcareous soils, and soils with jarosite are excluded from the Solonchaks and have a home in the Gypsisols, Calcisols, and Thionic Fluvisols, respectively (Spaargaren, 1994). These soils must also have a total salt concentration of the soil extract, expressed as the electrical conductivity (EC) within a depth of 125 cm of the surface. This minimum value, measured in a saturated paste extract (or in a 1 : 1 extract for very sandy soils) must be: (*a*) > 15 dS m^{-1} (or mS cm^{-1})

at 25 °C, if the pH is less than 8.5 (neutral salts) or (*b*) more than 8 dS m^{-1} if the pH is more than 8.5 (for alkaline carbonate soils) or less than 3.5 (for acid sulfate soils other than Thionic Fluvisols).

Chloride soils are of marine origin but influenced by the potential acidity of the soils under mangrove. The pH is very acid to acid (3.5–5) in reaction, calcium is almost lacking and sulfates, entirely derived from seawater, are present in only very small quantities compared to chloride. Sodium is dominant in the soil solution ($Cl \gg SO_4 > HCO_3$; $Na \gg Ca$). White salt deposits (NaCl, $CaCl_2$, $MgCl_2$) may occur at the soil surface as crusts or efflorescence, which seasonally can turn into brown powdery surface layers. Examples are noteworthy in Gambia and in the Casamance region of Senegal.

Neutral chloride-sulfate soils are mostly of marine origin, but can be enriched by sedimentary gypsum deposited by rivers. When the pH is near neutral, sulfates and chlorides occur and carbonates, sodium, calcium, and magnesium are in variable proportions and exceed bicarbonates present in variable quantities. Salt deposits are mostly NaCl, $CaCl_2$, and $MgCl_2$ associated with gypsum in the profiles. These soils are widespread and examples can be found in the alluvial plains, chotts, and sebkhas of North Africa, the Mexican Lagunas or playas, along the Euphrates River in Syria and Iraq, and in salt flats elsewhere.

Acid sulfate soils of marine origin are formed in potentially acid environments of mangrove vegetation (mangals) where acidification is promoted by dry periods in some tropical regions. When the environment becomes extremely acid ($pH < 3.5$), the result is acidolyse of clay and liberation of aluminum, iron, and magnesium; there is little calcium and chloride in these systems. The lack of bases and very low pH prevents the formation of jarosite. Examples occur in Gambia, the Casamance region of Senegal, and in Guinee Bissau. In reduced condition, these soils classify as Thionic Fluvisols as they have a sulfidic horizon; in oxidized and acidified states, these soils may classify as Salic Fluvisols if the EC is sufficiently high.

Carbonate soils include alkaline bicarbonate-sulfate soils and strongly alkaline carbonate soils. They form in aerobic environments with the production of sulfates from sulfides present in the original marine muds. The liberated acidity is neutralized by an excess of sodium and calcium carbonates in the biogeochemical system. Variations of these soils are found in the polders of Tchad, New Caledonia, the Balkan region, and Australia. The Solonchaks occupy the lower parts of landscapes where runoff, seepage, and shallow groundwater can accumulate; they are separated from most other soils by having a high salt content at or near the ground surface.

Podzols

The term *podzol*, meaning ‘white earth’ is derived form the Russian terms *pod* (beneath) and *zol* (ash). These soils are widely known as acid ashy gray sands over dark sandy loams (Buol et al., 1980). These two contrasting albic and spodic horizons, with an abrupt boundary between them, make these soils among the most dramatic, eye-catching, and photogenic soils in the world. The setting in which such a soil is produced requires the combination of soil-formation factors that yield necessary conditions where there is accumulation of iron, aluminum, and/or organic matter in a subsoil horizon. Podzols thus occupy large areas where there are sandy parent materials from the tropics to the boral climatic zone (485 million ha, Table S22). Many kinds of vegetation, including grasses, can yield certain organic compounds that enhance podzolization, but litter from a certain few species of plants in particular foster such accumulations viz. the hemlock tree (*Tsuga canadensis*) in forests of northern latitudes, the kauri tree (*Agathis australis*) of New Zealand, and heath (*Calluna vulgaris* and *Erica* sp.) in northern Europe. Podzols additionally occur under a wide variety of trees (e.g., *Picea*, *Pinus*, *Larix*, *Thuya*, *Populus*, *Quercus*, *Betula*) and understory plants in moist climatic zones that are cool (e.g., humid meso- and microthermal climates). Humic Podzols (cryohumods in Soil Taxonomy) occur as dominant soils in Canada, for example, in the Maritime Provinces (e.g., Cape Breton and Newfoundland), in the coastal forests of the British Columbia mainland, and on coastal islands (Clayton et al., 1977). Extensive areas of these soils occur on the humid subtropical coastal plain of the southeastern United States. Impressive are the 9 m thick Bh horizons in spodosols on the North Carolina Coastal Plain (Buol et al., 1980). Ages of these soils are extremely variable, some spodosols being able to form relatively quickly. Burges and Drover (1953), for example, reported evidence that 200 years were required to leach calcite from beach sand in New South Wales, Australia, but 2 000 years to produce an iron-Podzol, and 3 000 years to produce an iron-humus Podzol with pH as low as 4.5. An iron-Podzol in coastal California has been estimated at about 1 million years (Jenny et al., 1969). On coastal dunes in cooler climates, Podzols may develop within a few centuries, but in warmer or less humid climates Podzols require several millennia or longer periods to form (Sevink, 1991). Dune soils are easily leached because of their high permeability and low water storage capacity. Although sometimes high in carbonates, the acid buffering capacity of the non-calcareous fraction (e.g., quartz) is generally very low. As a consequence, acidification proceeds rapidly with concurrent changes in soil forming processes and profile characteristics. Rates of leaching and acidification are high in climates with a large precipitation surplus and low decomposition rates (because of low temperatures). In arid climates, leaching will be strongly reduced and mobile components such as carbonates and gypsum may accumulate within the solum. Accumulations of secondary carbonates (e.g., caliche, kunkar) are frequently cited in studies of Holocene dyer systems in drier coastal zones.

Podzolization is thus a bundle of processes that bring about translocation, under the influence of the hydrogen ion, organic matter, iron, and aluminum (and a small amount of phosphorus) from the upper part of the mineral solum to the lower part (Buol et al., 1980). Cheluviation, the dominant process of soil formation of Podzols, involves the combination of two processes: (1) weathering of primary minerals (especially phyllosilicates) by organic complexing acids and (2) translocation of organic matter both in the weathering of primary minerals and in the translocation of Al and Fe complexes. These processes lead to special morphological and analytical characteristics that are used to identify a soil materials as Podzolic. Cheluviation affects large areas of soils in the boreal zone. The process is also active in humid regions, especially in the temperate zone but also in the equatorial realm where many examples of Podzols have been described.

Podzols are soils characterized by the presence of an illuvial spodic horizon. In this horizon, amorphous compounds have accumulated consisting of organic matter and aluminum, with or without iron or other cations. The process of translocation and accumulation, known as cheluviation, is usually shown by the occurrence of an albic (bleached) horizon underlain by a spodic horizon. The illuviation of organic compounds can often be demonstrated by the presence of thick cracked organic coatings on the skeleton grains within the spodic horizon. In coarse sandy materials, Podzol morphology is well expressed and strong contrasts occur between eluvial (albic) and illuvial (spodic) horizons. In most Podzols, where clay percentage is often less than 10 percent, coarse texture ranges from sand to sandy loam. Accordingly, water retention capacity is low, less than 50 mm and, although Podzols develop in humid climates, they often show moisture stress. Podzols are very acid soils, with a pH ranging from 3.5 to 4.5 in surface horizons; the pH may increase up to 5.5 in lower horizons. The cation exchange capacity (CEC) is mostly due to the organic compounds present and base saturation is always very low. Organic matter has a high C/N ratio especially in the surface horizons (C/N = 25 or more) and in the spodic (C/N = 20 or more), indicative of low biological activity and slow degradation of organic matter.

The limits of the Podzols are determined by the minimum expression of the spodic horizon and the minimal contrast between the eluvial and illuvial horizons. Soils showing evidence of illuvial organo-Al/Fe complexes but lacking sufficient amounts of it to qualify for Podzols, form intergrades with Cambisols, Arenosols, and Gleysols. Podzols and intergrades are typical of a soil mantle on sandy coastal plains with poor quartzitic materials affected by a shallow water table.

Sesquisols, Ferralsols, Alisols, Acrisols, Lixisols

Sesquisols are soils either containing at shallow depth a layer indurated by iron (petroplinthite), or at some depth mottled material that irreversibly hardens after repeated drying and wetting (plinthite). *Plinthite* is a Fe-rich, humus-poor mixture of clay with quartz and other diluents that occurs as redoximorphic concentrations in platy, polygonal, or reticulate patterns (Shaw et al., 1997). These kinds of soils occur mainly in the tropics but examples are common to old landscapes in (sub)tropical and temperate regions. Those with a shallow petroplinthite horizon are known as (high level) laterites, ironstone soils, or sols ferrugineux tropicaux a cuirasse. They have widespread occurrence in western Africa, especially in the Sudano-Sahelian region where they cap structural tablelands; they are also common in central-southern India, the upper Mekong catchment, northern Australia, and the eastern part of the Amazon region (Table S22).

The sesquisols with plinthite are known as Plinthosols, groundwater laterite, sols gris lateritiques, or plinthaquox (Soil Survey Staff, 1992). They are found in extensively flat terrains with poor internal drainage, such as the late Pleistocene or early Holocene sedimentary basins of eastern and central Amazonia and the central Congo basin, but also on coastal plains such as in southwestern Western Australia (e.g., Swan Coastal Plain, Ridge Hill Shelf, Donnybrook Sunkland). Well-drained soils with loose ironstone concretions (sesquiskeletal material) are frequent nearly everywhere in the tropics and subtropics, in many landscape situations. The material is the result of former plinthite formation, subsequent hardening, and transport or re-weathering.

The central concept of sesquisols is one of a soil affected, at present or in the past, by groundwater or stagnating surface water in which iron has been segregated to such an extent that a mottled (redoximorphic) layer has been formed which irreversibly hardens when exposed to air and sunshine. Included in the concept are those soils that have a hardened layer at shallow depth. The most important characteristic of sesquisols therefore is the presence of plinthite and petroplinthite. Plinthite is an iron-rich, humus-poor mixture of kaolinitic clay with quartz and other diluents. It commonly occurs as red mottles in platy, polygonal or reticulate patterns, and changes irreversibly on exposure to a hardpan or to irregular aggregates on exposure and repeated wetting and drying with free access of oxygen. In a perennial wet soil, plinthite is usually firm but can be cut with a spade. A plinthic horizon is at least 15 cm thick in which plinthite takes up 10 percent or more by volume. Petroplinthite is a continuous layer of indurated material in which iron oxides are an important cement and in which organic matter is absent, ore present only in traces. The Fe_2O_3 content is generally greater than 30 percent. The continuous ferruginous duricrust layer may be either massive, reticulate, interconnected platy, or columnar pattern that encloses non-indurated material. The indurated layer may be fractured, but then the average lateral distances between fractures is 10 cm or more and the fractures themselves do not occupy more than 20 percent by volume within the layer.

Sesquisols dominantly occur in intertropical regions and have linkages with Ferralsols, Alisols, Acrisols, and Lixisols. Sesquisols may occur in distinctly different landscape positions. Petric sesquisols occupy the higher landscape positions, often as a result of landscape inversion due to lowering of the erosion base (McFarlane, 1976). They now form tablelands and are usually freely drained. The other sesquisols are found mainly in depressions or other areas with impeded drainage. On the Coastal Plain of Georgia (USA), for example, most soils have sandy surface horizons with high infiltration rates; many, however, have slowly permeable subsoil horizons with high concentrations of plinthite (Shaw et al., 1997) where only 10% platy plinthite is necessary to perch water (Daniels et al., 1978). These soils have developed from Miocene aged sediments and are classified in Soil Taxonomy in fine-loamy, siliceous, thermic families of plinthaquic, aquic, arenic plinthic, plinthic, and typic kandiudults. In Georgia, more than 1.5 million ha of soils containing plinthite have been mapped. Sesquisols are found in association with Gleysols and Stagnosols in areas condition by hydromorphy, and with Ferralsols, Alisols, Acrisols, and Lixisols, which occupy the better-drained positions in the landscape.

Ferralsols

Tropical weathering and pedogenesis produces Ferralsols that are characterized by a colloidal fraction dominated by low activity clays (1 : 1 alumino-silicate minerals) and sesquioxides. These highly weathered soils lack rock fragments with weatherable minerals and are characterized by the presence of low activity clays and a uniform morphology that lacks distinct horizonation. If there is sufficient iron in the original material, these soils are reddish in color and contain a weak pedal structure; there are few marks of other soil forming processes such as clay accumulation through translocation. Secondary accumulation of stable minerals such as gibbsite or iron oxyhydrates may be present in concretionary forms (e.g., pisolites) as part of the fine earth fraction. Typical soils are situated on old geomorphic surfaces, which formed through erosion and deposition, and occur today as relict landscapes over large areas (750 million ha, Table S22). Having formed in transported and reworked colluvial materials, these strongly weathered soils have little relationship with underlying geological strata. As a result of transport and deposition, the soils may be stratified (e.g., McFarlane, 1976; Finkl, 1980, 1984). In extreme stages of weathering in a free leaching environment, there is relative accumulation of sesquioxides and small amounts of 1 : 1 alumino-silicate minerals (e.g., kaolinite) as well as resistant minerals such as anatase and rutile. The sesquioxide minerals include goethite, hematite, and gibbsite; the alumino-silicate minerals are generally degraded kaolinites and some muscovite. In this weathering environment, neogenesis of alumino-silicates is rare with the possible exception of aluminum chlorite.

Occurring on geomorphically old surfaces, these soils are associated with Cambisols in areas with rock outcrops or where rock comes near to the surface. On the stable surface they occur together with Acrisols, which seem often to be related to the presence of more acidic parent materials (e.g., gneiss). On more basic rocks they occur associated with Nitisols, with no apparent relation to underlying rocks or topographic positions. Near valleys, Ferralsols merge into Gleysols.

Alisols (from L. *alumen*, alum), occurring in humid (sub)tropical and warm temperate regions, are acid soils with a dense layer of illuviated clay in the subsoil; they cover more than 100 million ha worldwide (Table S22). The intense weathering processes in these soils degrade 2 : 2 and 2 : 1 clay minerals and release large amounts of aluminum to create a very acid environment. Alisols correlate partly with aqults, humults, and udults in Soil Taxonomy (Soil Survey Staff, 1975, 1992), the ferialsols or sols fersiallitiques très lessive in French systems (e.g., AFES, 1992; CPCS, 1967), and red yellow podzolic soils with a high clay activity in the Brazilian soil classification.

Acrisols (from L. *acris*, very acid) are characterized by a subsurface accumulation of activated clays, a distinct clay increase with depth, and a base saturation (by 1 M NH_4Oac) of less than 50%. The soils have been named red-yellow podzolic soils, podzó licos vermelho-amarelo distróficos a argila de atividade baixa, sols ferrallitiques fortement ou moyennement désaturés (CPCS, 1967), red yellow earths, latosols and oxic subgroups of alfisols and ultisols. The later have been redefined as kand- and kanhapl- great groups in Soil Taxonomy (Soil Survey Staff, 1975, 1992). These soils are common in tropical, subtropical and warm climatic regions, on Pleistocene and older surfaces that take up more than 900 million ha worldwide (Table 22).

The dominant characteristic of Luvisols (from L. *luere*, to wash) is textural differentiation in the profile that forms a surface horizon depleted in clay and an accumulation of clay in the subsurface argic horizon. These soils are further characterized by moderate to high activity clays and low aluminum saturation. These soils are known as sols lessivés in France, Parabraunerde in Germany, pseudo-podzolic soils in Russia, gray-brown podzolic soils in earlier USA terminology or as alfisols in Soil Taxonomy.

Lixisols (from L. *lix*, lye) are characterized by a subsurface accumulation of low activity clays (cation exchange capacity is less than 24 cmol(+) kg^{-1}) and moderate to high base saturation. They show a distinct increase in clay content with depth. These soils have been named red-yellow podzolic soils, podzó licos vermelho-amarelo eutróficos a argila de atividade baixa, sols ferrugineux tropicaux lessives, and sols ferrallitiques faiblement désaturés appauvris (CPCS, 1967), red and yellow earths, latosols, and oxic subgroups in Soil Taxonomy (Soil Survey Staff, 1992). Limits and linkages of Lixisols, Acrisols, Alisols, and Luvisols are entirely based on analytical properties. Therefore, in areas where these kinds of soils have cation exchange capacities close to this value, they will merge into each other.

These soils, which are relict (out of pedogenic phase with the present environment) and not related to contemporary soil-forming processes in coastal zones, are nevertheless important pedogenic and geomorphic features along many coasts; they occur about 435 million ha worldwide (Table S22). Although commonly associated with truncated land surfaces that produce coastal cliffs such as those seen on marine sediments along the eastern boundary of the Guiana Shield in northeastern South America (Valeton, 1981); the coastal Trivandrum district in southern Kerala (India) (Karunakaran and Roy, 1981); Long Reef Beach near Sydney, New South Wales (Retallick, 1990); Darwin, Northern Territory (Australia) (McNally et al., 2000); and as lateritic spurs and benches along the Darling Fault Scarp in southwestern Australia (e.g., McArthur and Bettenay, 1960), these weathering profiles also occur as reefs on seaward sloping surfaces that extend below present MSL (Short, 2003) in the Northern Territory and into the Gulf of Carpentaria (Hays, 1967). Interestingly, these Tertiary and older weathering profiles extend from northern Australia to the southern boundary of Papua New Guinea but are now drowned by the eastern Arafura Sea and Torres Strait. Depending on the thickness of the weathering profile and its intersection with present MSL, a variety of materials may occur along the shore with beaches or marine terraces developed in saprolite, pallid zones, mottled materials, or ferruginous duricrust.

In the case of the Darwin porcellanite (Darwin Member of the Bathurst Island Formation), a siliceous duricrust that was produced by leaching and replacement of pre-existing rocks, the degree of alteration is less than that found in silcrete (McNally et al., 2000). Pisolithic ferricrete (lateritic or ironstone 'pea gravel') occurs in close association with the porcellanitic duricrust throughout the Darwin area. A karst-like relationship between the two types of duricrust (porcellanite vs. ferricrete) is exposed along road cuts in Darwin, as described by McFarlane et al. (1995) where the ferricrete fills cavities in the porcellanite. This ferricrete is pedogenetically unrelated to the old lateritic pallid zone that developed in the Cretaceous sulfide-bearing marine muds following the retreat of the Early Cretaceous Sea. Porcellanization around Darwin is mostly confined to Lower Cretaceous rocks that weathered to form the pallid zone of a laterite profile 50–70 million years ago. This deep weathering profile was later silicified in a number of cycles that were most intense during the Miocene (Milnes and Thierry, 1992). Both silicification and ferruginization continue to the present day, as evidenced by cliff-base 1940s junk that has been cemented together in a kind of 'bottlecrete' by iron-charged spring waters. Silicified and ferruginous 'beachrock' occurs at Fanny Bay (Darwin) between the present high and low tide lines. McNally et al. (2000) report that these beachrocks occur in a groundwater discharge zone, indicating that some duricrusts have developed since the postglacial sea-level stabilization around 6 000 yr B.P. Marine erosion along the Darwin coast cut marine benches and eroded cliffs into deep mantles of chemical weathering that retain lateritic and siliceous paleosols. Slumps of pallid zone materials at the cliff base provide residual lithogenic quartz and secondary (epidiagenetic) agglomerated porcellanized particles as beach materials. Parts of the beachface are silicified and ferruginized to form an unusual kind of 'beachrock'. Younger coastal soils have developed in the older deep weathering profiles that are exposed along the shore. Complicated polygenetic laterite profiles are also reported from Hong Kong (e.g., Wang, 2003) where pedogenic and groundwater origins represent paleosurfaces that require prolonged subaerial exposure, quiescent tectonism, and a certain level of climatic stability.

Planosols

Planosols (from L. *planus*, flat) have a bleached, light-colored eluvial horizon that abruptly passes into dense subsoil with significantly higher clay content. These soils typically occur in seasonally or periodically wet, level areas, often above normal flood levels of nearby rivers or estuaries. Planosols occur on nearly level river or marine terraces in southeast Asia from Bangladesh to Vietnam, southern Brazil, southern and eastern Africa, and southern Australia. On a global scale, Panosols occupy about 130 million ha (Table S22). Melanization, the addition of dark-colored organic matter, is the process by which a dark surface horizon extends down into the profile. This bundle of specific processes includes: (1) extension of roots from grasses in the profile, (2) partial decay of organic materials in the solum, (3) reworking of the soil and organic matter (bioturbation) by earthworms, ants, rodents with the development of krotovinas (folled burrows), (4) eluviation and illuviation of organic colloids along with some mineral colloids, and (5) formation of resistant 'ligno-protein' residues that give a dark color to these soils (Buol et al., 1980).

Cambisols

Cambisols (from L. *cambiare*, to change) are moderately developed soils that are characterized by slight to moderate weathering of parent materials. They do not contain appreciate amounts of illuviated clay, organic matter, aluminum and/or iron compounds. These soils are particularly common in temperate and boreal regions that were influenced by ice during recent glacial periods. The poorly developed profiles result because soil parent materials are young and because soil formation is slow under low temperatures (or even permafrost) of high latitudes in northern Russia and Canada. Cambisols also develop in pre-weathered, old parent materials where they occur in association with highly developed soils such as Acrisols and Ferralsols. The largest continuous surface of Cambisols in warm regions is found on young alluvial plains, terraces, and deltas of the Ganges-Brahmaputra River system. Cambisols are also quite common in arid climates, where they are closely associated with Calcisols. Cambisols cover an enormous are of about 1.5 billion ha worldwide (Table S22) and constitute the third largest major soil grouping in the FAO Revised Legend (FAO, 1991). The minimum degree of soil development present in Cambisols separates them from Regosols. Leptosols are not permitted to have a cambic horizon and the shallowness of Leptosols separates them from Cambisols. When the cambic horizon reaches its maximum expression, Cambisols border soils defined by an argic horizon (e.g., Luvisols, Alisols, Acrisols, Lixisols, Nitisols), a spodic horizon (Podzols), or ferralic horizon (Ferralsols). Definition of these horizons is such that the cambic characteristics are excluded.

Arenosols

Arenosols (from L. *arena*, sand) are sandy soils with slight to moderate profile development. These soils are widely distributed and form one of the more extensive major soil groups in the world. FAO (1991) estimates Arenosols to cover about 900 million ha (Table S22), or 7% of the land surfaces; if shifting sand and active dunes are included, the coverage is about 10%. Sandy coastal plains and coastal dune areas are, of course, of smaller extent but ecologically very important. Although Arenosols occur predominantly in arid and semiarid regions, they are typical azonal soils that occur in the widest possible range of climates from very arid to very humid and from hot to cold. Arenosols occur predominantly on aeolian sands, either dunes or flats, but have also formed on marine, littoral, and lacustrine sands of beach ridges, lagoons, deltas, lakes, etc. Other names for Arenosols include psamments (Soil-Survey Staff, 1975, 1992), sols mineraux bruts (France), siliceous, earthy and calcareous sands and various podzolic soils (Australia), red and yellow sands (Brazil), and raw sands (Britain and Germany), among others. Arenosols thus have linkages with most other major soil groups. Only a few groups, such as Vertisols, have no linkages. The limits are determined by either textural requirements or the occurrence of certain diagnostic horizons within specified depths. Of most importance in their development are factors that limit soil horizon development in wetlands, alluvial lands, sand lands, rocky areas, and various unconsolidated materials. The spatial distribution of Arenosols indicates that many factors are involved, which operate in various combinations to limit profile development: (1) dry but hot to warm to cold climates and microclimates that parse the amount and duration of water movement in the soils (Arctic, subarctic, Antarctic, and temperate and intertropical desert zones provide these conditions), (2) mass wasting and solifluction remove surficial material faster than most pedogenic horizons can form, (3) cumulization adds new material to the surface of the soil faster than new material can be assimilated into a pedogenic horizon, (4) immobilization of the soil plasma in inert materials, in carbonate-rich flocculated materials, and in some highly siliceous sediments to inhibit profile differentiation by illuviation, (5) exceptional resistance to weathering (pedologic inertia) of some initial materials, (6) infertility and toxicity of some initial materials to plant growth that inhibits biogenetic differentiation (for example, on serpentine barrens), (7) saturation with water or even submergence for long periods, (8) short exposure of initial material to active factors of soil formation (e.g., marine flats newly exposed by uplift), and (9) a recent drastic change in the biotic factor that initiates formation of a new pedogenic regime in an old one, which in turn serves as initial material (Buol et al., 1980).

Regosols

Regosols (from Gr. *rhegos*, blanket) are well-drained, medium textured, deep mineral soils that are derived from unconsolidated materials and which have been traditionally separated from shallow soils (Lithosols, Leptosols, etc.) and from those of sandy or coarser texture (e.g., Arenosols). A Regosol does not have assemblages of diagnostic horizons, properties, or materials that are definitive for any other group of soils. Most properties of Regosols are associated with the materials themselves and not with genetically developed soil features. Conceptually, Regosols are the initial state for pedogenesis representing recently deposited or recently exposed, earthy materials on a groundsurface; these weakly developed soils contain poorly defined horizons. Some soil materials, which represent a late stage of weathering with few distinguishing characteristics, are recognized as Regosols. For example, thin ferralitic materials that cannot go into Cambisols and may be classified with Regosols (Spaargaren, 1994). Although there are examples of initial stages of soil development in all landscapes throughout the world, the areal extent of regosols is often limited and these soils are often inclusions in other soil units. Although of generally limited extent on a global scale (Table S22), Regosols can be important soils in specialized environments (e.g., tundra), such as

Arctic plains in northern Canada where Cryic Regosols account for about 23.5% of Canada's land area (Clayton et al., 1977), extending from Labrador and Baffin Island on the east to the Mackenzie Delta in the west. Nearly 3 000 km^2 of Cumulic Regosols (dystric fluvisols in Soil Taxonomy) occur in tidal marshes adjacent to the Bay of Fundy in the Maritime Provinces as well as on coastal floodplains adjacent to the Yukon and Mackenzie deltaic river systems. In the terrain, Regosols are mostly associated with degrading or eroding areas, while other soils occur on aggrading, depositional, or stable areas. As time passes and soil formation proceeds, Regosols may develop into many other soils depending on the most important soil forming factor (s). Sand dunes on the central Delmarva Peninsula of Maryland and Delaware, for example, contain weathering zones that are represented by Regosols (entisols in Soil Taxonomy) with profiles that are only a meter or two in thickness (Denny and Owens, 1979). Basal horizons in the dunes constitute an ancient weathering profile, truncated at the top and overlain by a younger deposit of sand. These so-called two-cycle dunes thus contain an older basal dune that is Wisconsinan in age and the early episode of weathering may have been early Holocene, a comparatively warm Hypsithermal interval. The surface sand may be no more than a few hundred years old, the result of deforestation and cultivation in colonial times (Denny and Owens, 1979). The Sharon Coastal Plain in Israel is predominantly comprised by sand dune fields and eolianite ridges. Cliffs along the this plain contain three major sand accumulation periods between 65 to 50 ka, from 7 to 5 ka, and from 5 to 0.2 ka (Frechen et al., 2002), that in turn seem to correlate with periods of sapropel formation in the Mediterranean Sea and so with periods of strongly increased African monsoon activity. The uppermost eolianite (calcareous sandstone) seems to correlate with a sapropel formed at about 7.8 ± 4.0 ka B.P. Major phases of soil formation occurred 35 and 25 ka resulting in a rhodoxeralf soil (grumusolic dark brown soil) and between 15 and 12 ka forming a rhodoxeralf (hamra) soil. Frechen et al. (2002) identify at least seven weak pedogenic phases resulting in weakly developed horizons of Regosol-type soils that are intercalated in the eolianite sequences. The oldest eolianite layer contains kurkur (caliche) and seems to be about 55 ka B.P. in age.

Coastal plain soils

As a general rule, soils of younger landscapes are less differentiated (i.e., they contain simple sequences of horizonation and plasmic soil materials are unorganized) than those of older surfaces where weathering profiles tend to contain highly organized soil materials with complex horizonation (e.g., Butler, 1959; Huggett, 1975; Buol et al., 1980; Gerrard, 1981; Ollier and Paine, 1996). Because considerable time is needed to form differentiated soils where soil horizons and materials are highly organized, it is possible to sequentially arrange soils in chronological order with soils developed in young deposits placed before those formed later. Soils arranged in this way represent a sequence of development, referred to as a *chronosequence* (Jenny, 1941). If prior conditions of weathering continue, the young soils in time develop characteristics seen in the oldest (Gerrard, 1981; Ward and McArthur, 1983). This is a simplistic interpretation of uniform and uninterrupted development, but other more complicated (interrupted) sequences are possible, such as apparent trends due to secular changes in climate, drainage, or biota. Investigation of elemental mass balance trends, based on element translocation patterns in response to climate forcing, show promise for estimating the weathering flux under drier or wetter mean annual precipitation regimes (e.g., Stiles et al., 2003). Optical dating of young coastal dunes (e.g., Ballarini et al., 2003) provides a tool for reconstructing coastal evolution on a time scale of decades to a few hundred years. Quartz optically stimulated luminescence (OSL) dating is based on the fact that OSL dates of less than 10 years are very well zeroed prior to deposition and burial, as demonstrated by Ballarini et al. (2003) for an accretionary coastal segment near Texel, The Netherlands. Other luminescence sediment dating methods, more amenable to time scales of a very few thousand years, have found application in the study of the activation and stabilization of coastal dunes on a North Carolina barrier island (Berger et al., 2003). Here, the quartz SAR (single-aliquot regenerative-dose method) is preferred for photonic dating in this region because of the relative abundance of quartz. These kinds of dating methods provide tight controls for estimates of pedogenic phases and the estimation of time intervals required to produce specific horizonation sequences in coastal dunes.

Radiocarbon dating is limited by the availability of datable materials and the technique can be applied only to younger soils (<50 000 yr B.P.) that range from latest Pleistocene to Holocene in age (e.g., Vogel, 1980; Bowman, 1990). The prospect of dating and correlating coastal and bottom deposits as well as terrestrial-marine weathering sequences, as seen in coastal soils, is best achieved along the littoral where sedimentation and subsequent soil development are closely associated with changes in sea level (e.g., Karpytchev, 1993). Lake-level histories as well can sometimes be gleaned from radiocarbon dates for coastal dune fields, as demonstrated by Arbogast and Loope (1999) for Holocene coastal dunes on the shores of Lake Michigan. When marine deposits are correlated with terrestrial weathering sequences by stratigraphic linkage at the coast, pedogenesis can be related to sea-level change and erosion-deposition cycles (Kukla, 1977). If dates related to sea-level changes can be assigned to coastal landforms, then the chronology can be extended inland by using local markers (Ward and McArthur, 1983). At the coast, abundant shells can supplement wood and peat as a basis for radiocarbon dating (Mook and van de Plassche, 1986).

If there is uncrystallized coral present, then dates back to 200 000 years can be obtained from uranium decay methods, and on volcanic shores potassium/argon dating provides useful information. For coasts where these methods are not applicable, the principal means of dating refers to the correlation of stranded shorelines. If the former shores in one locality cannot be dated directly, it is sometimes possible to relate them to the shores in other localities where dates exist, assuming that changes in sea level are instantaneous and global (Ward and McArthur, 1983).

Because the earth's crust is in dynamic equilibrium with the asthenosphere and tectonic adjustments are always taking place, no coastal landmass can be regarded as completely stable, no matter how free it is from seismic activity or neotectonism. Few coasts are so mobile, however, that they contain no part of the eustatic record. Landforms in the coastal zone are complex and not all are only the product of terrestrial processes or marine action.

The apparent simplicity of most coastal plains is suggested by their lack of relief, which disguises these plains from their true nature as terminal geomorphic surfaces of complex transgressive-regressive depositional units laid down during glacioeustatic fluctuations. Bounded at the surface by terrestrial and marine erosional, transportational, and depositional landforms, the stratigraphic units (including paleosols) are limited below by unconformities of terrestrial and marine origin. Sedimentary facies between these surfaces reflect coastal plain (alluvial, palustrine, and aeolian), estuarine, and marine open-shelf environments (e.g., Curray, 1978; Davis, 1978). Their evaluation requires a complete stratigraphic examination, as offered by Haq (1995) in summaries of the principles and concepts of sequence stratigraphy (the study of rock relationships within a chronostratigraphic framework wherein the succession of rocks is cyclic and is composed of genetically related stratal units viz. sequences and systems tracts).

Ideally, two main sedimentary sequences occur within a transgressive-regressive unit (e.g., Blum et al., 2001). The terrestrial sequence, which develops as sea level regresses seaward through lowering, results from extension of alluvial erosion and sedimentation, and of soil formation, into the coastal zone. The marine sequence forms during subsequent landward transgressions or rise of sea level when marsh, estuarine, beach, dune, and deltaic sediments are introduced. The relative thickness, significance, and spatial extent of these sequences depend on the dynamics of coastal processes and on sediment volumes brought to the shore by rivers. When major rivers deposit large volumes of alluvium at the shore, the marine contribution to the sedimentary pile is limited. Coastal landforms thus result predominantly from alluvial distribution.

Coastal strand plains with no alluvial contribution, such as those forming in the Holocene landscape of Gippsland, Victoria, in Australia (Ward, 1977), lie at the other extreme of the scale. Relative placement of terrestrial and marine sediments here is determined by gradients at the coast, and by the history of eustatic fluctuations relative to the land. If, for example, sea level rises above a previous high stand, the earlier deposits will be truncated, buried, or partially submerged. Conversely, a eustatic fall will leave the earlier deposits stranded as a terrace.

Almost all the soils on the Swan Coastal Plain, southwestern Australia, are formed by material deposited by rivers (fluvial, alluvial soils) and wind (aeolian soils). The Yilgarn Block (part of the West Australian craton), east of the Darling Scarp bordering the Swan Coastal Plain, was epirogenically uplifted as part of cymatogenic movement and warping about 40 to 50 million years ago. This tectonic uplift increased the differential between base level and the plateau surface causing erosion of the craton by rivers and streams. Detritus from deep chemical weathering (e.g., laterite profiles) or saprolite was either deposited onto the Swan Coastal Plain or carried to the sea (Fairbridge and Finkl, 1980). The eroded material formed new parent materials for soil development on the Plain.

Broadly there are thus two major groups of soils on the Swan Coastal Plain. The first is a series of dune systems near the coast formed as a result of deposits from the sea, and including material originally derived from erosion of the Yilgarn block mixed with marine sediments. Once formed, the dunes can be eroded by strong winds. The sand is mostly eroded from the dunes nearest the coast, and is re-deposited on the dunes further inland. The second major soil types are a series of soils formed by deposits directly eroded from the Yilgarn block and which comprise soils on an alluvial (Pinjarra) plain, occurring between the dunes and the scarp. There is a third, very narrow strip of soil, called the Ridge hill shelf, next to the scarp, formed from material eroded from the scarp.

Although different conditions prevail in different locations, some general principles emerge from regional comparisons. It is impossible to review the development of all coasts, but some cases illustrate the salient principles that are involved.

Soils of coastal dune systems

Several distinct features characterize coastal sand dune systems (e.g., Cooper, 1966; Nordstrom et al., 1990). The dunes themselves often show a regular succession from the more active and unstable foredunes at the back of the beach to older, more stable vegetated dunes inland. The other major element is the system of slacks or swales (low-lying, narrow coastal wetlands) that occur between the main dune or beach-ridge trends. Dune slacks are low-lying areas within dune systems that are seasonally flooded and where nutrient levels are low. They occur primarily on the larger dune systems in the UK, for example, especially in the west and north where the wetter climate favors their development when compared with the generally warmer and/or drier dune systems of continental Europe. The range of plant communities found in slacks is considerable and depends on the structure of the dune system, the successional stage of the dune slack, the chemical composition of the dune sand, and the prevailing climatic conditions. When a coastal dune forms, dune sand accumulates seaward if there is an abundant sediment supply or the dune grows to its maximum height and then moves landwards (Gerrard, 1981). If the dunes are carbonaceous, leaching progresses with increasing age and when coupled with an increase in organic matter, there is a transition in soil reaction from alkaline to acid conditions. The rate of leaching is initially rapid but declines, as the amount of carbonate, rather than the amount of rainfall, becomes a limiting factor. The rate of leaching in the early stages also depends on the nature of the shell fragments and matrix grain size, being slower if the fragments are large. The process is temporarily halted if material is added to the dune system by wind action because leached and organic-rich layers are buried.

Differences in soil moisture between the younger and older dunes, and between dunes and swales direct soil formation in regard to oxidation of organic matter (Gerrard, 1981). Young swales are initiated with a considerable advantage because nutrients and other minerals accumulate in the wetlands, a situation that is ultimately reflected in the soil profiles and pH values. The rate of increase of organic content depends on the initial lime content of the dunes. On lime-deficient dunes, early colonization by vegetation takes place with a concomitant increase in the rate of litter accumulation. As more acid conditions prevail, litter breakdown is inhibited and organic matter buildup is promoted.

Swan Coastal Plain, southwestern Australia

The tectonically stable limestone coastline of southwestern Australia is well suited to preservation signals of former sea levels. The eustatic record is limited by the time frame when lithified dunes formed in middle to late Pleistocene times. Fairbridge (1961) interpreted the field evidence in calcarenite sequences and paleosols as fluctuation of sea level against the backdrop of a stable landmass, incorporating the curve in a proposed global standard. The sequence of former sea level stands was based on wave cut benches, submerged and stranded beach cobble deposits, karst, and marine bands associated with the Pleistocene limestone.

The Swan Coastal Plain in southwestern Western Australia presents a complex chronosequence of mid-Pleistocene to Holocene dune soils, the oldest interior sets (Bassendean dunes of siliceous sands with Podzol morphology) merging with a series of laterite-covered spurs of the Ridge Hill Shelf that form the foothills of the Darling Scarp (McArthur and Bettenay, 1979). The Bassendean Dune System is the oldest of the dune systems of marine origin and today consists of a series of low hills varying from 20 m to almost flat, which rise to 110 m above sea level. They were formed as a belt of coastal dunes and associated shoreline deposits that accumulated mostly during a period of high sea level, about 115 000 years ago during the Riss-Würm interglacial period (McArthur and Bettenay, 1974). Secondary or epidiagenetic calcrete commonly occurs in an interdunal area (between the Spearwood and Quindalup dunes), which is marine or estuarine in origin, as a cap on top of fossiliferous limestone that in turn is covered by a shallow sandy soil. The Swan Coastal Plain contains alluvium and dune sands (McArthur and Bettenay, 1960). The fluviatile deposits, displayed as coalesced alluvial fans, are of different ages and limited to the west by sequences of coastal dunes. The oldest Bassendean dune sequence is siliceous and Podzols have developed on them. The next Spearwood sequence has a core of eolianite beneath the weakly podzolized siliceous sand. The Quindalup dunes are calcareous and sequentially the youngest. Properties of the dune soils change in an orderly fashion with age. Assuming that the oldest was originally calcareous, there is progressive loss of carbonate, a lowering of the pH, and formation of podzols. Between the two younger dune sequences is a zone that is marine in origin.

In the southern extension of the Swan Coastal Plain, the Quindalup dune systems extends along the coast and are backed by soils of the Stirling Swale, a marsh environment, and soils developed on older dunes farther inland (McArthur and Bettenay, 1956). Alluvial and swamp soils occur still inland on the coastal plain. This sequence of dune systems, often calcareous near the coast and siliceous on the landward side of the coastal plain, separated by intervening swales is typical of many coastal plains around the world. Alluvial soils truncate these sequence as rives make their way to the coast and swamps often prevail in older degraded dune systems.

Gippsland Area, Victoria, Australia

The coastal zone south of the Dividing Range in Victoria is separated from the sea by a narrow sand barrier (Ward, 1977). Generally characterized as extensive lowland with broad, low-lying sand plains and swamps around lagoons, fourteen marine terraces elsewhere rise in shallow steps to the 130 m contour. Dune sands form low ridges on the marine terraces and alluvial terraces beside the main rivers terminate at former shorelines defined by stranded marine terraces, except for the youngest one that passes beneath present sea level. Three groups of soils are defined whether the parent sediment is aeolian sand, alluvium, or stranded marine terraces. The soils on the aeolian sands show progressive development of spodosol characteristics when viewed in order of age. In the other groups the most striking feature is the progressive development with increasing age of a contrast in texture between solum and subsoil. Changes in clay mineral suites and chemical composition accompany these changes in morphology.

Southeast South Australia, Australia

The most widespread soils of the Kingston–Mt. Gambier region in southeast South Australia are derived mainly form calcareous beach sands (Podzols and terra rossa profiles) or from estuarine and lacustrine deposits (groundwater rendzina and solodized Solonetz profiles) (Blackburn et al., 1965). The calcareous beach sands occur in about thirty stranded Quaternary beach ridges that comprise a soil chronosequence with the oldest soils occurring more than 80 km inland form the present coast. Variation in morphological properties of the main kinds of soils shows gradual transition in age sequence that is represented by depth of red soil, thickness of kunkar, and occurrence of ferruginous concretions (iron-rich pisolites). The time span for soil formation for some of the older soils appears to be on the order of several hundred thousand years (Blackburn et al., 1965). Most of the ridges are consolidated, immobile structures on which soil profiles show little evidence of truncation. In some places there is evidence of truncation in the form of secondary siliceous sand dunes and exposed kunkar. Most of the older land surfaces are represented by non-truncated soil profiles of sand podzolics.

Eolianites of tropical and subtropical coasts

Eolianite-paleosol sequences are commonly interpreted as evidence stable phases of soil formation that can be related to climatic change and fluctuating sea levels. Models of eolianite-paleosol formation have been developed for Bermuda and the Bahamas (e.g., Bretz, 1960; MacKenzie, 1964; Vacher and Harmon, 1987; Hearty et al., 1992; Hearty and Vacher, 1994). Eolianite lithofacies are massive to cross-bedded calcarenites that display similar skeletal assemblages to underlying beach rock. The majority of skeletal grains in eolianites tends to be highly abraded, are subangular to subrounded grains and are well sorted. Fletcher et al. (2005) report three caliche intervals in the Hawaiian Kaiehu Point sequence. Distinct, platey and laminar calcrete horizons are characteristic of the thicker caliche paleosols within the two dune successions. The beds here contain micritic and earthy iron-oxide coated grains that Fletcher et al. (2005) report as being indicative of vadose pedogenesis. These calcrete horizons are similar to 'vadose micritic envelopes' of southern Australia (Warren, 1983), to 'calcrete ooids' of Pleistocene dunes in Western Australia (Read, 1974) and to calcretes in coastal eolianites of South Africa (Seisser, 1973), as reported by Fletcher et al. (2005).

Soils of polar coastal plains

Cold soils occupy roughly one-third of the world's land area (Rieger, 1983). Maritime and continental climatic types are recognized, but each has varying degrees of expression. In maritime types, precipitation is high and uniformly distributed throughout the year, and temperature differences between winter and summer are minimal. Many sediments and soils in polar regions have a complex history, particularly as they relate to cyclic deposits, glacial activity, wind action, solifluction, as well as cryogenic processes (Tedrow, 1977; Allard, 2001). The coastal plain on the northern tip of Alaska is flat and the drainage pattern is poorly integrated. Barrow is a low-relief emergent region where lakes, marshes, or former lake basins occupy 50–75% of the region. The remainder of the coastal plain consists of initial surface residuals, areas that do not show evidence of thaw-lake activity. Black (1964) reports that the complexity of the surficial materials near Barrow makes it difficult to subdivide the geologic deposits. Beaches, bars, distributary deposits, and deltaic deposits are interspersed with shallow-water marine sediments and lagoonal, lacustrine, and fluvial deposits. The extremely low ground and air temperatures subdue chemical and biological activity that inhibits pedogenesis. Studying weathering in northeastern Greenland, Washburn (1969, 1973) defines the major weathering processes in terms of oxidation, formation of desert varnish, case hardening, rillenstein formation, carbonate coating, salt wedging, granular disintegration, differential weathering, exfoliation, cavernous weathering, frost cracking, frost wedging. More recently, Rieger (1983) pointed out the morphological impacts of freeze-thaw cycles, hydrostatic mounding and fissuring, and cryoturbation (viz. turbation accompanied by ice wedge formation), on soil formation in cold regions. Study of cryoturbated paleosols associated with past ice-wedge activity on late-Holocene sandy fluvial terraces in northern Québec (e.g., Allard, 2001), for example, corresponds with paleoclimatic information obtained form existing Arctic-wide and regional proxy records. The Little Ice Age stands out as a period of intense ice-wedge activity, followed by a warm thawing out interval during the first half of the twentieth century. From A.D. 1946 to 1991, climatic cooling reactivated ice wedge formation (Allard, 2001). In some situations, especially in the main coastal tundra zone, some of the physical and chemical weathering processes are inseparable from incipient soil-forming processes (Tedrow, 1977). Due to the adverse and specialized conditions in these cold lands, researchers recommend different kinds of soil classification systems, which are reviewed in Tedrow (1977). Modern soil classification systems tend to incorporate soil on cold coastal plains as part of more comprehensive approaches, rather than have separate systems for specialized soil environments. In the Canadian system (Clayton et al., 1977), for example, those cold region coastal soils that show weak profile development fall into the podzolic (Humo-ferric Podzol) great group. Mostly spodic (cryopsamments in Soil Taxonomy) and the brunisolic order (Cambisols in FAO/UNESCO; inceptisols, excluding aquepts in Soil Taxonomy) provide for the more normal soils. The regosolic order (equates to the concept of intisol, excluding aquents, in Soil Taxonomy) provides for various soils with little or no profile development. Gleysolic orders (aquepts, aquents, and some fluvaquents in Soil Taxonomy) include the gamut of poorly drained mineral soils with an organic layer up to 30 cm thick. Within the Canadian system, *cry* is attached to the names of 10 subgroups. The names Cryic Regosol and Cryic Gleysol indicate similarity to Regosol and Gleysol but also to those soils that are underlain by permafrost within a depth of 100 cm from the surface. The major genetic soils (excluding ranker) of the tundra zone can be arranged in caternary form as described by Tedrow (1977) viz. arctic brown, upland tundra, meadow tundra, and bog soil. The arctic brown represents zonal soils whereas the tundra soil is indicative of hydromorphic conditions. Organic soils occur in low-lying, poorly drained coastal areas referred to as bogs, swamps, marshes, or muskegs. Since many coastal landscapes have been free of glacial ice within the Holocene (past 10 000 years) there are many depressions in the landscape, water-impoundment areas, and flat plains with sluggish surface drainage. Recently deglaciated landscapes tend to exhibit poorly developed surface drainage patterns that result in water-saturated environments and the formation of bog soils. Russian investigators commonly refer to the presence of organic deposits in sectors that have 'sculpture-accumulative' relief (Tedrow, 1977). Where shorelines are elevated, the organic deposits are usually intermixed with windblown sand. South of Barrow in the Meade River basin, surficial deposits have a sandy character with numerous blowouts, sand dunes, and vegetative mats that are buried by blowing sand. The coastal plain west of the Colville Delta contains geologic materials that incorporate a marine facies with dunes and loess. Because floodplains and sandbars are exposed to the wind action in summer, soils in the vicinity of coastal rivers and deltas contain admixtures of windblown sediments. The sand and silt is blown inland by onshore winds and deposited along the banks. Soil properties are characteristic for a xeric, willow-vegetated dune system along the river but where the dunes merge with tundra inland, the terrain is poorly drained and wetland soils develop.

Interesting organic-rich soils of cold regions are the ornithogenic soils of coastal continental Antarctica (Casey Station, Wilkes Land) where penguin guano plays an important role in nutrient cycles in the ecosystem (Beyer et al., 1997). During the breeding season, seabirds bring huge amounts of organic matter from the sea to the land and this organic matter has accumulated to considerable thickness and consists of a friable layer of droppings, feathers, shells, bones, and dead penguins (Ugolini, 1972; Tedrow, 1977). On Signy Island (maritime Antarctica), 5% of the total snow-free surface is made up of ornithogenic soils from penguin guano. The chemical properties of the ornithogenic soils changes rapidly after the abandonment of the rookeries by the penguins, mainly because of CO_2^- evolution and N and P release in the sea (Tatur, 1989). Other processes include the formation of oxalic acids in the first few centimeters and simultaneous concentration of recalcitrant soil compounds such as chitin, urates, and phosphate minerals. Leaching of iron and organic P fractions and the accumulation into the subsoil in maritime Antarctica produces a spodic Bh dark brownish (5YR 3/1.5) horizon under a pale gray (10YR 5/2) Ae horizon, which are typical of Podzols in temperate regions (Beyer et al., 1997).

Coastal barriers and soils as transitional biophysical systems

Barrier systems are widespread throughout coastal areas (Jelgersma et al., 1970; Leatherman, 1979) and form the parent materials of soils. The barrier usually forms offshore, and a lagoon or backbarrier flat develops between the main barrier and the mainland; barrier – lagoon systems usually show transgressive, stationary, and regressive facies assemblages as seen along the coast of China (Li and Wang, 1991) and elsewhere. Distinctive soil suites similar in age develop on the barrier and the backbarrier flats (Daniels and Hammer, 1992). Some barriers form on the mainland, so only the soils seaward and those in the geomorphically equivalent estuaries or lagoons are the same age as the barrier. Goodwin (1987) describing coastal soil-landform relationships, reports that on the Coastal Plain of the Carolinas in the USA, soils on the landward Talbot Plain are older than the soils on the seaward Arapahoe Ridge or the Pamlico Plain. The Arapahoe Ridge and its association with the Talbot Plain is an example of why stratigraphic relations must be proven because form alone often leads to incorrect conclusions.

Barrier systems may be wide, such as those in South Carolina, or very narrow as the Arapahoe Ridge in North Carolina (Goodwin, 1987) or the Atlantic Coastal Ridge in southeastern Florida (Finkl, 1994). These systems may be very smooth, broad flats with little local relief, or irregular as in prograding beach ridge systems (e.g., Tanner, 1995; Rink and Forrest, 2003). Most barrier systems are a series of barrier and backbarrier flats where the seaward soils tend to develop on sandy parent materials.

Soils formed in the barrier sediments typically are 80 to 95 percent sand, with fine and medium sands dominating (Markewich et al., 1986). Spodic or humate horizons are common in the sandy barriers; in the Netherlands, peat and gytia interfinger with older dune systems and on top of the Older Dunes there is a strongly developed podzolic soil (Jelgersma et al., 1970). The Younger Dunes began to form in the 12th century and are weakly podzolized. The spodic horizons may be very few cm thick beneath dryer sites, or 6 or 7 meters thick beneath broad flats with deep-water movement. Most soils on the Arapahoe Ridge have spodic horizons, as do soils on the beach ridge complex. The soils on the beach ridge are complex sands. The A1 and spodic horizons on the ridge are often discontinuous and thin. The soils in the swales have thick organic-rich A horizons and distinct spodic horizons. Soils and vegetation change abruptly in response to differing hydrological gradients across the ridge and swale sequence.

Soils on the backbarrier flats can have a wide range of textures. Many backbarrier systems are extensive, have a nearly level surface and have finer textures than the adjacent barrier.

Coastal paleosols

Paleosols are soils that formed on landscapes of the past (Yaalon, 1971). They are identified on the basis of soil-forming processes, which produce the soil profile morphology, that no longer operate due to changes in climate, local environmental conditions, or because of burial by younger (terrestrial or marine) sediments, lava, or inundation (drowning) by the sea (Figure S65). Ruhe (1965) recognized three main types of paleosols: buried, exhumed, and relict. *Buried paleosols* form at the land surface but are subsequently covered by sediment or other materials, a process that separates and removes the soil from the contemporary soil-forming zone. The depth of burial or integrity of the covering layer (e.g., lava) must suspend the soil-forming processes and yet be rapid enough to prevent development of a cumulic soil profile. Common examples occur in coastal dune fields, on overwashed barrier flats or spits, or on chenier plains where the rate of episodic shifting sands is slow enough for soil formation to proceed and the new material to be incorporated into the soil profile. Epidiagenesis is common and resulting changes in original soil properties and horizons (formed prior to burial) must be considered in interpretation of paleosol composition. *Exhumed paleosols* occur at the land surface when a buried paleosol is uncovered by erosion of the blanketing material. These soils may be out of phase with existing environmental conditions, as they occur at the time of re-exposure. Exhumed paleosols are commonly found in calcarenite sequences or active (including periodically re-activated) dune environments. *Relict paleosols* formed on pre-existing landscapes but were never buried all the while environmental conditions changed to a different regime, leaving behind weathering products that characterized prior landscape conditions (Figure S65). Common examples occur in a variety of landscapes, but those associated with ancient tropical and subtropical land surfaces are exemplars viz. sesquisols, Ferralsols, Alisols, Acrisols, Luvisols, and Lixisols.

The Anastasia Formation in southeastern Florida contains intercalated paleosols that formed in the later Quaternary when environmental conditions are fluctuating, particularly rise and fall of glacioeustatic sea levels. Shown in Figure S66 is a paleosol developed on a bank deposit, when seal level fell about 120 000 years ago, and which subsequently became buried by aeolian deposits with steep bedding. A common example of buried coastal paleosols occurs in horizontally bedded sequences, as in tropical southern Florida where there are five distinct marine units punctuated by episodes of subaerial weathering (Enos and Perkins, 1977). Exposure to the atmosphere and chemical weathering of the exposed rock by dissolution resulted in the formation of discontinuous bands of dense caliche-type crusts (pedogenic calcrete as also reported in the Bahamas by Brown, 1986), paleosols, freshwater limestone, and laminated crusts (Enos and Perkins, 1977; Beach, 1982). Identification of subaerial exposure surfaces is an accepted means of identifying boundaries (unconformities) between different stratigraphic

Figure S65 Sea cliffs and marine platform developed in laterite deep weathering profile near Darwin, Northern Territory, Australia. These mantles of deep chemical alteration of bedrock formed in the late Tertiary when sea levels were lower and there was a land bridge to West Irian and Papua New Guinea. Subsequent sea-level rise drowned these deeply weather soil mantles that now form seafloor materials under the Coral Sea. Truncated by coastal erosion, these laterites now form coastal cliffs and marine platforms (center foreground) on continental margin of Australia. The ferruginous or mottled zone occurs in the coastal cliff in the foreground but kaolinitic clays of the pallid zone are exposed in the white cliffs in the background.

Figure S66 Road cut on the island of Palm Beach, Florida, showing coastal paleosols intercalated in the Anastasia Formation. The Anastasia Formation, consisting of alternating offshore bar, beach ridge, and dune system deposits at least 14 m thick along the coast, is divided into two distinct facies: an upper coquina facies and a lower shell rock facies. Shown here is the deepest road cut in southern Florida (*bicycle* for scale) where the upper part of the Anastasia Formation (late Pleistocene in age, about 120 000 years old) is weakly lithified and case hardened where exposed. A weakly developed carbonate soil developed along an unconformity (*diagonal undercut across the photo center*) prior to drowning by glacio-eustatic sea-level rise and deposition of additional bank deposits.

subdivisions of the Quaternary units. Interestingly, some of these weathering surfaces are radioactive and referred to as Secondary Depositional Crusts (SCD) (Krupa, 1999). These SDCs are typically associated with increased natural gamma radiation immediately below subaerial exposure surfaces. These SCDs seem to be related to the paleo-groundwater interface (Krupa, 1999; Harvey et al., 2002), which was formed by residual downward percolation of rainfall through the vadose zone. The SDCs exhibit elemental abundances (e.g., Ca, Mg, Al, Sr, Fe, U, Th, and K) above the natural background level for the area.

The Bermuda record is a complex mosaic of carbonate eolianites, shoreline-marine limestones, calcarenite *protosols* ('accretionary paleosols'), and terra rossa paleosols (Vacher and Hearty, 1989; Hearty and Vacher, 1994; Herwitz et al., 1996; Fletcher et al., 2005). Sayles (1931) was among the first to recognize that alternation of marine limestones, eolianites, and paleosols in local sections provides a record of Pleistocene sea-level fluctuations. Bretz (1960), drawing diverse observations into a comprehensive history, established the correlation that aeolian and marine limestones were deposited during Pleistocene interglacials when the shallow platform (–20 m) surrounding Bermuda was submerged and that terra rossa paleosols formed during glacial-age platform emergences. Solutional depressions often formed in the eolianites subsequent to dune stabilization and weathering to produce solution holes or pipes. These depressions were sometimes infilled with fine-grained sediment (Fe-rich dust) that weathered to red soils or Terra-Rossa (Herwitz and Muhs, 1995). The recurrent stratigraphic pattern, as reported by Vacher and Hearty (1989), features an erosional coastline marine deposit overlain by a regressive eolianite. Where the interglacial complex is entirely exposed above present sea level, high-stand erosional coastline deposits can be traced downdip into laterally extensive beach deposits of a depositional coastline. The beach deposits thus grade upward and laterally into eolianite, which in turn extends landward over the marine deposit and oversteps the erosional coastline deposits.

Bahamian paleosols, by way of another example of buried and exhumed paleosols, are predominantly calcium carbonate and contain minor amounts of mineral insoluble residue (quartz, plagioclase, and clay minerals) (Boardman et al., 1995; Hearty and Kindler, 1997). There are at least four megascopically distinct paleosols: laminated crusts, homogeneous crusts, breccia/conglomerate, and homogeneous matrix. All four types of Bahamian paleosols and all mineralogical varieties of paleosols are found on stratigraphically equivalent rock units (Boardman et al., 1995). The number and character of paleosol-bound parasequences on New Providence Island (Nassau), Bahamas, suggest that at least five interglacial cycles are distinguishable. Whole-rock amino acid racemization (AAR) ratios confirm the stratigraphic sequence and indicate that isotope Stages 1 through 11 are likely included among eight depositional packages (Hearty and Kindler, 1997). The Bahamian stratigraphic and pedogenic sequences, not unlike other calcarenite environments elsewhere, are complicated by the intricate stacking of similar materials in complex geomorphological settings that respond to fluctuating climates and sea levels (e.g., Carew and Mylroie, 1994). Similar late Pleistocene-Holocene coastal dune sequences and buried soils are described for the southeast Queensland coast by Ward and Grimes (1987), who suggest that Holocene sea level soon after 3 900 radiocarbon years B.P. was lower than present.

In addition to calcareous precipitates, other kinds of indurated materials related to ferruginous crusts and intensely weatherized materials are also common on coastal plains. Delaney (1966), for example, describes interesting mixed and contra-genetic sequences of caliche and laterite (Fe-duricrust) on the Rio Grande do Sul of southeast Brazil and northern Uruguay. Here, Quaternary units consist of a perched blanket of sand (the Itapoã Formation), arkosic sands and gravels (Graxaim Formation), the Serra de Tapes Laterite (a soil-stratigraphic unit), and a marine quartzose sand (Chuí Formation). The relict Serra de Tapes Laterite is not forming today and must have formed during a climate with high temperature and moderately high precipitation, conditions that do not exist on the coastal plain today. Pleistocene caliche was formed in a climate almost opposite to that of the Serra de Tapes Laterite.

Similar kinds of relationships are found in cold regions where ice-permafrost sequences on the Siberian coastal plain, with large polygonal ice wedges, represent excellent archives for paleoenvironmental reconstruction. Such deposits contain numerous well-preserved records (ground ice, paleosols, peat beds, fossils), which permit characterization of environmental conditions during a clearly defined period of the past 60 ka (Schirrmeister et al., 2002). Lake plains along the eastern shore of Lake Michigan provide analogous setups where buried soils occur in dune fields with cyclical development after relatively long (>100 yr) periods of low sediment supply (Loope and Arbogast, 2002). Because soil formation takes place during stable landscape conditions, the presence of buried soils facilitated construction of a general hypothesis for late Holocene interaction of foredune and perched dune models on this lake plain, as it relates to multicentury lake level fluctuations. It seems, on the basis of this study of thirty-two dune fields and included paleosols, that the modern landscape originated after the postglacial peak in lake level (i.e., after the Nipissing transgression, about 5 500–5 000 cal yr B.P.) (Loope and Arbogast, 2002).

The aforementioned descriptions feature Quaternary soils in contemporary coastal landscapes, but there are numerous other paleosolic developments along ancient shores where old weathering sequences persist in the form of deep weathering profiles of the lateritic or bauxitic type in senile landscapes. Salients among these examples are found in the formation of lateritic bauxites in Cretaceous and Tertiary coastal plains. Bauxites commonly form elongate belts hundred of kilometers long, parallel to Lower Tertiary shorelines in India and South America (Valeton, 1983). Typical sediment associations are found in India, Africa, South and North America that are characterized by: (1) red beds rich in detrital and dissolved material of reworked laterites, (2) lacustrine sediments and hypersaline precipitates, (3) lignites intercalated with marine clays, layers of siderite, pyrite, marcasite, and jarosite, and (4) marine chemical sediments rich in oolitic iron ores or glauconite. The geographic relationship between in situ lateritic bauxites and the shoreline at the time of bauxite formation are interesting, if not somewhat controversial. Occurrences of bauxites residing parallel to ancient coastlines is documented for the karst bauxites of the Mediterranean (Southern France, Greece, Yugoslavia). Most of these types of lateritic bauxites, which are soft at the time of formation, belong to the Aquox subgroup of the group of oxisols in Soil Taxonomy. The Fe-rich parts eventually form hard ferricretes whereas the Al-rich parts form hard alucretes (Goudie, 1973).

Alternating sequences of landscape stability and instability, as related to phases of soil formation in shield areas, are comprehended in the *cratonic regime* (Fairbridge and Finkl, 1980).

This model recognizes a thalassocratic-biostatic condition (a long-term stable phase) during which prolonged deep chemical weathering takes place. In contrast, the epeirocratic-rhexistatic condition is a shorter-term unstable phase when there is general ecological stress and erosion of weathering profiles. The dual-phased, long-term/short-term regime was developed from experience on the West Australian craton (Yilgarn Block) but is applicable to other cratonic margins around the world. The significance to coastal soils relates to occurrences of laterites, bauxites, and associated materials along contemporary coastlines and ancient shores. Phases of soil formation are related to landscape stability and high sea levels; erosional phases where there is stripping of weathered materials from the land surface is associated with low sea levels. This sequence of events along cratonic margins produces a wide range of distinctly contrasting coastal paleosols that include and which are derived from residual weathering that juxtaposes Quaternary coastal plain soils with relict Tertiary and older weathering profiles.

Epeirocratic-rhexistatic phases on the Yilgarn Block (West Australian craton) have, for example, resulted in the stripping of regolith materials form the craton surface to produce a series of etchplains that represent degrees of soil removal (Finkl and Churchward, 1973; Finkl, 1979). The least amount of stripping is associated with incipient etchplains, which occur on the seaward-most margins of the craton, along the North-South trending Indian Ocean coastal boundary and along the East-West trending Southern Ocean coastal fringe. Buried etchplains occur on the southern margin of the craton where deep chemical weathering profiles are intersected by present sea level and overrun by coastal dune systems.

Conclusion

Coastal soils are, in a certain sense, almost enigmatic because most soils occurring in coastal zones have complex histories and are related to environmental conditions that no longer predominate. This fact is perhaps not surprising because coasts themselves are extremely complex, resulting from combinations of land movements and fluctuations of sea level. Some coasts thus have histories of ingression where relative sea-level rise drowns pre-existing landscapes (Kelletat, 1995). The accompanying soils become drowned or are buried by younger coastal sediments and new phases of soil formation. In other cases, the seabed becomes emergent by sea-level fall or neotectonic uplift providing new parent materials for soil formation. In other situations, the land-sea boundary remains more or less stable long enough for soils to develop in coastal deposits such as mangrove muds. Whatever the mechanisms involved, there exists a diverse range of soils in coastal zones. Some are clearly ‘coastal’ in the sense that they are closely related to present shoreline materials and conditions; they are therefore younger Holocene in age. Other soils occurring in coastal zones are not strictly ‘coastal’ because they can form independently of maritime conditions. The complex array of coastal zone soils is not easily comprehended without careful study and some background in pedological concepts, principles, practices, and field experience. Complex terminologies of different soil classification systems also tend to confound all but the most intent coastal researchers who make the effort to ferret out the details. Coastal soils are an interesting topic that offers scope for studying coastal change or evolution as recorded in the pedological record.

It is seen that coastal zones contain the youngest soils on Earth as well as some of the oldest. Newly exposed seafloor muds form parent materials for acid sulfate soils (Thionic Luvisols) and Solonchaks; recently stabilized coastal dunes host youngest Holocene Regosols whereas some older dunes feature strongly differentiated Pleistocene Podzols. Holocene Gleysols and Histosols form in juxtaposed swales and slacks where drainage is poor. Planosols and Solonetz occur on marine terraces and deltaic regions along with Histosols whereas Cryosols and Leptosols characterize cold region coastal lowlands. Developed on older coastal plains in the low to middle humid latitudes there is a range of pedogenic formation that includes Podzols, Planosols, Alisols, Luvisols, and Arenosols and Calcisols in drier realms. Deltaic plains often feature Fluvisols, Planosols, Solonetz, and Histosols. Ancient surfaces truncated by coastal erosion, especially in intertropical regions, show sesquisols, Ferralsols, Alisols, Acrisols, and Lixisols. Last but not least there are Anthrosols and Technosols that characterize pedogenic regimes in coastal areas where there has been a long record of human habitation and cultivation of field crops. This description of coastal soils may seem like a long digression, but it is actually a light vignette because the situation is far more complex than what has been alluded to here.

This overview nevertheless provides a fair indication of the range and complexity of pedogenesis in coastal zones as well as indicating the close interrelationships between coastal processes, landforms, vegetation, hydrology, maritime climates, sediments, and the imprint of biochemical weathering on coastal landscapes and seascapes. More importantly, however, is the fact that coastal soils provide much biophysical information that is useful in attempts to unravel some of the major events in coastal evolution, especially phases of soil formation that correspond to sea-level stillstands and landscape stability.

Charles W. Finkl

Bibliography

AFES (Association Française pour l’Etude du sol), 1992. *Référentiel pédologique, principaux sols d'Europe*. Paris: INRA, 220 pp.

Allard, M., 2001. Late-Holocene climatic changes as detected by the growth and decay of ice wedges on the southern shore of Hudson Strait, northern Québec, Canada. *Holocene*, **11**(5): 563–578.

Amador, J.A., and Jones, R.D., 1995. Carbon mineralization in pristine and phosphorus-enriched peat soils of the Florida Everglades. *Soil Sci.*, **159**(2): 129–135.

Arbogast, A.F., and Loope, W.L., 1999. Maximum-limiting ages of Lake-Michigan coastal dunes: their correlation with Holocene lake level history. *J. Great Lakes Res.*, **29**: 372–382.

Ballarini, M., Wallinga, J., Murray, A.S., van Heteren, S., Oost, A.P., Bos, A.J.J., and van Eijk, C.W.E., 2003. Optical dating of young coastal dunes on a decadal time scale. *Quatern. Sci. Rev.*, **22**(10–13): 1011–1018.

Beach, D.K., 1982. *Depositional and Diagenetic History of Pliocene–Pleistocene Carbonates, Northwestern Great Bahama Bank: Evolution of a Carbonate Platform.* Miami, FL: University of Miami, Doctoral Dissertation, 600 pp.

Berger, G.W., Murray, A.S., and Havholm, K.G., 2003. Photonic dating of Holocene back-barrier coastal dunes, northern North Carolina, USA. *Quatern. Sci. Rev.*, **22**(10–13): 1043–1051.

Beyer, L., Knicker, H., Blume, H-P., Bölter, M., Vogt, B., and Schneider, D., 1997. Soil organic matter of suggested spodic horizons in relic ornithogenic soils of coastal continental Antarctica (Casey Station, Wilkes Land) in comparison with that of spodic soil horizons in Germany. *Soil Sci.*, **162**(7): 518–527.

Black, R.F., 1964. Gubik formation of Quaternary age in northern Alaska. *U.S. Geological Survey Professional Paper, 302-C*, pp. 59–91.

Blackburn, G., Bond, R.D., and Clarke, A.R.P., 1965. *Soil Development Associated with Stranded Beach Ridges in South-East South Australia.* Melbourne, Victoria: CSIRO, Soil Publication No. 22, 65 pp.

Bloom, A.L., and Stuvier, M., 1963. Submergence of the Connecticut coast. *Science*, **139**: 333–334.

Bloom, A.L., and Yonekura, N., 1985. Coastal terraces generated by sea-level change and tectonic uplift. In Woldenberg, M.J., ed., *Models in Geomorphology.* Binghamton Symposium on Geomorphology International Series No. 14. Boston, MA: Allen & Unwin, pp. 139–154.

Blum, M.D., Carter, A.E., Zayac, T., and Goble, R., 2001. Middle Holocene sea-level and evolution of the Gulf of Mexico Coast (USA). *J. Coast. Res.*, **36**: 65–80.

Boardman, M.R., McCartney, R.F., and Eaton, M.R., 1995. Bahamian paleosols: origin, relation to paleoclimate, and stratigraphic significance. In Curran, A., and White, B., eds., *Terrestrial and Shallow Marine Geology of the Bahamas and Bermuda.* Boulder, CO: Geological Society of America Special Paper 300, pp. 33–49.

Boesch, D.F., Josselyn, M.N., Mehta, A.J., Morris, J.T., Nuttle, W.K., Simenstad, C.A., and Swift, D.J.P., 1994. Scientific assessment of coastal wetland loss, restoration and management in Louisiana. *J. Coast. Res.*, **20**: 103.

Bowman, S., 1990. *Radiocarbon Dating.* Berkeley, CA: University of California Press and the British Museum, 64 pp.

Bretz, J.H., 1960. Bermuda: a partially drowned late mature Pleistocene karst. *Geol. Soc. Am. Bull.*, **71**: 1729–1754.

Brown, T.W., 1986. *The Formation of Pedogenic Calcrete: Its Stratigraphic and Diagenetic Significance in the Quaternary Limestones on San Salvador Island, Bahamas.* Bloomington, IN: Indiana University, Master's Thesis, 226 pp.

Brown, R.B., Stone, E.L., and Carlisle, V.W., 1990. Soils. In Myers, R.L., and Ewel, J.J., eds., *Ecosystems of Florida.* Orlando, FL: University of Central Florida Press, pp. 35–69.

Buol, S.W., Hole, F.D., and McCracken, R.J., 1980. *Soil Genesis and Classification.* Ames, IA: University of Iowa Press, 404 pp.

Burges, A., and Drover, D.P., 1953. The rate of Podzol development in sands of the Woy Woy District, N.S.W. *Aust. J. Bot.*, **1**: 83–94.

Butler, B.E., 1959. Periodic phenomena in landscapes as a basis for soil studies. *C.S.I.R.O. (Australia) Soil Publication No. 14*.

Butler, B.E., 1967. Soil periodicity in relation to landform development in southeastern Australia. In Jennings, J.N., and Mabbutt, J.A., eds., *Landform Studies from Australia and New Guinea.* Canberra: Australian National University Press, pp. 231–255.

Callaway, J.C., DeLaune, R.D., and Patrick, W.H., Jr., 1997. Sediment accretion rates from four coastal wetlands along the Gulf of Mexico. *J. Coast. Res.*, **13**(1): 181–191.

Carew, J.L., and Mylroie, J.E., 1994. Discussion of Hearty, P.J., and Kindler, P., 1993. New perspectives on Bahamian geology: San Salvador Island, Bahamas. *J. Coast. Res.*, **10**(4): 1087–1094.

Clague, J.J., Hutchinson, I., Mathews, R.W., and Patterson, R.T., 1999. Evidence for late Holocene tsunamis at Catala Lake, British Columbia. *J. Coast. Res.*, **15**(1): 45–60.

Clayton, J.S., Ehrlich, W.A., Cann, D.B., Day, J.H., and Marshall, I.B., 1977. *Soils of Canada, Volume 1: Soil Report; Volume II: Soil Inventory.* Ottawa: Supply and Services Canada, Vol. I, 243 pp; Vol. II, 239 pp.

Cook, P.J., Colwell, J.B., Firman, J.B., Lindsay, J.M., Schwebel, D.A., and Von Der Borsch, C.C., 1977. Late Cainozoic sequence of South East Australia and sea level changes. *BMR J. Geol. Geophys.*, **2**: 81–88.

Cooper, W.S., 1966. *Coastal Sand Dunes of Oregon and Washington.* Boulder, CO: Geological Society of America Memoir 72, 168 pp.

CPCS, 1967. *Classification des sols*. Grignon, France: ENSA, 87 pp.

Curray, J.R., 1978. Transgressions and regressions. Reprint of Original 1964 Paper. In Swift, J.P., and Palmer, H.D., eds., *Coastal Sedimentation.* Stroudsburg, PA: Dowden, Hutchinson & Ross, Benchmark Papers in Geology No. 42, pp. 97–203.

Daniels, R.B., and Hammer, R.D., 1992. *Soil Geomorphology.* New York: Wiley, 236 pp.

Daniels, R.B., Perkins, H.F., Hajek, B.F., and Gamble, E.E., 1978. Morphology of discontinuous phase plinthite and criteria for its field identification in the southeastern United States. *Soil Sci. Soc. Am. J.*, **42**: 944–949.

Darmody, R.G., and Foss, J.E., 1979. Soil–landscape relationships of the tidal marshes of Maryland. *Soil Sci. Soc. Am. J.*, **43**: 534–541.

Davis, R.A., 1978. *Coastal Sedimentary Environments.* New York: Springer, 420 pp.

Delaney, P.J.V., 1966. *Geology and Geomorphology of the Coastal Plain of Rio Grande do Sul, Brazil and Northern Uruguay.* Baton Rouge, LA: Louisiana State University Press, Coastal Studies Series Number 15, 58 pp.

DeLaune, R.D., Smith, C.J., Patrick, W.H., and Roberts, H.H., 1987. Rejuvenated marsh and bay-bottom accretion on the rapidly subsiding coastal plain of the U.A. Gulf Coast: a second-order effect of the emerging Atchafalaya Delta. *Estuar., Coast. Shelf Sci.*, **25**(4): 381–389.

DeLaune, R.D., Pezeshki, S.R., Pardue, J.H., Whitcomb, J.H., and Patrick, W.H., 1990. Some influences of sediment addition to deteriorating marshes in the Mississippi River Deltaic Plain: a pilot study. *J. Coast. Res.*, **6**(1): 181–188.

Denny, C., and Owens, J.P., 1979. Sand Dunes on the Central Delmarva Peninsula, Maryland and Delaware. Washington, DC: U.S. Government Printing Office, Geological Survey Professional Paper 1067-C, 15 pp.

Dent, D.L., 1986. Acid sulfate soils: a baseline for research and development. Wageningen, The Netherlands: International Institute for Land Reclamation and Improvement (ILRI), ILRI Publication No. 39.

Dent, D.L. and Pons, L.J., 1995. Acid sulphate soils: A world view. *Geoderma*, **67**: 263–276.

Dreissen, P.M., and Dudal, R. eds., 1989. *The Major Soils of the World. Lecture Notes on their Geography, Formation, Properties and Use.* Wageningen/ Belgium: Agricultural University/Katholieke Universiteit Leuven, 310 pp.

Enos, P., and Perkins, R.D., 1977. *Quaternary Sedimentation in South Florida.* Boulder, CO: Geological Society of America, Memoir 147, 198 pp.

Fairbridge, R.W., 1950. The geology and geomorphology of Point Peron, Western Australia. *J. R. Soc. West. Aust.*, **34**: 35–72.

Fairbridge, R.W., 1961. Eustatic changes in sea level. In Ahrens, L.H., Press, L., Rankema, K., and Runcorn, S.K., eds., *Physics and Chemistry of the Earth,* Vol. 4. Oxford: Pergamon, pp. 99–185.

Fairbridge, R.W., and Finkl, C.W., 1980. Cratonic erosional unconformities and peneplains. *J. Geol.*, **88**: 69–86.

FAO, 1991. *World Soil Resources. An Explanatory Note on the FAO World Soil Resources Map at 1:25 000 000 scale.* Rome: Food and Agriculture Organization of the United Nations, Report No. 66, 58 pp.

FAO–UNESCO–ISRIC, 1988. *Soil Map of the World. Revised Legend.* World Soil Resources Report No. 60. Rome: Food and Agricultural Organization of the United Nations, 119 pp.

Finkl, C.W., 1979. Stripped (etched) land surfaces in southern Western Australia. *Aust. Geogr. Stud.*, **17**(1): 33–52.

Finkl, C.W., 1980. Stratigraphic principles and practices as related to soil mantles. *Catena*, **7**(2/3): 169–194.

Finkl, C.W. ed., 1981. *Soil Classification.* Stroudsburg, PA: Hutchinson Ross, Benchmark Papers in Soil Science, Vol. 1, 391 pp.

Finkl, C.W., 1982a. The geography of soil classification. *Quaestiones Geographicae*, **8**: 55–59.

Finkl, C.W., 1982b. Toward a comprehensive soil classification system. *Geogr. Bull.*, **21**: 41–47.

Finkl, C.W., 1984. Chronology of weathered materials and soil age determinations in pedostratigraphic sequences. *Chem. Geol.*, **44**(1/3): 311–335.

Finkl, C.W., Jr. ed., 1994. Disaster mitigation in the South Atlantic Coastal Zone (SACZ): a prodrome for mapping hazards and coastal land systems using the example of urban subtropical southeastern. In Finkl, C. W., ed., *Coastal Hazards: Perception, Susceptibility and Mitigation.* Charlottesville, VA: Coastal Education and Research Foundation, pp. 339–366.

Finkl, C.W., 1995. Water resources management in the Florida Everglades: are 'lessons from experience' a prognosis for conservation in the future? *J. Soil Water Conserv.*, **50**: 592–600.

Finkl, C.W., 2000. Identification of unseen flood hazard impacts in southeast Florida through interpretation of remote sensing and geographic information system techniques. *Environ. Geosci.*, **7**(3): 119–136.

Finkl, C.W., and Churchward, H.M., 1973. The etched land surfaces of southwestern Australia. *J. Geol. Soc. Aust.*, **20**(3): 295–307.

Fletcher, C.H., and Sherman, C.E., 1995. Submerged shorelines on Oahu, Hawaii: archive of episodic transgression during the deglaciation? In Finkl, C.W., ed., *Holocene Cycles: Climate, Sea Level, and Sedimentation.* West Palm Beach: Coastal Education and Research Foundation, Journal of Coastal Research Special Issue No. 17, pp. 141–152.

Fletcher, C.H., III, Murray-Wallace, C.V., Glenn, C.R., Sherman, C.E., Popp, B., and Hessler, A., 2005. Age and origin of late Quaternary Eolianite, Kaiehu Point (Moomomi), Molokai, Hawaii. In Finkl, C.W., ed., *The Sun, Earth and Moon.* West Palm Beach, FL: Journal of Coastal Research, Special Issue No. 44, pp. 97–112.

Frechen, M., Neber, A., Dermann, B., Tsatskin, A., Boenigk, W., and Ronen, A., 2002. Chronostsratigraphy of aeolianites from the Sharon Coastal Plain of Israel. *Quatern. Int.*, **89**(1): 31–45.

Gerrard, A.J., 1981. *Soils and Landforms: An Integration of Geomorphology and Pedology.* London: Allen and Unwin, 219 pp.

van Ghent, P.A.M., and Ukkerman, R., 1993. The Balanta rice farming system in Guinea Bissau. In Dent, D.L., and van Mensvoort, M.E.F., eds., *Selected Papers of the Ho Chi Minh City Symposium on Acid Sulfate Soils.* Wageningen, The Netherlands: ILRI Publication No. 53, pp. 103–112.

Gleason, P.J., Cohen, A.D., Smith, W.G., Brooks, H.K., Stone, P.A., Goodrick, R.L., and Spackman, W., Jr., 1984. The environmental significance of Holocene sediments from the Everglades and saline tidal plain. In Gleason, P.J., ed., *Environments of South Florida: Past and Present, II.* Coral Gables: Miami Geological Society, pp. 297–351.

Goodwin, R.A., 1987. *Soil Survey of Pamlico County, North Carolina.* Washington, DC: U.S. Department of Agriculture, Soil Conservation Service.

Goudie, A., 1973. *Duricrusts in Tropical and Subtropical Landscapes.* Oxford: Clarendon, 174 pp.

Haq, B.U. ed., 1995. *Sequence Stratigraphy and Depositional Response to Eustatic, Tectonic and Climatic Forcing.* Dordrecht: Kluwer, 400 pp.

Harvey, J.W., Krupa, S.L., Gefvert, C., Mooney, R.H., Choi, J., King, S.A., and Giddings, J.B., 2002. Interactions between surface water and ground water and effects on mercury transport in the north-central Everglades. Reston, VA: U.S. Geological Survey, Water-Resources Investigations Report 02-4050, 82 pp.

Hays, J., 1967. Land surfaces and laterite sin the north of the Northern Territory. In Jennings, J.N., and Mabbutt, J.A., eds., *Landform Studies from Australia and New Guinea.* Canberra: Australian National University Press, pp. 182–210.

Hearty, P.J., and Kindler, P., 1997. The stratigraphy and surficial geology of New Providence Island and surrounding islands, Bahamas. *J. Coast. Res.*, **13**(3): 798–812.

Hearty, P.J., and Vacher, H.L., 1994. Quaternary stratigraphy of Bermuda: a high-resolution pre-Sangamon rock record. *Quatern. Sci. Rev.*, **13**: 685–697.

Hearty, P.J., Vacher, H.L., and Mitterer, R.M., 1992. Aminostratigraphy and ages of Pleistocene limestones of Bermuda. *Geol. Soc. Am. Bull.*, **104**: 471–480.

Hearty, P.J., Kaufman, D.S., Olson, S.L., and James, H.F., 2000. Whole-rock amino acid geochronology of key Holocene and Last Interglacial carbonate deposits in the Hawaiian Islands. *Pac. Sci.*, **54**: 423–442.

Herwitz, S.R., and Muhs, D., 1995. Bermuda solution pipe soils: a geochemical evaluation of eolian parent materials. In Curran, H.A., and White, B., eds., *Terrestrial and Shallow Marine Geology of the Bahamas and Bermuda.* Geological Society of America Bahamas-Bermuda Special Paper 300, pp. 311–323.

Herwitz, S.R., Muhs, D., Prospero, J., and Vaughn, B., 1996. Origin of Bermuda's clay-rich paleosols and their climatic significance. *J. Geophys. Res. – Atm.*, **101**: 23389–23400.

Huggett, R.J., 1975. Soil landscape systems: a model of soil genesis. *Geoderma*, **13**(1): 1–22.

Huiskes, A.H.L., 1990. Possible effects of sea level changes on salt-marsh vegetation. In: Beukema, J.J., et al., eds., *Expected Effects of Climatic Change on Marine Coastal Ecosystems.* Dordrecht: Kluwer, pp. 167–172.

Hussein, A.H., and Rabenhorst, M.C., 2001. Tidal inundation of transgressive coastal areas: pedogenesis of salinization and alkalization. *Soil Sci. Soc. Am. J.*, **65**(2): 536–545.

Inman, D.L., and Nordstrom, C.E., 1971. On the tectonic and morphologic classification of coasts. *J. Geol.*, **79**(1): 1–21.

Inubushi, K., Furukawa, Y., Hadi, A., Purnomo, E., and Tsuruta, H., 2003. Seasonal changes of CO_2, CH_4 and N_2O fluxes in relation to land-use change in tropical peatlands located in coastal area of South Kalimantan. *Chemosphere*, **52**(3): 603–609.

Jelgersma, S., De Jong, J., Zagwijn, W.H., and Van Regteren Altena, J.F., 1970. The coastal dunes of the western Netherlands; geology, vegetational history and archaeology. *Mededelingen Rijks Geologische Dienst*, Nieuwe Serie No. 21, 166 pp.

Jenny, H., 1941. *Factors of Soil Formation. A System of Quantitative Pedology.* New York: McGraw Hill, 281 pp.

Jenny, H., Arkley, R.J., and Schultz, A.M., 1969. The pygmy forest-Podzol ecosystem and its dune associates in the Mendocina Coast. *Madrono*, **20**: 60–74.

Johnson, M.E., 1992. Ancient rocky shores: a brief history and annotated bibliography. *J. Coast. Res.*, **8**: 797–812.

Johnson, M.E., and Baarli, B.G., 2005. Erosion and buried of granite rocky shores in Recent and late Pleistocene of the Seychelles Islands: physical and biological perspectives. *J. Coast. Res.*, **21**(5): 867–879.

Karpytchev, Yu.A., 1993. Reconstruction of Caspian sea-level fluctuations: radiocarbon dating coastal and bottom deposits. *Radiocarbon*, **35**(3): 400–420.

Karunakaran, C., and Sinha Roy, S., 1981. Laterite profile development linked with polycyclic geomorphic surfaces in south Kerala. In Krishnaswamy, V.S., ed., *Lateritisation Processes* (Proceedings of the International Seminar on Lateritisation Processes, 11–14 December 1979, Trivandrum, India). Rotterdam: Balkema, pp. 221–231.

Kelletat, D.H., 1995. *Atlas of Coastal Geomorphology and Zonality.* West Palm Beach, FL: Coastal Education and Research Foundation, 286 pp.

Krupa, S.L., 1999. *Recognition and Analysis of Secondary Depositional Crusts in the Surficial Aquifer System of Southeast Florida.* Boca Raton, FL: Florida Atlantic University, Master's Thesis, 277 pp.

Kukla, G.J., 1977. Pleistocene land–sea correlations. I. Europe. *Earth Sci. Rev.*, **13**: 307–374.

Leatherman, S.P., 1979. *Barrier Islands: From the Gulf of St. Lawrence to the Gulf of Mexico.* New York: Academic Press, 325 pp.

Less, B.G., and Lu, Y., 1992. A preliminary study on formation of the sand dune systems in the northern Australian coastal zone. *Chin. Sci. Bull.*, **37**(7): 587–592.

Li, C., and Wang, P., 1991. Stratigraphy of the late Quaternary barrier – lagoon depositional systems along the coast of China. *Sediment. Geol.*, **72**: 189–200.

Libbey, L.K., and Johnson, M.E., 1997. Upper Pleistocene rocky shores and intertidal biotas at Playa La Palmita (Baja California Sur, Mexico). *J. Coast. Res.*, **13**(1): 216–225.

Lissman, J.C., and Oxenford, R.J., 1975. Eneabba rutile-zircon-ilmenite sand deposit, WA. In Knight, C.L., ed., *Economic Geology of Australia and Papua New Guinea. 1 Metals.* Melbourne, Victoria: Australian Institute of Mining and Metallurgy, Monograph No. 5, pp. 1062–1088.

Liu, C., and Walker, H.J., 1989. Sedimentary characteristics of cheniers and the formation of the chenier plains of east China. *J. Coast. Res.*, **5**: 353–368.

Lodge, T.E., 1994. *The Everglades Handbook: Understanding the Ecosystem.* Delray Beach, FL: St. Lucie Press, 228 pp.

Loope, W.L., and Arbogast, A.F., 2002. Dominance of an ~150-year cycle of sand-supply change in late Holocene dune-building along the Eastern Shore of Lake Michigan. *Quatern. Res.*, **54**: 414–422.

MacKenzie, F.T., 1964. Bermuda Pleistocene eolianite and paleowinds. *Sedimentology*, **3**: 52–64.

Markewich, H.W., et al., 1986. *Soil Development and Its Relation to the Ages of Morphostratigraphic Units in Horry County, South Carolina.* Reston, VA: U.S. Geological Survey Bulletin No. 1589.

Maroukian, H., Gaki-Papanastassiou, K., Papanastassiou, D., and Palyvos, N., 2000. Geomorphological obersvations in the coastal zone of Kyllini Peninsula, NW Peloponnesus-Greece, and their relation to the seismotectonic regime of the area. *J. Coast. Res.*, **16**(3): 853–863.

McArthur, W.M., and Bettenay, E., 1956. *The Soils and Irrigation Potential of the Capel-Boyanup Area, Western Australia.* Melbourne, Victoria: CSIRO Soils and Land Use Series No. 16, 31 pp.

McArthur, W.M., and Bettenay, E., 1960. The Development and Distribution of the Soils of the Swan Coastal Plain, Western Australia. CSIRO Australia Soil Publication No. 16.

McArthur, W.M., and Bettenay, E., 1979. The land. In O'Brien, B.J., ed., *Environment and Science.* Nedlands: University of Western Australia Press, pp. 22–52.

McCollum, S.H., Cruz, O.E., Stem, L.T., Wittstruck, W.H., Ford, R.D., and Watts, F.C., 1978. *Soil Survey of Palm Beach County Area, Florida.* Washington, DC: U.S. Department of Agriculture, Soil Conservation Service, 96 pp.

McFarlane, M.J., 1976. *Laterite and Landscape.* London: Academic Press, 151 pp.

McFarlane, M.J., Ringrose, S., Giusti, L., and Shaw, P.A., 1995. The origin and age of karstic depressions in the Darwin-Koolpinyah area, N.T. In

Brown, A.G., ed., *Geomorphology and Groundwater.* New York: Wiley, pp. 93–120.

McNally, Clarke, G., and Weber, B.W., 2000. Porcellanite and the urban geology of Darwin, Northern Territory. *Aust. J. Earth Sci.*, **47**: 35–44.

Mendelssohn, I.A., and McKee, K.L., 1988. *Spartina alterniflora* die-back in Louisiana: time-course investigation of soil waterlogging effects. *J. Ecol.*, **76**: 509–521.

Milliman, J.D., and Meade, R.H., 1983. World-wide delivery of river sediment to the oceans. *J. Geol.*, **91**: 1–21.

Milnes, A.R., and Thierry, M., 1992. Silcretes. In Martin, I.P., and Chesworth, W., eds., *Soils and Paleosols.* Amsterdam: Elsevier, pp. 349–377.

Mook, W.G., and van de Plassche, 1986. Radiocarbon dating. In van de Plassche, O., ed., *Sea-Level Research: A Manual for the Collection and Evaluation of Data.* Norwich: Geo Books, pp. 525–560.

Nelson, A.R., and Kashima, K., 1993. Diatom zonation in southern Oregon tidal marshes relative to vascular plants, foraminifera, and sea level. *J. Coast. Res.*, **9**(3): 673–697.

Nordstrom, K., Psuty, N., and Carter, W., 1990. *Coastal Dunes: Form and Process.* Chichester: Wiley, 392 pp.

Nyman, J.A., Delaune, R.D., Roberts, H.H., and Patrick, W.H., Jr., 1993. Relationship between vegetation and soil formation in a rapidly submerging coastal marsh. *Mar. Ecol. Prog. Ser.*, **96**: 269–279.

Ollier, C., and Pain, C., 1996. *Regolith, Soils and Landforms.* Chichester: Wiley, 316 pp.

Otvos, E.G., and Price, W.A., 1979. Problems of chenier genesis and terminology – an overview. *Mar. Geol.*, **31**: 251–263.

Petit, M., 1985. A provisional world map of duricrust. In Douglas, I., and Spencer, T., eds., *Environmental Change and Tropical Geomorphology.* London: Allen & Unwin, pp. 269–279.

Playford, P.E., and Leech, R.E.J., 1977. Geology and Hydrology of Rottnest Island. Geological Survey of Western Australia Report No. 6.

Pons, L.J., and van Breeman, N., 1982. Factors influencing the formation of potential acidity in tidal swmaps. In Dost, H., and van Breeman, N., eds., *Proceedings of the Bangkok Symposium on Acid Sulphate Soils.* Wageningen, The Netherlands: International Institute for Land Reclamation and Improvement (ILRI), ILRI Publication No. 31, pp. 37–51.

Quarto, A., and Cissna, K., 1997. The mangrove action project. In Peck, D., ed., *Ramsar Convention on Wetlands*, 2 pp. [ramsar@ramsar.org; Ramsar Convention Bureau, Rue Mauverney 28, CH-1196 Gland, Switzerland].

Rabenhorst, M.C., 1997. The chrono-continuum: an approach to modeling pedogenesis in marsh soils along transgressive coastlines. *Soil Sci.*, **167**: 2–9.

Radtke, U., 1989. Marine Terrassen und Korallenriffe – Das Problem der quartären Meeresspiegelschwankungen erläutert an Fallstudien aus Chile, Argentinien und Barbados. *Düsseldorfer Geographische Schriften*, 27 (Düsseldorf).

Read, J.F., 1974. Calcrete deposits and Quaternary sediments, Edel Province, Shark Bay, Western Australia. In Logan, B.W., ed., *Evolution and Diagenesis of Quaternary Carbonate Sequences, Shark Bay, Western Australia. Am. Assoc. Petrol. Geol. Mem.*, **22**: 250–282.

Rebenhorst, M.C., and Swanson, D., 2000. Histosols. In Sumner, M.E., ed., *Handbook of Soil Science.* Boca Raton, FL: CRC Press, pp. E183–E209.

Redfield, A.C., 1972. Development of a New England salt marsh. *Ecol. Monogr.*, **42**: 201–237.

Rieger, S., 1983. *The Genesis and Classification of Cold Soils.* New York: Academic Press, 230 pp.

Rink, W.J., and Forrest, B., 2003. Dating evidence for the accretion history of beach ridges on Cape Canaveral and Merritt Island, Florida, USA. *J. Coast. Res.*, **19**(4).

Ritsema, C.J., van Memsvoort, M.E.F., Dent, D.L., van den Bosch, H., and van Wijk, A.L.M., 2000. Acid sulfate soils. In Sumner, M.E., ed., *Handbook of Soil Science.* Boca Raton, FL: CRC Press, pp. G121–G154.

Roberts, H.H., and Coleman, J.M., 1996. Holocene evolution of the deltaic plain: a perspective – from Fisk to present. *Eng. Geol.*, **45**: 113–138.

Ruhe, R.V., 1965. Quaternary paleopedology. In Wright, H.E., and Frey, D.E., eds., *The Quaternary of the United States.* Princeton, NJ: Princeton University Press, pp. 755–764.

Runge, E.C.A., 1973. Soil development sequences and energy models. *Soil Sci.*, **115**: 183–193.

Rutter, H., Schnack, E.J., Fasano, J.L., Isla, F.I., Del Rio, J., and Radtke, U., 1989. Correlation and dating of Quaternary littoral zones along the coast of Patagonia and Tierra del Fuego. *Quater. Sci. Rev.*, **8**: 213–234.

Saito, Y., Wei, H., Zhou, Y., Nishimura, A., Sato, Y., and Yokota, S., 2000. Delta progradation and chenier formation in the Huanghe (Yellow River) delta, China. *J. Asian Earth Sci.*, **18**: 489–497.

Sayles, R.W., 1931. Bermuda during the Ice Age. *Am. Acad. Arts Sci.*, **66**: 183–190.

Schellmann, G., and Radtke, U., 2001. Neue Ergebnisse zur Verbreitung und Altersstellung gehobener Korallenriffterrassen im Süden von Barbados. In Schellmann, G., ed., Von der *Nordseeküste bis Neuseeland – Beiträge zur* 19. *Jahrestagung des Arbeitskreises "Geographie der Meere und Küsten vom 24–27 Mai 2001 in Bamberg. Bamberger Geographische Schriften*, **20**: 201–224.

Schellmann, G., and Radtke, U., 2003. Coastal terraces and Holocene sea-level changes along the Patagonian Atlantic coast. *J. Coast. Res.*, **19**(4).

Schirrmeister, L., Siegert, C., Kunitzky, V.V., Grootes, P.M., and Erlenkeuser, H., 2002. Late Quaternary ice-rich permafrost sequences as a paleoenvironmental archive for the Laptev Sea Region in northern Siberia. *Int. J. Earth Sci.*, **91**: 154–167.

Schlichting, E., 1973. Pseudogleye und Gleye – Genese und Nutzung hydromorpher Böden. In Schlichting, E., and Schwertmann, U., eds., *Pseudogley and Gley* (Transactions of Commissions V and VI of the International Society of Soil Science). Weinheim, Germany: Verlag Chemie, pp. 1–6.

Searle, D.J., and Woods, P., 1986. Detailed documentation of Holocene sea-level record in the Perth region, South Western Australia. *Quatern. Res.*, **26**: 299–308.

Searle, D.J., Semeniuk, V., and Woods, P.J., 1988. Geomorphology, stratigraphy and Holocene history of the Rockingham-Becher Plain, South-western Australia. *J. R. Soc. West. Aust.*, **70**(4): 89–109.

Seisser, W.G., 1973. Diagenetically formed ooids and intraclasts in South Africa calcretes. *Sedimentology*, **20**: 539–551.

Sevink, J., 1991. Soil development in the coastal dunes and its relation to climate. *Landscape Ecol.*, **6**(1/2): 49–56.

Shaw, J.N., West, L.T., Truman, C.C., and Radcliffe, D.E., 1997. Morphologic and hydraulic properties of soil with water restrictive horizons in the Georgia Coastal Plain. *Soil Sci.*, **162**(12): 875–885.

Short, A.D., 2003. Cross-shore sediment transport around Australia – sources, mechanisms, rates, and barrier forms. ASCE International Conference on Coastal Sediments (Clearwater Beach, Florida, 18–23 May 2003). *Coastal Sediments Book of Abstracts*, pp. 216–217.

Sibirtzev, N.M., 1901. Russian soil investigations. In Finkl, C.W., ed., *Benchmark Papers in Soil Science 1. Soil Classification.* Stroudsburg, PA: Hutchinson Ross Publishing Company, pp. 15–35.

Spaargaren, O.C. (compiler and ed.), 1994. *World Reference Base for Soil Resources.* Rome: FAO, Land and Water Development Division, 161 pp.

Spaargaren, O.C., 2000. Other systems of soil classification. In Sumner, M.E., ed., *Handbook of Soil Science.* Boca Raton, FL: CRC Press, pp. E137–E174.

Spackman, W., Dolsen, C.P., and Riegel, W., 1966. Phytogenic organic sediments and sedimentary environments in the Everglades – Mangrove complex. Part I: evidence of a transgressing sea and its effects on environments of the Shark River area of Southeastern Florida. *Paleontographica*, **117**(B): 135–152.

Soil Survey Staff, 1975. *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys*. Washington, DC: U.S. Department of Agriculture, Agriculture Handbook No. 436, 754 pp.

Soil Survey Staff, 1992. *Keys to Soil Taxonomy.* U.S. Department of Agriculture, Soil Management Support Services, Technical Monograph No. 19, 541 pp.

Stevens, J.C., Allen, L.H., Jr., and Chen, E.C., 1984. Organic soil subsidence. *Geol. Soc. Am. Rev. Eng.*, **6**: 107–122.

Stiles, C.A., Mora, C.I., Driese, S.G., and Robinson, A.C., 2003. Distinguishing climate and time in the soil record: Mass-balance trends in Vertisols from the Texas coastal prairie. *Geology*, **31**(4): 331–335.

Tanner, W.F., 1995. Origin of beach ridges and swales. *Mar. Geol.*, **129**: 149–161.

Tatur, A., 1989. Ornithogenic soils of maritime Antacrtica. *Polar Res.*, **10**: 481–532.

Tedrow, J.C.F., 1977. *Soils of the Polar Landscapes.* New Brunsiwck, NJ: Rutgers University Press, 638 pp.

Thorp, J., and Smith, G., 1949. Higher categories of soil classification: order, suborder and great group. *Soil Sci.*, **67**: 117–126.

Ugolini, F.C., 1972. Ornithogenic soils of Antacrtica. In Liano, G.A., ed., Antarctic terrestrial biology. *Am. Geophys. Union Antarctic Res. Ser.*, **20**: 181–193.

Vacher, H.L., and Hearty, P., 1989. History of Stage 5 sea level in Bermuda: review with new evidence of a brief rise to present sea level during Substage 5A. *Quatern. Sci. Rev.*, **8**: 159–168.

Valeton, I., 1981. Bauxites on peneplained metamorphic and magmatic rocks, on detrital sediments and on karst topography, their similarities and contrasts of genesis. In Krishnaswamy, V.S., ed., *Lateritisation Processes* (Proceedings of the International Seminar on Lateritisation Processes, 11–14 December 1979, Trivandrum, India). Rotterdam: Balkema, pp. 15–23.

Valeton, I., 1983. Palaeoenvironment of lateritic bauxites with vertical and lateral differentiation. In Wilson, R.C.L., ed., *Residual Deposits: Surface Related Weathering Processes and Materials.* London: Balckwell, pp. 77–90.

Van Mensvoort, M.E.F., and Dent, D.L., 1997. Acid sulfate soils. In Lal, R., et al., eds., *Methods for Assessment of Soil Degradation.* Boca Raton, FL: CRC Press, pp. 301–333.

Vepraskas, M.J., and Sprecher, S.W., 1997. *Aquic Conditions and Hydric Soils: The Problem Soils.* Madison, WI: Soil Science Society of America, Special Publication No. 50, 156 pp.

Vogel, J.C., 1980. Accuracy of the radiocarbon time-scale beyond 15000 B.P. *Radiocarbon*, **22**(2): 210–218.

Wang, Y., 2003. Coastal laterite profiles at Po Chue Tam, Lantau Island, Hong Kong: the origin and implication. *Geomorphology*, **52**(3/4): 335–347.

Wang, J., and Luo, S., 2002. Sulfur and its acidity in acid sulfate soil of Taishan coastal plain in southern China. *Commun. Soil Sci. Plant Anal.*, **33**(3/4): 579–586.

Wanless, H.R., Parkinson, R.W., and Tedesco, L.P., 1994. Sea level control on stability of wetlands. In Davis, S.M., and Ogden, J.C., eds., *Everglades: The Ecosystem and Its Restoration.* Delray beach, FL: St. Lucie Press, pp. 199–223.

Ward, W.T., 1977. *Geomorphology and Soils of the Stratford-Bairnsdale Area, East Gippsland, Victoria.* Australia CSIRO Division of Soils, Soils and Land Use Series No. 57.

Ward, W.T., and Grimes, K.G., 1987. History of coastal dunes at Triangle Cliff, Fraser Island, Queensland. *Aust. J. Earth Sci.*, **34**: 325–333.

Ward, W.T., and McArthur, W.M., 1983. Soil formation on coastal lands and the effects of sea-level changes. In Division of Soils, CSIRO, *Soils: An Australian Viewpoint.* London: Academic Press, pp. 101–105.

Warren, K.K., 1983. Pedogenic calcrete in Quaternary calcareous dunes in coastal southern Australia. *J. Sediment. Petrol.*, **53**: 787–796.

Washburn, A.L., 1969. Weathering, frost action, and patterned Ground in the Mesters Vig District, northeast Greenland. *Meddel. Om Gronland*, **176**(4): 303 pp.

Washburn, A.L., 1973. *Periglacial Processes and Environments.* London: Arnold, 320 pp.

Yaalon, D.H., 1971. Soil-forming processes in time and space. In Yaalon, D.H., ed., *Paleopedology.* Jerusalem: Israel University Press, pp. 29–40.

Yan, Q., Xu, S., and Shao, X., 1989. Holocene cheniers in the Yangtze Delta, China. *Mar. Geol.*, **90**: 337–343.

Yatsko, A., 2000. Of marine terraces and sand dunes: the landscape of San Clemente Island. *Pacific Coast Archaeol. Soc. Q.*, **36**(1): 26–30.

SOILS, NON-AGRICULTURAL USES

One of the primary purposes of the soil classification program of the USDA has been its use in soil surveys, the principal use of which has been oriented toward interpretations for technical assistance in soil conservation programs, for planning agricultural programs, and as a basis for credit. As the agricultural uses of the land intensified and grew more complex, it became obvious that the combination of soil properties responsible for a specific soil having a characteristic crop production and management potential also determined its suitability for a variety of non-agricultural uses.

Simonson (1968) has reviewed the early concepts and recognition of soils as components of the natural resource base. Early civilizations, while often located near major transportation routes, were also conscious of soils suitable for agriculture. The pattern of prehistoric occupation of soils in Western Europe suggests that Neolithic people recognized distinctions between soils (Clark and Evans, cited by Simonson, 1968). Early Chinese, Egyptian, Mesopotamian, Indus, and Roman civilizations recorded soil classification systems that were based on productivity (Simonson, 1968).

Early non-agricultural soil uses while not well documented nevertheless recognized the importance of soil. The early brickmakers and potters must have appreciated the amount and types of clay contained in certain soils and deposits. Examination of many American Indian camps reveals that they were often located on the higher and better-drained soils.

The early attempts in the United States at applying the basic soil classification system to non-agricultural land uses began in the mid and late 1920s. By 1930 the system began to guide highway construction and was later applied in defense planning (Kellogg, in Bartelli, et al., 1966). As non-agricultural land use intensified after World War II, soil survey interpretations accelerated in the areas of community planning, engineering, transportation, and waste-disposal technology (e.g., Silberstein and Maser, 2000; Caldwell and Brown, 2003; Randolph, 2003).

Aitchison et al. (1954) began a study in 1945 on the urban-related soil problems of Adelaide, South Australia, indicating the control exerted on the city's expansion pattern by the nature of the soil. Of particular interest to Aitchison in the 1954 report and subsequent applications of soil survey principles to urban planning uses was the correlation of soil types with building foundation behavior and design. Aitchison concluded "*that the soil profile could serve as the basis for the quantitative extrapolation of knowledge basic to foundation design*". Such information and its extrapolation to similar soils has proved valuable to engineers and architects and aided in the development of building codes and practices to overcome soil limitations.

One of the earliest soil surveys made specifically for planning the expanding non-agricultural land uses on the fringes of suburban areas in the United States was in Fairfax County, Virginia (Kellogg, in Bartelli, et al., 1966). The soil mapping, begun in 1953 at the request of the county, was completed in 1955 with the final report published by the Soil Conservation Service (SCS) in 1963. This county was the first in the United States to hire a full-time soil scientist for multipurpose interpretations.

The use of soil surveys and soil data for regional planning in a seven-county area of southeast Wisconsin has been reviewed in detail by Bauer (in Simonson, 1974). Bauer states that, to help avoid further abuse and misuse of the soil element of the natural resource base, a need exists in any comprehensive regional planning program to examine not only how land and soils are currently used but how they can *best* be used and managed. This effort requires definitive data and knowledge about the geographic location and extent of the various soils; about their physical, chemical, mineralogical, and biological properties; and about the capability of these soils to support various kinds of both rural and urban uses.

Modern soil surveys in the United States provide a variety of interpretive tables for many non-agricultural soil uses. These interpretations usually take the form of indicating the suitability (good, fair, poor) or limitations (slight, moderate, severe) of the soils for the use being considered (see section H of Sumner, 2000).

Legal aspects of the use of soils information in land use planning are covered by Juergensmeyer and Roberts (2003).

Non-agricultural uses of soil information

Floodplains

Because urban development often encroaches on floodplains of streams and rivers, it is necessary to develop restrictions preventing such unwise land use in the interest of public welfare and safety. To delineate the various floodplain boundaries with respect to maximum probable flood events, expensive hydrologic surveys are required to determine the various limits of the floodplain. Because soils in a floodplain are unique and distinct from other upland soils, a floodplain can be delineated from soil maps. Local jurisdictions have used soil maps as tools in delineating floodplain zones. In the humid regions of the United States, most floodplains delineated from soil maps would correspond to the 25- to 40-year frequency flood event.

Waste disposal

Power (2000) details the use of soils as a receptacle for the wastes of human society, from simple septic systems to industrial and urban landfills. Septic tank effluents contain suspended solids, BOD (biochemical oxygen demand) components, bacteria, virus and salts, including nitrogen and phosphorous. The soil medium is used as the recipient and renovator of the effluent.

The major criteria in evaluating soils for their suitability as a medium for effluent renovation are: (1) hydraulic conductivity; (2) adequate unsaturated soil volume or depth beneath the discharge point; and (3) lack of constraints such as flooding, stoniness, and concave landscape position.

Because soils differ in their ability to transmit liquids (hydraulic conductivity) and their depth as well as drainage condition under a particular moisture (climate) regime, their suitability or potential as a medium for waste disposal and renovation also varies. A septic system with a properly operating soil absorption field in a deep, medium-textured soil will result in a highly purified effluent by the time the effluent reaches the water table. Virus, bacteria, solids, phosphates and the BOD load are effectively absorbed or deactivated by the soil. Only a portion of the nitrate and salts eventually reach the groundwater – a condition of little concern unless there is a high density of such systems.

Soils are also being used as a medium for other wastes and waste-disposal systems. More communities are going to land disposal of the centrally collected effluent, either spraying it on the land or flooding certain soil areas for infiltration and renovation. This practice has been used in Europe and Australia since the 1800s. The environmental constraints on ocean dumping and incineration are forcing sewage utilities in metropolitan areas to look at the land as a medium for disposing of sewage sludge. This sludge contains primarily the organic residues of the treatment process as well as nutrients such as nitrogen, phosphorous, and small amounts of potash and some micronutrients. This waste product can be beneficial to agricultural crops. But the sludge also contains heavy metals such as zinc, copper, nickel, cadmium, and lead that can be toxic to plants and the food chain if certain concentrations are exceeded. Again soils differ in their ability to accommodate such sludges, and those responsible for using sludges on agricultural or other lands must be mindful of the limitations of the soil medium in degrading this product.

The soil medium is also used as a receptacle for solid waste. Where large volumes of wastes are buried, these sites are called *landfills*. Pesticide containers, radioactive wastes, organic compounds, and other wastes are often discharged to the soil. Soil scientists are called on to interpret soil data and evaluate soils for their capability to handle such wastes without contaminating adjacent ecosystems. As soils are disturbed and mixed with these solid wastes, new or manmade soils result, requiring special management and care when used for parks or recreation areas after the landfill operation is complete.

This use of soil information for site selection, soil behavior, and effluent renovation under various systems of waste disposal is reviewed by Miller and Miller (2000) and Power (2000).

Engineering

Soils differ not only in their capacity to grow crops and accept wastes but also in their ability to support loads and remain stable when disturbed or graded into embankments and earthen dams. Engineers run complex soil tests to determine suitability as a foundation or building material for a large building or other major project. But for most non-agricultural land uses, there is no on-site engineering determination of the soil's suitability for the specific use.

Many residential streets, houses, small or low-load buildings, and other urban-oriented land uses are placed on soils without on-site soil sampling and testing. These types of land uses are protected to a degree by building codes and other ordinances that require minimum foundation and subbase standards to minimize the dangers of soil failure.

Over the years soil scientists and engineers have learned a great deal about the soil properties responsible for a soil's stability and shear strength under various loads and slopes. These properties include the soil's texture or particle size distribution. Texture in turn is related to the amount and size of the pores within the soil matrix. The amount, size, and shape of the pore space determine the soil's permeability and the amount of water the soil can hold against gravity. The amount and type of clay mineral in the soil will determine the soil's potential to swell when wetted and shrink when dried. Furthermore, the texture and permeability of the various horizons or layers within the soil profile affect the soil's behavior.

Engineers have developed several soil classification schemes that relate the soil's behavior to its texture under various moisture levels (Atkins, 2003). These include the Unified System (ASTM, 2006), the AASHTO system (American Association of State Highway and Transportation Officials, 2004), and several others. Knowing the properties then of the various horizons in each type of soil, one can predict to a degree how the soil will respond or behave when loaded or used as a material for a road subbase or a dam, for example (Brockenbroughand Boedecker, 2003). It is this technique that soil scientists and engineers use when considering an area for a non-agricultural use when on-site testing is either impractical or too costly for the proposed use (American Association of State Highway and Transportation Officials, 2004).

Interpretive maps can be made of an area, showing the soil depth, water-table limits, permeability classes, shrink-swell classes, and engineering classes. These and other data can be used to predict the soil's corrosion potential and depth constraints for pipelines, suitability for road fill and foundation loads, reservoir site suitability, grading limitations and constraints for other uses. These engineering soil properties can be and have been used to predict a soil's behavior and susceptibility to damage under earthquake shocks. Soil maps and data have been used for military purposes to determine trafficability and potentials and limitations of lands for certain types of equipment.

Again the principle of extending the application of knowledge about one kind of soil to other areas with similar soils is used. Since each kind of soil can occur over a large area, there is a wide potential application for all information and data relevant to the specific behavior of each soil. Building codes, subdivision specifications, urban zoning ordinances, and highway engineering standards have incorporated soil maps and information as a basis for avoiding and/or correcting problem soils (Gunaratne, 2006; Budhu, 2007).

Other uses

Numerous other non-agricultural uses of soil information and surveys can be cited. Soil information and data are used as criteria in park and recreation area planning, wildlife habitat management, identification of sand and gravel sources, analyzing the pattern of insurance claims from earthquake damage, and for environmental-impact statements and site analysis. Geochemists use anomalies in the chemistry of soils as clues to the presence of ore bodies at depth in the practice of geochemical propecting. The disciplines of geology and archeology use soil information in determining the age relationships of specific sites and layers such as the alluvial infilling of basins, migration of shorelines, ash accumulation from volcanic activity, and history of vegetation in swamps. Old geologic faults penetrating into the subsoil horizons can assist the geologist in dating the fault's occurrence, a critical measurement now required in the location of nuclear power plants. Soil science has also been applied in criminology and in forensic science to verify or link an act or individual to a specific area via the soil characteristics unique to the region.

The future

The future of soil survey interpretation and utilization of soil data seems pointed in the direction of not just describing soil conditions and indicating soil suitability but also attempting to predict the potentials of soils for alternative land uses including the measures and costs involved in making the soils more suitable for a particular use.

The costly land-use mistakes of the past, the increasing concern for preserving prime agricultural lands in the United States and elsewhere, and the desire among planners to expand urban areas onto known soil conditions have all played a role in forcing soil scientists to be more quantitative and precise in their predictions and more interdisciplinary in considering alternatives. Soil properties will be weighed as criteria for different use potentials. As more soil data are obtained, computers will be able to digest the information, assigning different, or perhaps relative, weights for each property. Eventually information will be available on which planners and others can decide which soil to use for what purpose and how much energy and cost will be required to accommodate that soil for the particular use. Furthermore, the alternative soil use decisions can be made on cost-benefit analysis with the potential costs and trade-offs known before the soil is disturbed.

A final consideration for the future relates to current concerns about global change. A good deal of information about global change is archived in the soil and is readily amenable for the reconstruction of past changes, (see for example Fabregas et al., 2003) as a harbinger of things to come.

Fred P. Miller

Bibliography

Aitchison, G.D., Sprigg, R.C., and Cochrane, G.W., 1954. The soils and geology of Adelaide and suburbs. *Geol. Surv. So. Aust. Bull.*, **32,** 130 pp.

American Association of State Highway and Transportation Officials, 2004. AASHTO provisional standards. Washington, DC: American Association of State Highway and Transportation Officials. 1 v (various pagings).

ASTM, 2006. Active Standard: D2487-06 Standard Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System). West Conshohocken, PA: American Society for Testing Materials, 12 pp.

Atkins, H.N., 2003. *Highway Materials, Soils, and Concretes*, 4th edn. Upper Saddle River, NJ: Prentice-Hall, 383 pp.

Bartelli, L.J., Klingebiel, A.A., Baird, J.V., and Heddleson, M.R., 1966. *Soil Surveys and Land Use Planning.* Madison, WI: Soil Science Society of America and American Society of Agronomy, 196 pp.

Brockenbrough, R.L., and Boedecker, K.J., Jr. eds., 2003. *Highway Engineering Handbook: Building and Rehabilitating the Infrastructure*, 2nd edn. New York: McGraw-Hill. 1 v (various pagings).

Budhu, M., 2007. *Soil Mechanics and Foundations*, 2nd edn. Hoboken, NJ: Wiley, 634 pp.

Buol, S.W., 2003. *Soil Genesis and Classification*, 5th edn. Ames, IA: Iowa State Press, 494 pp.

Caldwell, R.E., and Brown, R.B., 2003. *The Nature and Use of a Soil Survey.* Gainsville, FL: Soil and Water Science Department, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida Fact Sheet SL-11, 8 pp.

Fábregas Valcarce, R., Martinéz Cortizas, A., Blanco Chao, R., and Chesworth, W., 2003. Environmental change and social dynamics in the second-third millenium B.C. in NW Iberia. *J. Archaeol. Sci.*, **30**: 859–871.

Gunaratne, M., 2006. *The Foundation Engineering Handbook.* Boca Raton, FL: CRC/Taylor & Francis, 608 pp.

Juergensmeyer, C.J., and Roberts, T.E., 2003. *Land Use Planning and Development Regulation Law.* St. Paul, MN: Thomson/West, 934 pp.

Miller, D.M., and Miller, W.P., 2000. Land application of wastes. *Sumner*, G217–G245.

Power, J.F., 2000. *Land Application of Agricultural, Industrial, and Municipal By-Products.* Madison, WI: Soil Science Society of America, 653 pp.

Randolph, J., 2003. *Environmental Land Use Planning and Management.* Washington, DC: Island Press, 576 pp.

Silberstein, J., and Maser, C., 2000. *Land-Use Planning for Sustainable Development.* Boca Raton, FL: Lewis Publishers, 203 pp.

Simonson, R.W., 1968. Concept of soil. *Adv. Agron.*, **20**: 1–47.

Simonson, R.W. ed., 1974. *Non-Agricultural Applications of Soil Surveys.* New York: American Elsevier, 178 pp.

Soil Survey Staff, 1993. *Soil Survey Manual.* Washington, DC: U.S. Dept. of Agriculture, 437 pp.

Sumner, M.E. (ed. in chief), 2000. *Handbook of Soil Science.* Boca Raton, FL: CRC Press, 1 v (various pagings).

SOIL-SOLVENT INTERACTIONS

See *Soil Solution*.

SOLIFLUCTION

The slow movement or creep downhill of water saturated soil overlying frozen subsurface material. With freeze-thaw and cryoturbation, a characteristic soil forming process of soils of the tundra (Cryosols).

Cross-references

Cryosols
Ice Erosion

SOLONCHAKS

Solonchaks are soils with a high concentration of 'soluble salts' at some time of the year. The following account is based on FAO (2001).

Connotation. Saline soils; from R. *sol*, salt, and R. *chak*, salty area.

Synonyms. Appear as Solonchaks in most national classifications. Known generally as saline soils and salt-affected soils.

Definition. Defined by FAO (2001) as soils:

1. with a *salic* horizon starting within 50 cm from the soil surface; and
2. with no diagnostic horizons other than a *histic*, *mollic*, *ochric*, *takyric*, *yermic*, *calcic*, *cambic*, *duric*, *gypsic* or *vertic* horizon.

Parent material. Virtually any unconsolidated soil material.

Environment. Solonchaks are largely confined to the arid and semi-arid climatic zones, though in coastal regions they may occur in all climates.

Distribution. There are between 260 million (Dudal, 1990) and 340 million ha (Szabolcs, 1989) of Solonchaks, worldwide, the estimates differing in terms of the level of salinity taken to be diagnostic. The largest areas are in the Northern Hemisphere, in arid and semi-arid parts of northern Africa, the Middle East, the former USSR and central Asia. They also occur in the (semi)arid regions of Australia and North and South America. In all cases, Solonchaks can be expected to be associated with other soil types with salic horizons (e.g., salic varieties of Histosols, Vertisols and Fluvisols). Figure S67 shows the global distribution.

Characteristics. AC or ABC profiles are the commonest, with *gleyic* properties likely at depth. A distinction is made between external Solonchaks (with shallow water tables, and salt accumulation or crust, strongest at the surface) and internal Solonchaks of the soil (with a deep water table and the greatest accumulation of salts below the surface). It is not uncommon for internal Solonchaks in a high catenary position to provide at least part of their salt content to external Solonchaks in bottomland downslope. The deepest depressions, collecting drainage from the surrounding region, can develop extreme salinity and deep surface crusts. The resulting soils are called 'flooded' Solonchaks.

The high salt content of Solonchaks generally gives a stronger soil structure than comparable non-saline soils. Small crystals of salt are usually present on the faces of peds. Clay rich varieties may lose their structure if the surface becomes wet and peptized. The peptized layer can then dry to a hard crust. Re-wetting (by winter rains for example) often produces an impermeable surface. Diurnal temperature fluctuations can result in repeated phase changes between salt minerals so that a 'fluffy' character is imparted to any salt crust present.

The salt content of Solonchaks is normally measured as the electric conductivity of a saturation extract (the EC_e value). For a salic soil horizon EC_e values must be greater than 15 $dS\ m^{-1}$ at 25 °C at some time of the year, or more than 8 $dS\ m^{-1}$ if the soil-pH (H_2O, 1:1) lies above or below the limits 8.5 (alkaline carbonate soils) or less than 3.5 (acid sulfate soils).

Because of the high salt content, faunal activity is subdued or non-existent. Vegetation is restricted to halophytic species in the saltier soils.

Origin. The distinctive feature of the genesis of Solonchaks is the precipitation of calcium, magnesium, or sodium salts, or some combination of the foregoing, by reason of the evaporation of soil water. This requires water added by atmospheric precipitation to be in annual deficit to that lost by evapotranspiration, though over short periods of the year input may be temporarily greater than losses. Dissolution and crystallization are the operative physico-chemical processes, possibly accompanied by solid-state phase changes (temperature driven), especially in Sabkha environments.

Use. The principal limitation is the presence of salt in solution, which will cause drought in plants that are not adapted to the condition, by 'reverse' osmosis. Solonchaks may be used for low intensity grazing, or the less intensively salinized variety may have some use in the cultivation of salt tolerant crops,

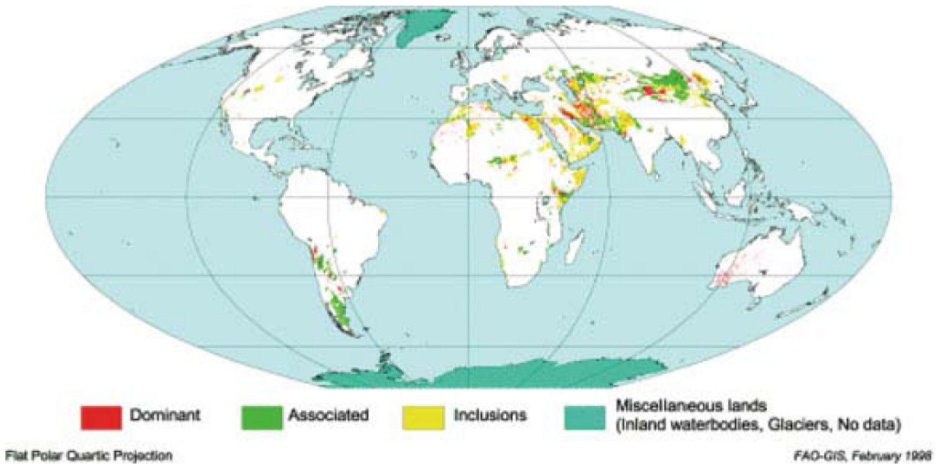


Figure S67 Global distribution of Solonchaks.

but in general their agricultural potential, if it exists at all, is severely limited.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

Fitz Patrick, E.A., 1986. *An Introduction to Soil Science*, 2nd edn. Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World*. Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Alkaline Soils
Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles

---

SOLONETZ

The Reference Soil Group of the Solonetz contains soils with a horizon of clay illuviation that is dense and strongly structured, and has a high concentration of sodium and/or magnesium ions on the exchange complex. The following description follows FAO (2001).

Connotation. From R. *sol*, salt, and *etz*, strongly expressed.

Synonyms. Internationally, Solonetz are referred to as 'alkali soils' and 'sodic soils', 'sols sodiques à horizon B et solonetz solodisés' (France), natrustalfs, natrustolls, natrixeralfs, natrargids or nadurargids (Soil Taxonomy) as solonetz (USDA, 1938, USSR, FAO) and solonetzic soils (Canada).

Definition. FAO (2001) defines Solonetz as soils having a *natric* horizon within 100 cm of the soil surface.

The natric horizon has an ESP of 15 or more in the upper 40 cm of the horizon, where ESP is the percentage of the cation exchange capacity that is accounted for by Na ions:

$$\mathrm{ESP} = \frac{\text{exchangeable Na}}{\mathrm{CEC}} \times 100$$

In cases where exchangeable Mg + Na is greater than Ca plus exchange acidity (at pH 8.2) within this depth, then ESP can be less than 15, provided that ESP exceeds 15 in some sub-horizon within 200 cm of the surface.

The natric horizon commonly shows signs of clay translocation.

The name 'Solonetz' is a little confusing in that most saline soils, whether of not they have a high proportion of adsorbed Na^+, classify as Solonchaks in the WRB classification. In the past, Solonetz were frequently lumped into one broad soil group with Solonchaks: the "salt-affected soils". However, Solonetz need not be saline and Solonetz and Solonchaks often have quite different morphological and physico-chemical properties, and consequently also different management requirements. At present, Solonetz and Solonchaks are separated at a high taxonomic level in most national soil classification systems.

Parent material. Unconsolidated materials, mostly fine-textured sediments. In particular in flat lands with impeded vertical and lateral drainage.

Environment. Solonetz are normally associated with flat lands in a climate with hot, dry summers, or with (former) coastal deposits that contain a high proportion of sodium ions. Major concentrations of Solonetz are in flat or gently sloping grasslands with loess/loam or clay in semi-arid, temperate and subtropical regions.

Distribution. There are 150 million ha of Solonetz worldwide (see Figure S68) mostly in regions of steppic climate (total annual rainfall no more than 400 or 500 mm, hot dry summers) for example the drier parts of the prairie states of the USA and contiguous provinces in Canada, and similar areas in Eurasia, particularly in the Ukraine, Russia Kazakhstan and China, as well as in Australia. Smaller areas occur on the inherently saline materials found for example on marine flats.

Characteristics. Solonetz are mostly hard in the dry season and sticky in the wet. Typically a thin loose litter layer overlies about 2–3 cm of black humified material and profiles of ABtC or AEBtC type. The A is a granular, easily eroded, black or brown surface soil overlying a columnar or prismatic, natric B within 100 cm of the soil surface. Illuviation is indicated by the presence of clay and/or organic cutans on structural elements of the B, and mature Solonetz may have the beginning

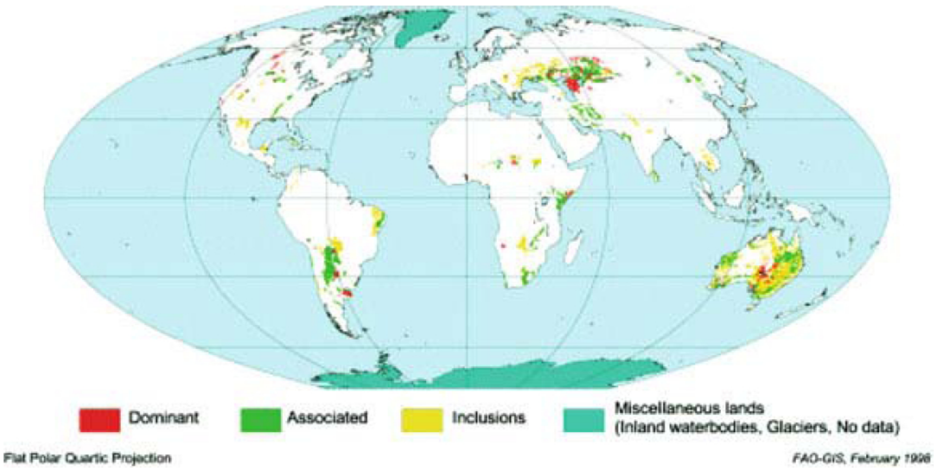


Figure S68 Global distribution of Solonetz.

of an albic horizon above the B. There may be a *calcic* or *gypsic* horizon below the natric horizon.

Solonetz that contain sodium carbonate (‘free soda’) are strongly alkaline with a field pH above 8.5.

Origin. The first requirement in the genesis of Solonetz is a high Na content in the soil forming system. In those Solonetz formed on marine flats (current or former), the high Na may be inherited. Alternatively it may be introduced as ground waters that are geologically charged with Na via hydrothermal activity (as for example in the Rift Valley of East Africa), or that may have picked up Na from older geological formations (as is the case with oil-field brines). Even where such extraneous sources are unavailable, soil water will inevitably built up to a relative Na enhancement, if evaporation reaches a stage where Ca minerals precipitate. The most common precipitating phase is calcite, followed by gypsum, and it has even been suggested that fluorite may contribute to this Na-enrichment effect (Barbiero and van Vliet-Lanoe, 1998).

Continued evaporation leads to the precipitation of Na salts, the specific minerals formed depending upon what anions are present in the local environment. The commonest precipitates are sodium sulfates ($Na_2SO_4 \cdot xH_2O$) or ‘soda’ $Na_2CO_3 \cdot xH_2O$ in inland locations, with chlorides a possibility on marine parent. Co-precipitation with Mg into more complex salts is also known.

Soda can form also by the bacterial reduction of Na_2SO_4 under hydromorphic conditions. The sulfate is reduced to sulfide, which reacts with CO_2 (from decaying organic matter) to form sodium carbonate. S leaves the system as H_2S gas.

During wet periods there will be some leaching of salts, and where this becomes emphasized, perhaps in an episode of climate change, H^+ replaces Na^+ on exchange sites and a bleached eluvial horizon of low pH forms. The soil is then called a solod.

Use. A high salt content is the main constraint on the productive use of Solonetz in agriculture. This is directly toxic to Na^+-sensitive plants, and indirectly disadvantageous by disrupting soil structure. The dense natric horizon impedes the movement of water and root-growth. Attempts at amelioration directed towards these two problems, include deep ploughing, addition of gypsum and of course, irrigation. Small areas have been cropped, especially in temperate regions where a humus-rich surface soil may be present. However but most of the world’s Solonetz lie idle or are used as rangeland.

Otto Spaargaren

Bibliography

Barbiero, L., and van Vliet-Lanoe, B. 1998. The alkali soils of the middle Niger valley: origins, formation and present evolution. *Geoderma* **84,** 323–343

FAO. 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

FitzPatrick, E.A. 1986. *An Introduction to Soil Science*. 2nd ed. Essex, England/New York: Longman Scientific & Technical Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World*. Heidelberg Berlin: Springer-Verlag, 130 pp.

Cross-references

Alkaline Soils
Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles

SOLUM

The upper part of a soil profile, the A, B, but not the C horizons, in which the soil-forming processes predominantly occur.

SOLUTE SORPTION-DESORPTION KINETICS

The reactivity of solutes and their mobility in soils play a significant role in their leaching losses beyond the root zone, availability to uptake by plants and the potential contamination of groundwater. The ability to predict the mobility of dissolved chemicals in the soil is a prerequisite in minimizing leaching losses, managing land disposal of wastes and fertilizer applications. Such predictive capability requires knowledge of the physical, chemical as well as biological processes influencing solute behavior in the soil environment. In order to assess the potential mobility of reactive solutes in the soil, models that account for the reactivities or retention of solutes with the soil matrix are needed.

Solute retention and release reactions in the soil environment include ion exchange, adsorption/desorption, precipitation/dissolution, and other mechanisms such as chemical or biological transformations. Retention and release reactions are influenced by several soil properties, including bulk density, soil texture, water flux, pH, organic matter, and type and amount of dominant clay minerals. Adsorption is the process where solutes bind or adhere to soil matrix surfaces to form outer- or inner-sphere solute surface-site complexes. In contrast, ion exchange reactions represent processes where charged solutes replace ions on soil particle surfaces. Adsorption and ion exchange reactions are related in that an ionic solute species may form a surface complex and may replace another ionic solute species already on surface sites. Retention or the commonly used term sorption should be used when the mechanisms of solute removal from soil solution are not known, and the term adsorption should be used only to describe the formation of solute-surface site complexes.

Over the last three decades, retention of solute by the soil matrix has been quantified by several scientists along two different lines. One represents equilibrium reactions and the second kinetic or time-dependent type reactions. Equilibrium models are those where solute reaction is assumed to be fast or instantaneous in nature and “apparent equilibrium” may be observed in a relatively short reaction time. Langmuir and Freundlich models are perhaps the most commonly used equilibrium models for the description of fertilizer chemicals such as phosphorus and for several organics and heavy metals. These models include the linear and Freundlich (nonlinear) and the one- and two-site Langmuir type. Kinetic models represent slow reactions where the amount of solute sorption or transformation is a function of contact time. Most common is the first-order kinetic reversible reaction for describing time-dependent adsorption/desorption in soils. Others include linear irreversible and nonlinear reversible kinetic models. Recently, combination of equilibrium and kinetic type (two-site) models, and consecutive and concurrent multireaction type models has been introduced. Several of these models have been successful in describing the adsorption as well as release of several organics in several soils.

In this section, major features of kinetic type models, which govern retention reactions of solutes in the soil, are presented. Single reaction models of the reversible and irreversible kinetic type are first discussed. Subsequently retention models of the multiple reaction type including the two-site equilibrium-kinetic models, the concurrent and consecutive multireaction models, and the second-order approach along with examples of their applications are presented (see also Table S23).

Single reaction models

Linear and Freundlich

The first-order kinetic approach is perhaps one of the earliest single form of reactions used to describe the sorption versus time for several dissolved chemicals in soils This may be written as,

$$\frac{\partial S}{\partial t} = k_{\mathrm{f}} \left(\frac{\theta}{\rho} \right) C - k_{\mathrm{b}} S \tag{1}$$

where S is the amount of solute retained by the soil (μg/g soil), C is the solute concentration in the soil solution (μg ml^{-1}), θ is the soil moisture content (cm^3 cm^{-3}) and ρ is the soil bulk density (g cm^{-3}), and t is time (h). In addition, the parameters k_{f} and k_{b} represent the forward and backward rates of reactions (h^{-1}) for the retention mechanism, respectively. The first-order reaction was first incorporated into the classical convection-dispersion equation by Lapidus and Amundson (1952) to describe solute retention during transport under steady state water flow conditions. Integration of Equation (1) subject to initial conditions of $C = C_{\mathrm{i}}$ and $S = 0$ at $t = 0$, for several C_{i} values, yields a system of linear sorption isotherms. That is, for any reaction time, t, a linear relation between S and C is obtained. Linear isotherms are not often encountered except for selected cations, heavy metals and herbicides at low concentrations. Isotherms, which exhibit nonlinear or curve linear retention behavior is commonly observed for several reactive chemicals as depicted by the nonlinear isotherms for copper and arsenic shown in Figures S69 and S70. To describe such nonlinear behavior, the single reaction given in Equation (1) is commonly extended to include nonlinear kinetic such that (Selim and Amacher, 1997),

$$\frac{\partial S}{\partial t} = k_{\mathrm{f}} \left(\frac{\theta}{\rho} \right) C^m - k_{\mathrm{b}} S \tag{2}$$

where m is a dimensionless parameter commonly less than unity and represents the order of the nonlinear reaction. For both linear and nonlinear reactions (Equations 1 and 2), the above reactions are fully reversible where the magnitudes of the rate coefficients dictate the extent of kinetic behavior of retention of the solute from the soil solution. For small values of k_{f} and k_{b}, the rate of retention is slow and strong kinetic dependence is anticipated. In contrast, for large values of k_{f} and k_{b}, the retention reaction is a rapid one and should approach quasi-equilibrium in a relatively short time. In fact, at large times ($t \rightarrow \infty$), when the rate of retention approaches zero, Equation (2) yields,

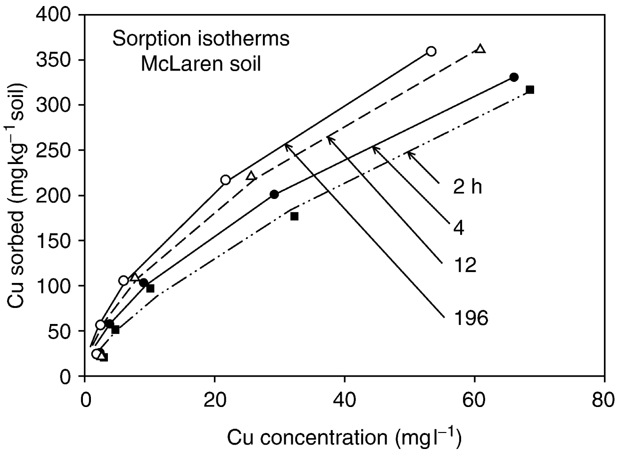


Figure S69 Adsorption isotherms for Cu on McLaren soil at different retention times. The *solid curves* are based on the Freundlich Equation.

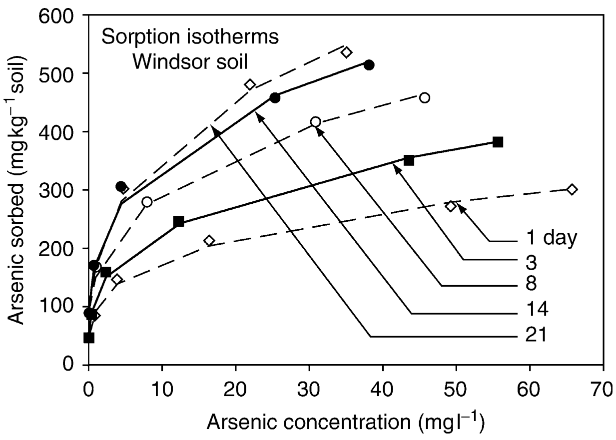


Figure S70 Adsorption isotherms for As on Windsor soil at different retention times.

Table S23 Selected equilibrium and kinetic type models for solute retention in soils (adapted from Selim and Amacher, 1997, with permission)

Model	Formulation[a]
Equilibrium type	
Linear	$S = K_{\mathrm{d}} C$
Freundlich (nonlinear)	$S = K_{\mathrm{f}} C^b$
Langmuir	$S = \omega\ C\ S_{\mathrm{T}}/[1 + \omega C]$
Langmuir with sigmoidicity	$S = \omega\ C\ S_{\mathrm{T}}/[1 + \omega C + \sigma/C]$
Kinetic type	
First-Order	$\partial S/\partial t = k_{\mathrm{f}}(\theta/\rho)C - k_{\mathrm{b}} S$
n-th Order	$\partial S/\partial t = k_{\mathrm{f}}(\theta/\rho)C^n - k_{\mathrm{b}} S$
Irreversible (sink/source)	$\partial S/\partial \mathrm{t} = ks(\theta/\rho)C - C_{\mathrm{p}}$
Langmuir kinetic	$\partial S/\partial t = k_{\mathrm{f}}(\Theta/\rho C)(S_{\mathrm{r}} - S) - k_{\mathrm{b}} S$
Elovich	$\partial S/\partial t = A \exp(-BS)$
Power	$\partial S/\partial t = K(\theta/\rho)C^n\ S^m$
Mass transfer	$\partial S/\partial t = K(\theta/\rho)(C - C^*)$

[a] $A, B, b, C^*, C_{\mathrm{p}}, K, K_{\mathrm{d}}, k_{\mathrm{f}}, k_{\mathrm{b}}, k_{\mathrm{f}}, k_{\mathrm{s}}, n, m, S_{\mathrm{T}}, \omega$, and σ are adjustable model parameters.

$$S = K_f C^m \quad \text{where} \quad K_f = \frac{\theta k_f}{\rho k_b} \tag{3}$$

which is analogous from to the Freundlich equilibrium equation where K_f is the solute partitioning coefficient (cm^3 g^{-1}). Therefore, one may regard the parameter K_f as the ratio of the rate coefficients for sorption (forward reaction) to that for desorption or release (backward reaction). For the case where $m = 1$, we have the simple linear form

$$S = K_d C \quad \text{where} \quad K_d = \frac{\theta k_f}{\rho k_b} \tag{4}$$

where the parameter K_d is the solute distribution coefficient (cm^3 g^{-1}) and of similar form to the Freundlich parameter K_f. There are numerous examples of cations and heavy metals retention, which were described successfully by use of the Freundlich Equation (Sparks, 1989; Buchter et al., 1988). In addition, an extensive list of K_d values for hundreds of pesticides have been compiled by Wauchope et al. (1992).

Kinetic second-order model

An alternative to the above first- and *n*th-order models is that of the second-order kinetic approach. Such an approach is commonly referred to as the Langmuir kinetic and has been recently used for predictions of phosphorus retention (van der Zee and van Riemsdijk, 1986), heavy metals (Selim and Amacher, 1997), and herbicides (Selim et al., 1999). Based on second-order formulation, it is assumed that the retention mechanisms are site-specific where the rate of reaction is a function of the solute concentration present in the soil solution phase (C) and the amount of available or unoccupied sites ϕ (μg/g soil), by the reversible process,

$$C + \phi \underset{k_b}{\overset{k_f}{\rightleftarrows}} S \tag{5}$$

where k_f to k_b are the associated rate coefficients (h) and S the total amount of solute retained by the soil matrix. As a result, the rate of solute retention may be expressed as,

$$\rho \frac{\partial S}{\partial t} = k_f \theta \phi C - k_b \rho S = k_f \theta (S_T - S) C - k_b \rho S \tag{6}$$

where S_T (μg/g soil) represents the total amount of specific sorption sites. As the sites become occupied by the retained solute, the amount of vacant sites approaches zero ($\phi \rightarrow 0$) and the amount of solute retained by the soil approaches that of the total capacity of sites, i.e., $S \rightarrow S_T$. Vacant specific sites are not strictly vacant. They are assumed occupied by hydrogen, hydroxyl or by other specifically sorbed species. As $t \rightarrow \infty$, i.e., when the reaction achieves local equilibrium, the rate of retention becomes,

$$k_f \theta \phi C - k_b \rho S = 0 \tag{7a}$$

or

$$\frac{S}{\phi C} = \left(\frac{\theta}{\rho}\right) \frac{k_f}{k_b} = \omega \tag{7b}$$

Upon further rearrangement, the second order formulation, at equilibrium, obeys the widely recognized Langmuir isotherm equation,

$$\frac{S}{S_T} = \frac{KC}{1 + KC} \tag{8}$$

where the parameter K ($= \theta k_f / k_b \rho$) is now equivalent to ω of Equation (6) and represents Langmiur equilibrium constant. Sorption/desorption studies showed that highly specific sorption mechanisms are responsible for solute retention for low concentrations. The general view was that metal ions have a high affinity for sorption sites of oxide minerals surfaces in soils. In addition, these specific sites react slowly with reactive chemicals such as heavy metals and are weakly reversible.

Hysteresis

To illustrate solute retention behavior (adsorption–desorption) when the first-order or the nonlinear kinetic reactions are used, we present several simulations in Figures S71 and S72 (Selim et al., 1976). As shown in Figure S71 (*top*), the linear kinetic adsorption isotherms are strongly time-dependent and even after more than 50 h only 90 % of equilibrium were achieved. The slow attainment of equilibrium can be attributed primarily to the magnitude of the reaction rate coefficients k_f and k_b. Figure S72 (*bottom*) also shows simulated adsorption curves for 10 and 50 h and desorption (*dashed*) curves initiated after 10 and 50 h of adsorption. The simulated desorption isotherms shown were obtained by reducing the solute solution concentration one half successively, every 10 h (or 50) until the solution concentration was less than 5 μg l^{-1}. This procedure is similar to that used in desorption studies in the laboratory.

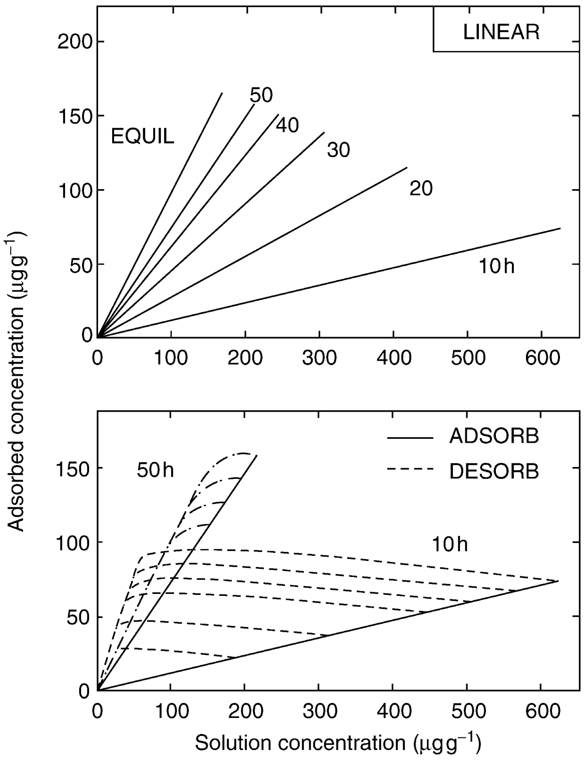


Figure S71 Simulated adsorption-desorption isotherms using linear kinetic retention. Desorption was initiated after 10 and 50 h for each successive sorption step (from Selim et al., 1976, with permission).

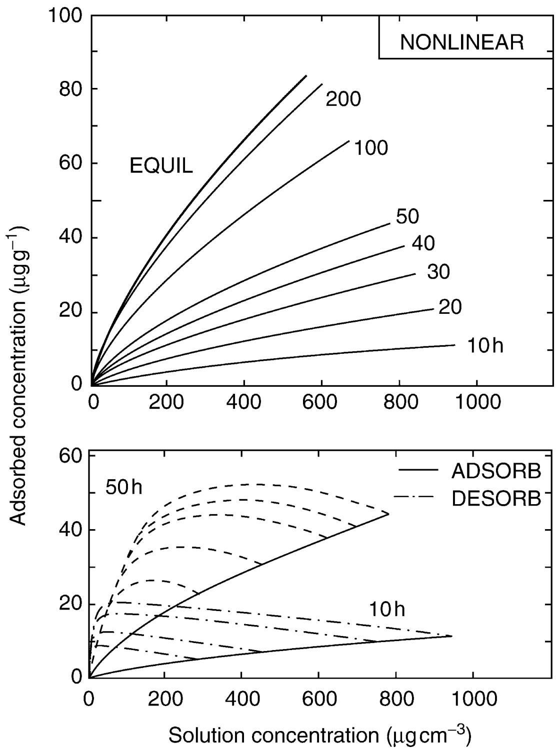


Figure S72 Simulated adsorption-desorption isotherms using nonlinear kinetic retention. Desorption was initiated after 10 and 50 h for each successive sorption step (from Selim et al., 1976, with permission).

As seen from the family of (*dashed*) curves, desorption did not follow the same path (i.e., nonsingularity) as the respective adsorption isotherm (*solid curves*). Obviously, this singularity or hysteresis results from failure to achieve equilibrium adsorption prior to desorption. If adsorption as well as desorption were carried out for times sufficient for equilibrium to be attained, or the kinetic rate coefficients were sufficiently large, such hysteretic behavior would be minimized.

Adsorption-desorption results are presented as isotherms in the traditional manner in Figures S73 and S74 that clearly indicate considerable hysteresis for copper and arsenic retention in two different soils. Such hysteretic behavior resulting from discrepancy between adsorption and desorption isotherms was not surprising in view of the strong kinetic retention behavior of these heavy metals in soils. Several studies indicated that observed hysteresis in batch experiments might be due to kinetic retention behavior and slow release and/or irreversible adsorption conditions. Adsorption–desorption isotherms indicate that the amount of irreversible or nondesorbable phases increased with time of reaction. Heavy metals may be retained by heterogeneous type sites having a wide range of binding energies. At low concentrations, binding may be irreversible. The irreversible amount almost always increased with time. It is suggested that hysteresis for heavy metals is probably due to extremely high energy bonding with organic matter and layer silicate surfaces. The fraction of nondesorbable solutes is often referred to as specifically sorbed. Others suggested that several solutes were fixed in a nonexchangeable form, which resulted in lack of reversibility as well as hysteretic behavior. Moreover, several researchers reported that the magnitude of hysteresis increases with longer sorption incubation periods. Increasing hysteretic behavior upon aging has been observed consistently for several pesticides and heavy metals.

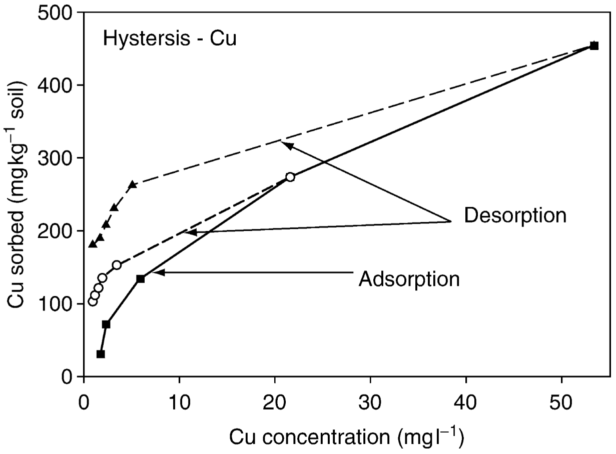


Figure S73 Adsorption and desorption isotherms illustrating hysteresis behavior of Cu retention in McLaren soil.

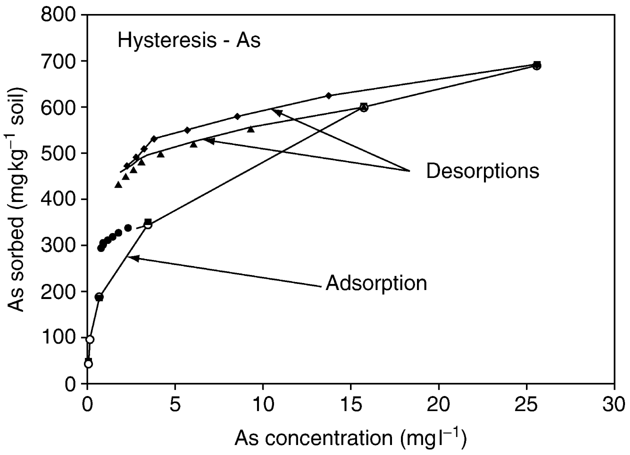


Figure S74 Adsorption and desorption isotherms illustrating hysteresis behavior of As retention in Sharkey clay soil.

Hysteresis has also been observed in ion exchange reactions for several cations, where the exchange of one sorbed cation with another is not completely reversible, i.e., the forward and reverse exchange reactions do not result in the same isotherms. The hysteretic behavior of cation exchange is abundantly reported in the literature. Verburg and Baveye (1994) provide a critical review. From a survey of the literature they were able to categorize several elements into three categories. The elements in each category were found to show hysteretic exchange between groups, but not within groups. They proposed that exchange reactions are most likely a multi-stage kinetic process in which the later rate-limiting processes are a result of physical transformation in the system, e.g., surface heterogeneity, swelling hysteresis, and formation of quasi-crystals, rather than simply a slow kinetic exchange process where there exists a unique thermodynamic relationship for forward and reverse reactions. While this may be true in some circumstances, an apparent (pseudo) hysteresis also can result from slow sorption and desorption reactions, i.e., lack of equilibrium (Selim et al., 1976). Regardless of the different reasons for hysteresis, it is evident that kinetic models such as those proposed in this study need to be complimented by detailed information on the mechanism(s) responsible for the slow kinetic reaction(s).

Multiple reaction models

Several studies showed that the use of single-reaction models, such as those described above is not adequate since such models of the equilibrium or kinetic type. Failure of single reaction models is not surprising since they only describe the behavior of one species with no consideration to the simultaneous reactions of others in the soil system. Multi-component models consider a number of processes governing several species including ion exchange, complexation, precipitation/dissolution, and competitive adsorption, among others. Multi-component models rely on the basic assumption of local equilibrium of the governing reactions where possible kinetic are ignored.

Multisite or multireaction models deal with the multiple interactions of one species in the soil environment. Such models are empirical in nature and based on the assumption that a fraction of the total sites are highly kinetic whereas the remaining fraction of sites interacts slowly or instantaneously with that in the soil solution (Selim et al., 1976; Selim and Amacher, 1997). Nonlinear equilibrium (Freundlich) and first- or *n*th-order kinetic reactions were the associated processes. Such a two-site approach proved successful in describing observed extensive tailing of breakthrough results. Amacher et al. (1988) developed a multireaction model that includes concurrent and concurrent-consecutive processes of the nonlinear kinetic type. The model was capable of describing the retention behavior of Cd and Cr^{VI} with time for several soils. In addition, the model predicted that a fraction of these heavy metals was irreversibly retained by the soil. A schematic representation of the multireaction model is shown in Figure S75. In this model we consider the solute to be present in the soil solution phase (C) and in four phases representing solute retained by the soil matrix as S_e, S_1, S_2, S_3 and S_{irr}. We further assume that S_e, S_1 and S_2 are in direct contact with the solution phase and are governed by concurrent type reactions. Here we assume S_e as the amount of solute that is sorbed reversibly and is in equilibrium with C at all times. The governing equilibrium retention/release mechanism was that of the nonlinear Freundlich type as discussed previously.

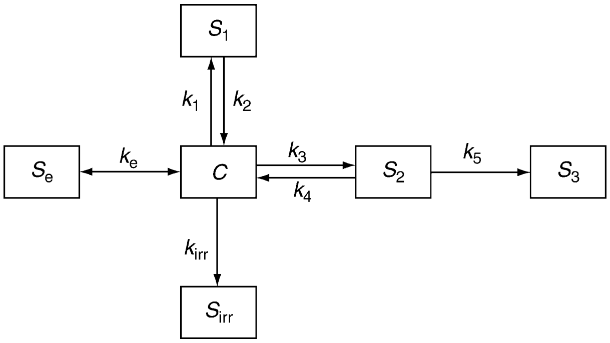


Figure S75 A schematic representation of the multireaction kinetic model.

The retention/release reactions associated with S_1 and S_2 were considered to be in direct contact with C and reversible processes of the (nonlinear) kinetic type govern their reactions:

$$S = S_e + S_1 + S_2 + S_{irr} \tag{9}$$

$$S_e = K_e\left(\frac{\theta}{\rho}\right)C^b \tag{10}$$

$$\frac{\partial S_1}{\partial t} = k_1\left(\frac{\theta}{\rho}\right)C^n - k_2 S_1 \tag{11}$$

$$\frac{\partial S_2}{\partial t} = k_3\left(\frac{\theta}{\rho}\right)C^m - k_4 S_2 \tag{12}$$

where k_1 to k_4 are the associated rates coefficients (h^{-1}). These two phases (S_1 and S_2) may be regarded as the amounts sorbed on surfaces of soil particles and chemically bound to Al and Fe oxide surfaces or other types of surfaces, although it is not necessary to have a priori knowledge of the exact retention mechanisms for these reactions to be applicable. Moreover, these phases may be characterized by their kinetic sorption and release behavior to the soil solution and thus are susceptible to leaching in the soil. In addition, the primary difference between these two phases not only lies in the difference in their kinetic behavior but also on the degree of nonlinearity as indicated by the parameters n and m. The multireaction model also considers irreversible solute removal via a retention sink term Q in order to account for irreversible reactions such as precipitation/dissolution, mineralization, and immobilization, among others. We expressed the sink term as a first-order kinetic process:

$$Q = \rho\frac{\partial S_{irr}}{\partial t} = k_{irr}\theta C \tag{13}$$

where k_{irr} is the associated rate coefficient (h^{-1}).

The multireaction model also includes an additional retention phase (S_3) which is governed by a consecutive reaction with S_2. This phase represents the amount of solute strongly retained by the soil that reacts slowly and reversibly with S_2 and may be a result of further rearrangements of the solute retained on matrix surfaces. Thus, inclusion of S_3 in the model allows the description of the frequently observed very slow release of solute from the soil. The reaction between S_2 and S_3 was considered to be of the kinetic first-order type, i.e.,

$$\frac{\partial S_3}{\partial t} = k_5 S_2 \tag{14}$$

where k_5 (h^{-1}) are the reaction rate coefficients. If a consecutive reaction is included in the model, then Equation (12) must be modified to incorporate the reversible reaction between S_2 and S_3. As a result, the following equation

$$\rho\frac{\partial S_2}{\partial t} = k_3\theta C^n + \rho(k_4 + k_5)S_2 \tag{15}$$

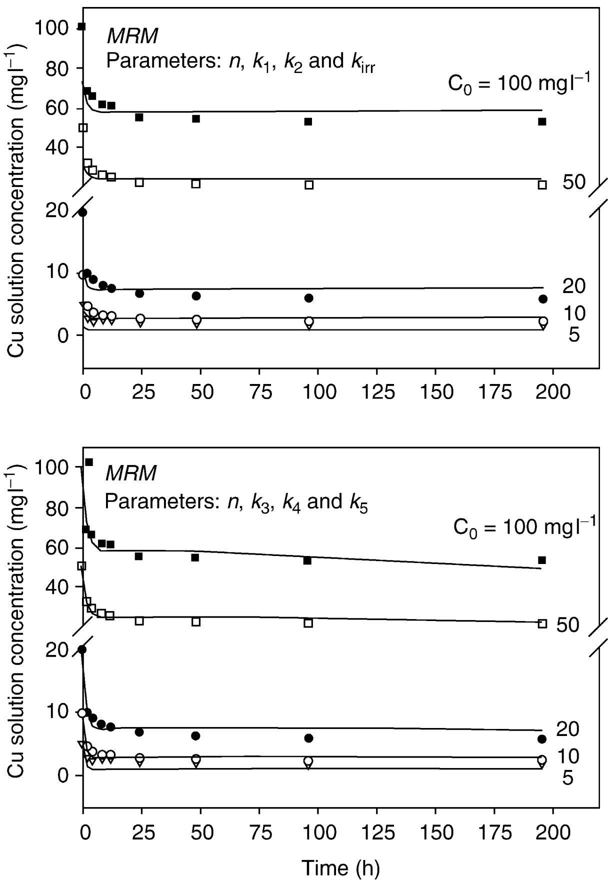


Figure S76 Experimental results of Cu in soil solution for McLaren soil versus time for a wide range of initial concentrations (C_0). The *solid curves* were obtained using the multireaction model with concurrent (*top panel*) and consecutive (*bottom panel*) irreversible reactions. Necessary model parameters were n, k_1, k_2, and k_{irr} (*top*) and n, k_3, k_4, and k_5 (*bottom*).

must be used in place of Equation (12). The above reactions are nonlinear in nature and represent initial-value problems that are typically solved based on numerical approximations. In addition, the above retention mechanisms were incorporated, in a separate model, into the classical convection-dispersion equation in order to predict solute retention as governed by the multireaction model during transport in soils (Selim et al., 1992).

The capability of the multireaction approach discussed above in describing experimental batch data for copper retention is shown by the solid curves of Figure S76. The results and model predictions are given for the various initial concentrations (C_i). Over all, good model predictions were observed for the wide range of input concentrations values considered. The multireaction model used here accounts several interactions of the reactive solute species (Cu) within the soil system. Specifically, the model assumes that a fraction of the total sites is highly kinetic whereas the remaining fraction interacts slowly or instantaneously with solute in the soil solution. As illustrated in Figure S75, the model also accounts for irreversible reactions of the concurrent and consecutive type. As a result, different versions of the multireaction model shown in Figure S75 represent different reactions from which one can deduce retention mechanisms.

In our simulations, the multireaction model was fit to Cu vs. time for all input concentrations (C_i) simultaneously. As a result an '*overall*' set of model parameters for the appropriate rate coefficients, applicable for the entire data set, was achieved. The examples shown in Figure S76 are for two different model versions. In the first version, the simulations in Figure S76 (*top*), a kinetic phase (S_1) and an irreversible phase (S_{irr}) were considered where the necessary model parameters were n, k_1, k_2, and k_{irr}. In the second version, the simulations in Figure S76 (*bottom*), a kinetic phase (S_2) as well as a consecutive irreversible reaction represented by (S_3). The presences of a consecutive S_3 phase may occur as a result of further surface rearrangement of the adsorbed phase (see Figure S75). For this version, model parameters considered were n, k_3, k_4, and k_5 where all other model parameters were set equal to zero. It is obvious from the simulations shown in Figure S76, a number of model versions were capable of producing indistinguishable simulations of the data. Similar conclusions were made by Amacher et al. (1988) for Cd and Cr^{VI} for several soils. They also stated that it was not possible to determine whether the irreversible reaction is concurrent or consecutive, since both model versions provided similar fit of their batch data. For the example shown in Figure S76, the use of a consecutive irreversible reaction provided an improved fit of Cu retention than other model versions. This finding is based on goodness-of-fit (r^2 and root mean square errors) as well as visual observation of measured data and model simulations.

H. M. Selim

Bibliography

Amacher, M.C., Selim, H.M., and Iskandar, I.K., 1988. Kinetics of chromium (VI) and cadmium retention in soils: a nonlinear multireaction model. *Soil Sci. Soc. Am. J.*, **52**: 398–408.

Buchter, B., Davidoff, B., Amacher, M.C., Hinz, C., Iskandar, I.K., and Selim, H.M., 1988. Correlation of Freundlich Kd and n retention parameters with soils and elements. *Soil Sci.*, **148**: 370–379.

Lapidus, L., and Amundson, N.R., 1952. Mathematics of adsorption in beds, VI: The effect of longitudinal diffusion in ion exchange and chromatographic column. *J. Phys. Chem.*, **56**: 984–988.

Selim, H.M., and Amacher, M.C., 1997. *Reactivity and Transport of Heavy Metals in Soils*. Boca Raton, FL: CRC/Lewis, 201 pp.

Selim, H.M., Davidson, J.M., and Mansell, R.S., 1976. Evaluation of a 2-site adsorption–desorption model for describing solute transport in soils. *Proc. Summer Computer Simulation Conf.*, Washington, DC, 12–14 July 1976. La Jolla, CA: Simulation Councils Inc., pp. 444–448.

Selim, H.M., Buchter, B., Hinz, C., and Ma, L., 1992. Modeling the transport and retention of cadmium in soils: multireaction and multicomponent approaches. *Soil Sci. Soc. Am. J.*, **56**: 1004–1015.

Selim, H.M., Ma, L., and Zhu, H., 1999. Predicting solute transport in soils: second-order two-site models. *Soil Sci. Soc. Am. J.*, **63**: 768–777.

Sparks, D.L., 1989. *Kinetics of Soil Chemical Processes*. San Diego, CA: Academic Press, 210 pp.

Van der Zee, S.E.A.T.M., and Van Riemsdijk, W.H., 1986. Sorption kinetics and transport of phosphate in soils. *Geoderma*, **38**: 293–309.

Verburg, K., and Baveye, P., 1994. Hysteresis in the binary exchange of cations on 2 : 1 clay minerals: a critical review. *Clays Clay Miner.*, **42**: 207–220.

Wauchope, R.D., Buttler, T.M., Hornsby, A.G., Augustijn-Beckers, P.W.M., and Burt, J.P., 1992. The SCS/ARA/CES pesticide properties database for environmental decision-making. *Rev. Environ. Contam. Toxicol.*, **123**: 1–164.

SORPTION PHENOMENA

Introduction

The word "*ad*sorption" is familiar to most of us. It simply means that a substance is attached to the outside of a solid. Or to use more formal language, the concentration of a substance is greater at the surface of a phase than it is in the bulk. However, sometimes it is not clear that the substance is really restricted to the outside. Because it can be difficult to separate the *ad*sorbed material from the *ab*sorbed, the noncommittal term "sorption" is often preferred. The term has a long scientific history going back to 1909 (McBain, 1909). In soil science it is used to indicate all processes that result in the transfer of material from the soil solution to the solid phase. It therefore includes adsorption. In this entry "*ad*sorption" will be used in the strict sense and therefore with a more limited meaning than sorption.

Easily the most significant aspect of the important sorption phenomena in soils is that they involve the reaction of ions (that is, charged molecules) with charged surfaces. We tend to think of these reactions in two categories: those in which electrostatic forces are dominant and those in which chemical specificity is also involved. However, these categories are not quite as sharply separate as we like to think.

The classic case in which electrostatic forces dominate is that of the attraction of cations to the negatively charged surface of clay particles – cation exchange. But even within the alkali metals, not all cations are equal: the heavier members of the series are less likely to retain their sheath of water molecules when they are adsorbed (Shainberg and Kemper, 1966). Consequently, on average, the center of charge of the cation is closer to the surface. This could reasonably be regarded as showing a degree of chemical specificity.

The classical case in which chemical specificity is involved is that of reaction of certain anions (including phosphate) with soil. Here the specificity may be so great that reaction can occur on negatively charged surfaces despite the electrostatic repulsion. Again, not all anions are equal. For some, such as sulfate and selenate, the chemical specificity is not as great and so electrostatic forces may have some effect.

Thus, rather than two sharp categories, we have a spectrum of kinds of adsorption with predominantly electrostatic forces at one end and predominantly chemical forces at the other. Although there is a continuum, the development of the two ends of the spectrum has been rather different and it is convenient to treat them separately. This entry is mainly concerned with reactions in which chemical forces are important; see *Exchange phenomena* for reactions involving mainly electrostatic forces.

Sorption curves

Why do we need to measure the amount of sorption? Because, at least in the short term, sorbed nutrient is not free to move. The proportion in the soil solution is therefore the main factor determining the rate of movement of nutrients to plant roots, or out of the soil in leachate. Much of this article is concerned with the factors, which determine the amount of sorption – that is, the partitioning between the solid phase and the soil solution. One of the most important of these is the amount added. These effects are conveniently described by plotting the amount sorbed by the soil against the concentration in solution. Such curves are often called "adsorption isotherms". This is unfortunate. First, we can seldom be sure that the process involved really is adsorption. Second, the word "isotherm" is borrowed from chemistry where it is used for reactions that depend solely on temperature and pressure (or for reactions in solution, concentration). Hence, if we have fixed the temperature – isotherm – we define the equilibrium fully by specifying concentration. This is not the case for soil reactions. A somewhat better term is "Q/I" curves – quantity/intensity. However I prefer the term "sorption curves".

In almost all cases, sorption is described by simple curves with the proportion in the soil solution increasing as the amount added increases. There are, however, some exceptions. Sorption of metals can sometimes give sigmoid curves such that there is an initial increase in concentration without much increase in sorption (Neal and Sposito, 1986; Barrow and Cox, 1992b). This seems to arise when substances in solution get first call on the metal ions so that little sorption occurs until these reactions have been satisfied. Another exception sometimes occurs at very low concentrations; a linear relation between sorption and concentration may be observed (McLaren et al., 1983; Jarvis, 1981). For trace elements in many soils the concentrations may be so low that this is a common situation. Nevertheless this straight initial section is the bottom part of a curve and this should be kept in mind when describing (and explaining) the curve.

Describing sorption curves

Two main motives for describing sorption curves may be discerned. One is to summarize a large set of numbers by a few numbers. The few numbers might then be used to characterize the soil or as an input for a fertilizer or leaching model. This motive is essentially pragmatic and the method should be chosen on the pragmatic grounds of efficiency and effectiveness. Measurement of sorption curves is somewhat tedious and is therefore seldom undertaken by soil testing laboratories. In Australia, there has therefore been interest in developing short-cut methods involving just a single-point measure rather than the several measures required for a curve (Barrow, 2000; Allen et al., 2001; Burkitt et al., 2002).

The other motive is to understand the process involved. In this case also, the description must be efficient and effective, but it should also take into account verifiable theories about the processes involved. It should also be comprehensive; it should explain all of the observations. We will therefore postpone discussion of this kind of description until after we have considered all of the factors which affect sorption.

Despite many criticisms, the Langmuir Equation is still widely used to describe reactions with soil. To understand its deficiencies, consider how it may be derived. Imagine a simple adsorption reaction in which sites on the surface of particles adsorb a reactant, x. The equilibrium equation could then be represented:

$$\text{site} + x \rightleftharpoons \text{site} - x \tag{1}$$

If the initial concentration of sites is a and the equilibrium concentration of x is c and of the product *site-x* is y, (all in convenient units) then the equilibrium constant b is given by:

$$b = \frac{y}{(a-y)c} \tag{2}$$

Re-arranging gives:

$$y = \frac{abc}{1 + bc} \tag{3}$$

This is the Langmuir adsorption equation. It may be derived in other ways (Elprince and Sposito, 1981) but this simple derivation shows that it is compatible with adsorption on one uniform surface on which all sites are equal. Further, it is not compatible with a reaction that changes the properties of the surface or of the solution. The Langmuir Equation may therefore fail for two separate reasons. It always fails when ions react specifically with surfaces – that is, when charged particles with a specific affinity for the surface react. It fails because the charge on the reacting ion must be balanced. It may be partly balanced by changing the charge on the surface. Changes in surface charge are marked with anions such as phosphate. These changes in charge change the effective value of *b*. The charge may also be partly balanced by displacing ions from the surface. This is often marked with metallic cations, which displace H^+ from the surface. These may be regarded as competing ions (Harter and Baker, 1977) and again the required conditions are not met. The Langmuir Equation also fails when the reaction is not with a uniform surface. This is commonly the case for reactions with soils. It can also be the case for reactions with surfaces that appear to be uniform.

Perhaps the most direct test of the Langmuir Equation is to plot the observed sorption against concentration. The Langmuir Equation requires that sorption reach a well-defined plateau represented by the parameter *a*. Especially for soil data; this is seldom the case (see Harter, 1984 for some examples.).

A second test is to plot the data according to one of the four linearized forms of the equation (Kinniburgh, 1986). These linearized forms are unfortunately still being used to fit Langmuir Equations using ordinary linear regressions. The most-commonly used form involves plotting concentration against a function of concentration and therefore always gives high correlation coefficients (Harter, 1984). However, because the transformations cause unacceptable changes in the variance, and because modern computers permit better techniques, these methods should be avoided for fitting regressions (Kinniburgh, 1986). Nevertheless, plotting the data in this way provides a simple test of the appropriateness of the equation. If the data plot as curves, then the Langmuir Equation is inappropriate.

Because the Langmuir Equation is frequently unsatisfactory for soil data, several modifications of it have been used. Gunary (1970) was responsible for one that involves introducing an extra term to the Langmuir formulation (Barrow, 1978). This extra term modifies the sorption curve so that it is closer to observed curves. However, the same result may be achieved with fewer terms using the Freundlich Equation (Barrow, 1978) – see later.

Another way of modifying the Langmuir Equation is to assume that the surface can be divided into two, or even three, separate regions each with characteristic, but differing, affinities for the reactant. Within each region, a Langmuir Equation is supposed to hold and the overall behavior is obtained by summing the behavior of the regions – that is multiple Langmuir Equations are assumed. This has been criticized on both theoretical and practical grounds. The theoretical grounds were concerned with the reality of the postulated surfaces (Posner and Bowden, 1980; Sposito, 1982). The practical grounds are that it is inefficient because it requires more coefficients to describe the results than other methods and that it has poor statistical properties. (Barrow, 1978; Ratkowsky, 1986)

The other widely used equation – the Freundlich Equation – can also be considered as a modification of the Langmuir Equation. It has been known for some time that the Freundlich Equation is consistent with a distribution of values for the parameters of the Langmuir Equation. More recently (Sposito, 1980, 1984) showed that a Freundlich Equation was obtained if the logs of the equilibrium coefficients of a series of Langmuir Equations were assumed to be distributed in a fashion rather similar to a normal distribution. The Freundlich Equation may be written:

$$y = a_1 c^{b_1} \tag{4}$$

where a_1 and b_1 are coefficients. If this equation is followed, a straight line will be obtained on a log-log scale. The log transformation involved is often also acceptable from a statistical point of view because the variance of both *y* and *c* often increases as the measured value increases. For soils, such plots are often close to linear over a concentration range of about 100-fold. The equation is therefore very convenient for describing such data. However if a wider range of data is available, it often becomes clear that the log-log plots are gentle curves. A sufficient range of data is seldom available for a single reactant but the principle can be well illustrated by plotting sorption of selenate, selenite, and phosphate on an adjusted scale (Figure S77). Usually the limiting slope for the left side of such curves is unity because, at this value, simple plots of sorption versus concentration are straight lines. Thus the contention that log plots are really gentle curves is consistent with linear sorption at low concentration. One way of describing such data is to make the exponent term (b_1) of the Freundlich Equation also vary with concentration (Sibbesen, 1981). However, curvature on a log scale can also have another cause.

Suppose sorption of, say, phosphate is measured on a soil that already contains some available phosphate (*q*). Then the Freundlich Equation would become:

$$y + q = a_1 c^{b_1} \tag{5}$$

and hence:

$$y = a_1 c^{b_1} - q \tag{6}$$

Plots of Equation (6) on a log scale are also curved (Figure S78). Hence care should be taken in interpreting curved plots on a log scale. Where possible, an independent measure of *q* should be made.

The effects of time of reaction on sorption

Much chemical thinking is dominated by equilibria and there is a desire to measure sorption at equilibrium – so much so, that the word “equilibrate” is widely used to describe *mixing* of soil with a reactant. However, it is wiser to take it as a general rule that reactions with soil continue for a very long period so that a measure of sorption after a given time is merely one possible measure. Rather than thinking of a sorption curve, we should think of a sorption “surface” with time as the extra dimension. A sorption curve measured at a given time is merely one of many possible curves that together make the surface.

Farmers have, of course, been aware of the continuing reaction for a very long time. It is one of the important reasons why

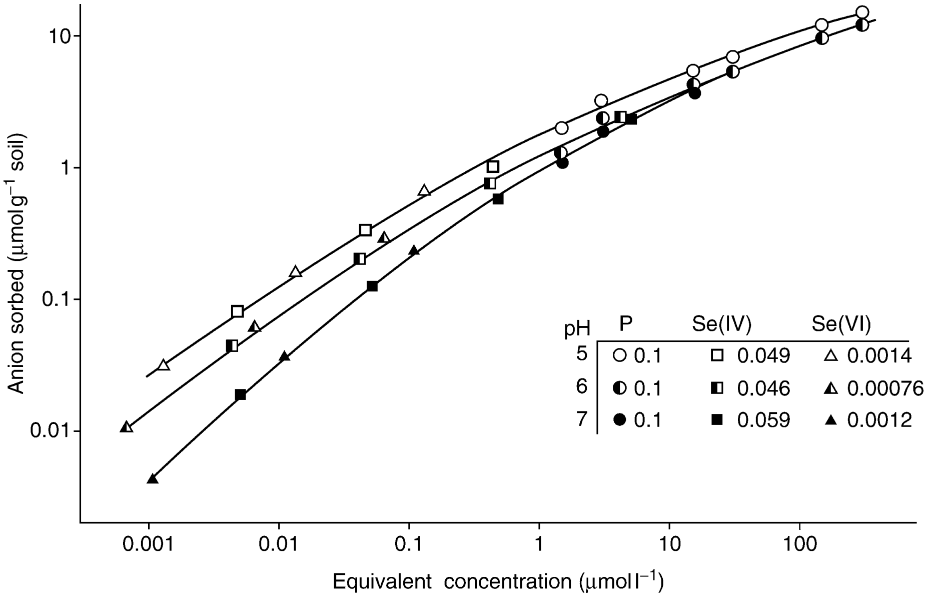


Figure S77 An extended sorption curve constructed by plotting sorption of phosphate, selenite and selenate on the same axis. Selenite and selenate are less strongly sorbed than phosphate and their concentrations have been multiplied by the factors shown to make the *lines* correspond. Thus, at pH 5, the factor for selenite was 0.049 and for selenate was 0.0014 (from Barrow and Whelan, 1989).

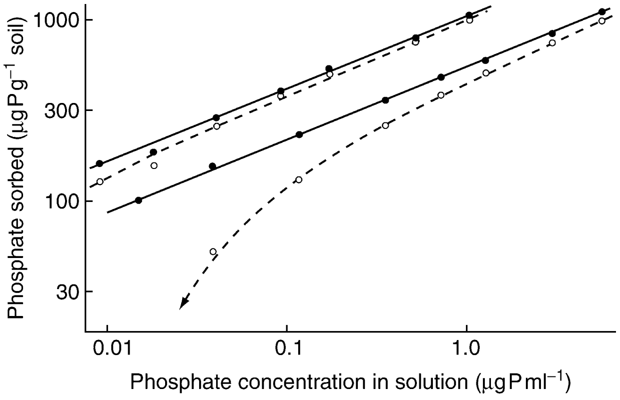


Figure S78 Sorption curves for phosphate showing that some of the curvature on a log scale can be due to phosphate present in the soil. In each case, the *hollow symbols and broken lines* are plots of Equation (4) and the *solid symbols and lines* are plots of Equation (6). The *upper pair* is for a soil, which had never been fertilized; the *lower pair* is for a sample of the same soil that had been incubated with phosphate at 400 mg P g^{-1} soil for a year at 25 °C (from Barrow, 1978).

they re-apply fertilizers. Because the rate of the reaction affects the need to re-fertilize, it is important to characterize it.

The rate of any reaction may be followed by measuring either the disappearance of the reactants or the accumulation of the products. For reactions with soil, it is obviously easier to measure the rate of disappearance of the reactant. Two kinds of methods are possible.

In one method, a small amount of soil is mixed with a large volume of solution containing the reactant and, at various times, the concentration remaining in solution is measured. The advantages are that good mixing is obtained and it is easy to separate soil and solution to measure the solution concentration. The disadvantages are that too vigorous mixing can cause breakdown of soil particles and spurious results (Barrow and Shaw, 1979), and it is often inconvenient to continue for periods of months, or years, that are relevant to agriculture.

In the other kind of method, soil is mixed with just sufficient solution containing the reactant to bring the moisture content to near the field water content and the mixture is incubated for various periods. The advantages are that conditions are closer to those of agriculture; little space is required and so incubation can continue for as long as desired; and it is easy to incubate at a range of temperatures. Like most reactions, the rate is increased by increasing the temperature and, by using moderate temperatures, the equivalent of rather long periods at lower temperature can be achieved. The disadvantages are that the rate may be limited by lack of mixing and it is more difficult to measure the remaining concentration in solution. Extraction procedures are undesirable because they involve desorption. We have used a “null-point” method. This involves briefly mixing the soil with a series of solutions containing a range of concentrations of the reactant. Some will be too dilute and so desorption will occur. Some will be too concentrated and so further sorption will occur. The null-point is the interpolated intermediate value at which neither sorption nor desorption occurs. For a fuller discussion of these points, see Barrow (1983b).

For many reactants, the rate of reaction can be described by including a term for time in the Freundlich Equation

$$y = a_1 c^{b_1} t^{b_2} \qquad (7)$$

The three-dimensional surface described by this equation is a plane on a log scale. Like the Freundlich Equation itself, it is a convenient summary of a set of data since only three parameters are needed. It has been shown to apply to phosphate reaction with a range of non-calcareous soils. For calcareous soils, it also applies at first, but precipitation of calcium phosphates may cause concentrations to decrease to a value determined by the solubility product. For further details, see Barrow (1989).

The continuing reaction is the main reason for the use of the term "sorption". There is much evidence that there is an initial *ad*sorption reaction on the surface of the soil particles and that this is relatively rapid and reaches equilibrium within, at most, a matter of hours. This is then followed by a much slower reaction – and hence the term sorption to encompass both reactions. The mechanism of the slow reaction will be considered later.

The effects of temperature on sorption

If we accept that there is a relatively rapid adsorption reaction followed by a slower reaction, temperature can have separate effects on the separate reactions. As the adsorption reaction is fairly rapid, the effects of temperature are mainly seen on the position of its equilibrium – rather than on its rate. The adsorption reaction involves ions reacting with charged surfaces. There can be effects of temperature on: the electric potential of the surface; on the ions in solution; and on the constant describing the affinity of the ions for the surface. The magnitude, and even the direction of the effects, can vary according to the reactants. Barrow (1992) discusses this further.

In contrast, the effects of temperature on the slow reaction are mainly on its rate. They are much simpler: increasing temperature increases the rate. The Arrhenius Equation may be used to relate the rate coefficient (k) of a reaction to temperature:

$$k = A\exp\left(-\frac{E}{\mathrm{R}T}\right) \tag{8}$$

where E is the activation energy, R is the gas constant, T the temperature (K), and A is a constant. Modifying Equation (7) to include this gives:

$$y = a_2 c^{b_1}\left[\exp\left(-\frac{E}{\mathrm{R}T}\right)t\right]^{b_2} \tag{9}$$

The exponential term is included in the bracket raised to the power b_2 because the rate is thought to be limited by a diffusion process. However the power term b_2 is less than the value of 0.5 expected for a diffusion process for reasons to be discussed later. With this formulation, the value of the activation energy appropriate to the pragmatic description is the same as that for the mechanistic model. The value of the activation energy E can be an important clue to the mechanism of a reaction. For most reactants with soil it has been found to be about 80 to 100 kJ per mole. It is also an indication of the acceleration to be achieved by increasing the temperature. If E is 80 kJ per mole, the rate at 60 °C is 91 times that at 15 °C and four days at 60 °C is equivalent to a year at 15 °C. By using moderate temperatures it is therefore possible to simulate in the laboratory the equivalent of much longer periods at field temperature.

The effects of salt concentration and of pH on sorption

All measurements of sorption by soil are made in the presence of some background electrolyte. This is true even if water is used as the medium because some ions will be desorbed from the soil. In most cases, measurements are made in the presence of a fairly dilute salt – such as 0.01 M calcium chloride. This means that differences in the concentration of the reactant itself have little effect on the activity coefficient because they are swamped by the background electrolyte. Practical considerations are that soil and solution are easier to separate in the presence of an electrolyte and that comparisons between soils are made in a uniform environment. However the measured value for sorption depends on the identity and the concentration of electrolyte used. Further, the magnitude and even the direction of the effect of electrolyte concentration depend on the pH (Figure S79). This figure shows that increasing the electrolyte concentration increases sorption of borate, selenite and phosphate at moderate to high pH but decreases it at low pH. We might also say that the effect of pH depends on the electrolyte used. This has been the source of some confusion about the effects of pH but it is also important in understanding the mechanisms involved (see later).

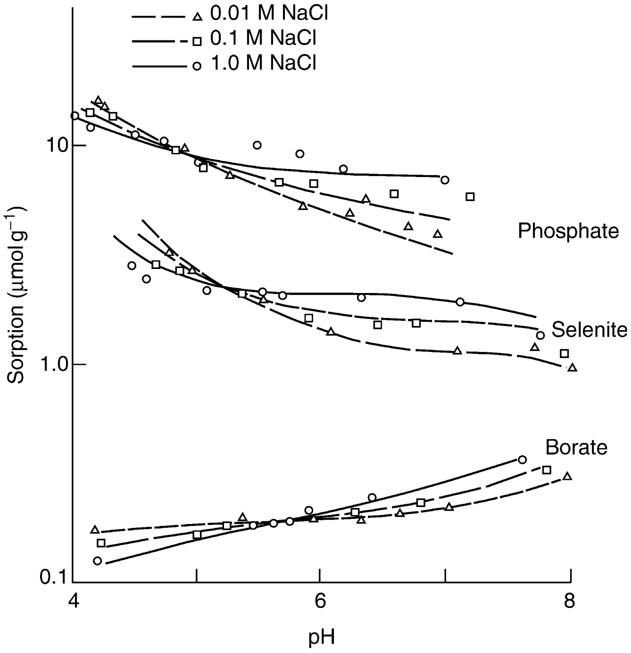


Figure S79 Comparison of the effects of pH and of background electrolyte concentration on the sorption of phosphate, selenite and borate by a soil. In each case, sorption was measured at a solution concentration of 100 mM. The lines were fit to the data using the mechanistic model described in the text and presented in detail in Barrow (1987) (from Barrow, 1989).

Despite the interaction with electrolyte concentration, some general statements may be made about the effects of pH on sorption. For most of the metal cations that react specifically with soil, sorption increases markedly with increases in pH. This is true for copper, zinc, cobalt, nickel, cadmium and manganese. An important exception is mercury. In the absence of chloride, there is gentle decease in sorption with increasing pH; in the presence of chloride, sorption increases at first then decreases (Barrow and Cox, 1992a). The behavior of the anions is more diverse. Molybdate sorption decreases sharply with increasing pH; fluoride sorption increases up to about pH 5.5, then decreases; sulfate and selenate both decrease;

borate increases and selenite decreases slightly. I have left phosphate until last because the effects are controversial. Partly this is because the effects of pH are small relative to those of say molybdate. The direction of the effect is therefore more sensitive to the conditions. When a dilute electrolyte with a monovalent cation is used, sorption is likely to decrease with increasing pH (Figure S79). When a more concentrated electrolyte, or a divalent cation is used, sorption may increase with increasing pH at least in part of the pH range. For more information on the several factors, which may influence the outcome of a particular experiment, see Barrow (1984).

The problems of desorption

In a typical experiment, sorption of a reactant might be induced by mixing soil with a solution containing the reactant for an arbitrary period – say 24 hours. Soil and solution would then be separated and desorption induced by adding a solution containing zero concentration of the reactant. A typical result is that the desorption limb does not follow the same path as the sorption limb (Figure S80). And a typical conclusion is that "adsorption was irreversible". This is an oxymoron – an impossible combination of words. The usual meaning of an irreversible reaction is that there is virtually no back reaction. The reaction therefore goes to completion. A good example is the oxidation of hydrogen to give water. But for an adsorption reaction – such as that represented by Equation (1) – there must be a back reaction. If this were not so, the reaction would go to completion; there would be no reactant left in solution; and we could not draw sorption curves. If *ad*sorption appears to be not reversible, then it is not adsorption – or at least, not only adsorption. This is one of the lines of evidence that leads us to argue that there is a slow reaction, which follows an initial adsorption reaction – and leads us to call the whole process sorption.

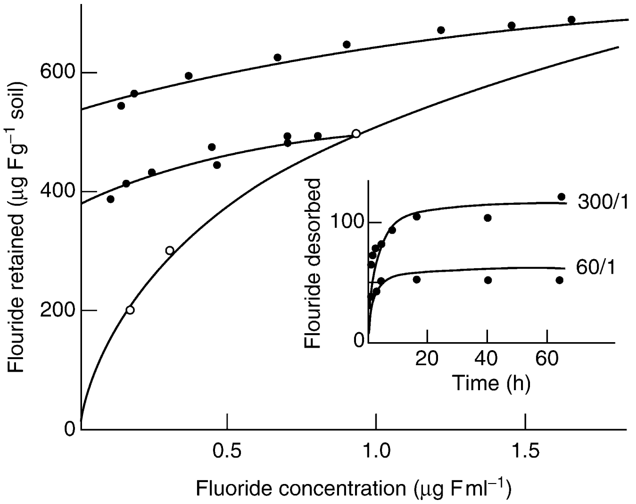


Figure S80 Sorption and desorption of fluoride from a soil. The soil had been incubated with fluoride for 4 days at 80 °C. *Open circles* indicate the concentration required to prevent both sorption and desorption – the null point concentration. The *line* for these points is therefore the sorption curve. *Closed circles* show desorption measured 40 hours after mixing samples of the soil with increasing volumes of 0.01 M calcium chloride. The *line* for these points is therefore the desorption curve at this time. The *inset* shows the rate of desorption at two solution : soil ratios. The *lines* are the output of a model fit to the rate of the sorption reaction (from Barrow, 1986).

The apparent irreversibility occurs because it has been assumed that equilibrium has been reached and this is seldom the case. Rather than thinking of sorption and desorption curves, we should be thinking of pathways across different parts of the time-concentration surface. If we define that surface by taking into account the rate of the reaction, the observed outcome can be explained (Barrow and Shaw, 1975, 1977). In simple terms, the slow reaction takes time to reverse. This is why the sorption and desorption limbs do not coincide.

If desorption involves the reversal of the slow reaction, we would expect that there would be an effect of temperature on the rate. I found (Barrow, 1979) that the activation energy for desorption was similar to that for sorption. For most chemical reactions, the activation energy for the forward reaction differs from that for the back reaction. That is, the product has a different energy content than the reactants. That this is apparently not the case for the slow reaction is an important clue to its nature.

Work with model systems

So far, this entry has described the sorption of a range of reactants with soil. Any explanation of these observations has to apply to all of them and it has to contain understanding of the reactions involved. As is not unusual in science, this understanding comes from study of simplified systems.

It has become clear that the variable charge components of soil are important in most of the reactions treated above. The variable charge components in soil include soil organic matter, the oxides (and hydroxides) of iron, aluminum, manganese and titanium, and the edges of clay minerals. The charge on organic matter varies with pH because there are many different functional groups with different dissociation characteristics. The charge on the other components varies for a different reason. Consider first the flat surfaces of the clay minerals. These are rather unusual crystal surfaces because the atoms on the surface have all their bonds satisfied. The atoms at the surface of most crystals cannot complete the pattern present in the body of the crystal. The metal atoms at the surface of oxides, and those at the edges of clay minerals attempt to complete their bonds by reacting with water molecules. These may, in turn, gain or lose protons so that their charge varies with pH – it is a pH dependent charge. However, the charge also varies as a result of reactions with reactants such as phosphate and the term variable charge is more general.

There has been much study of simplified systems containing just one oxide. Often this has been the iron oxide goethite (αFeOOH), which is one of the important reactants in many soils. Ideally, the advantages of such work are: a uniform homogeneous reactant can be studied and the same reactant can be studied in different laboratories; its charge can be measured and included in models; and the initial content of reacting ions (q) should be zero. These ideals are not always met. It is difficult to grow exactly the same goethite crystals even for successive batches in the same laboratory, and it is difficult to prevent the goethite reacting with carbon dioxide and even with silicates. Even so, such work has led to important understanding.

Crucial to this understanding is the assumption that the ions near the surface can be allocated to mean planes of adsorption. These planes are meant to be understood in terms of a time-averaged basis and to refer to the center of charge of the ion. As we move from the surface out into the bulk solution, the electric potential changes. The various adsorption planes therefore experience different potentials. Published models differ in the number of planes specified and in the way the reactions in each plane are written. Some models restrict the number of planes to which ions can be allocated. I prefer a model which permits such diverse ions as F^-, HPO_4^{2-}, Cl^-, and $ZnOH^+$ to reside in different planes and therefore to experience different electric potentials and different changes in potential with change in pH. Comparisons of the models can be found in Barrow (1985) and Barrow and Bowden (1987).

All models include terms such that the amount of reaction depends not only on the solution concentration of the reacting ion but also on the electric potential in the plane of adsorption – although the derivation of this relationship and the way that is specified differs between models. The model of Bowden et al. (1977) uses the surface activity function (a_{is}):

$$a_{\mathrm{is}} = \alpha\gamma c K_i \exp\left(-\frac{z\mathrm{F}\Psi}{\mathrm{R}T}\right) \tag{10}$$

where α is the proportion of the reactant present as the reacting species, γ is the activity coefficient, c is the total concentration, K_i is the binding constant of the reacting species i, z is the charge (including sign) on the reacting ion, and F is the Faraday. The surface activity function is used instead of the term for concentration in Equation (3). This concept is the key to the diverse behavior of the differing reactants and we need to consider the terms of Equation (10) in detail.

The term α is included because it is argued that reaction depends on specific ions in solution rather than the total concentration. Many of the important reactants with soil can be considered as weak acids. That is, they dissociate either within, or just outside, the normal range of soil pH. This means that there may be at least two different kinds of molecules present. There may also be ion pairs present – such as between metals and chloride. The various molecules do not have equal affinity for the surface – the value of K_i differs. It is the product αK_i that determines the relative importance of the species. This means that a species can be very important even if α is small provided K_{i} is large. In many cases, αK_i is much greater for one of the species than the others. This species therefore dominates the reaction. Why should one species in solution be more important than another? It depends on the nature of the bond with the surface. Thus for phosphate, the adsorbed ion links to the surface through two of its oxygen atoms. No matter which pathway is postulated for the formation of these bonds, the amount of reaction can be related to the concentration of the divalent ion in solution (Barrow, 1999).

Within the bracket of Equation (10), the z term adjusts the direction of the effect of the exponential term so that, if ions are reacting with a like-charged surface, the contents of the bracket are negative. The exponential term then has a value less than unity. Thus, reaction with a like-charged surface can occur – provided that the product of $\alpha K_i c$ is large enough to counter-balance the small value of the exponential term. The value of the term for electric potential Ψ varies with pH. Depending on the properties of the particular surface, Ψ will tend to be positive at low pH and negative at high pH. However, the rate of change with pH will depend on how closely the adsorbing ion approaches the surface. The closer the adsorption plane to the surface, the steeper the change in Ψ with pH. Reaction between an ion and a surface usually changes the charge on the surface and thus the value of Ψ. This introduces a feedback effect that is important in determining the shape of the adsorption curves on oxides.

Changes in charge with sorption

When an ion reacts with a variable charge surface, the charge on the ion must be balanced. There are two possibilities. One is that some of the surface charge will be displaced. For example, reaction with an anion would displace hydroxyl ions and reaction with a cation would displace protons. If this were the only mechanism, there would be no change in surface charge but there would be changes in the pH of the solution. The other possibility is that the surface charge would change. If a cation were adsorbing, the surface would become more positive; if an anion, more negative. These changes would be balanced by changes in ions in the outer layers – in a sodium chloride solution, by gains or losses in the sodium and chloride ions. There would be no changes in the pH of the solution.

The balance between these two mechanisms depends a great deal on the reactants. For reacting species for which the plane of adsorption is close to the surface, displacement of surface charge will predominate. Thus the divalent metals tend to displace protons and so decrease the pH – an important factor in the shapes of their sorption curves. Similarly fluoride tends to displace hydroxyls and raise the pH. This is used as a quick test in rating soils for sorption capacity. For a given reactant, the balance between the two options depends on such factors as the initial concentration of the reactants, the pH and the ionic strength (Bolan and Barrow, 1984). This means that it is seldom possible to write a simple stoichiometric chemical equation for the reaction because the stoichiometric relations vary with the conditions and the extent of the reaction.

The rate of reaction in model systems

The initial adsorption reaction may be considered as “site plus ion gives product”. That is, a second order forward reaction opposed by a first order back reaction. However, it is important to remember that it involves ions approaching and leaving charged surfaces and the electric potential of the surface has an effect on the rate of the adsorption reaction. It has been argued that the rate of adsorption of phosphate will decrease as the pH rises because of the slowing down due to the more negative potential (Barrow et al., 1981). Recent work supports this (Strauss et al., 1997b).

Although very interesting from a theoretical point of view, the rate of the initial adsorption reaction is of little practical importance. Of much greater practical importance is the slow reaction that can follow adsorption. Perhaps the clearest evidence that the slow reaction can also occur in model systems was provided by Brümmer et al. (1988) who showed that sorption of nickel, zinc and cadmium by goethite continued for many weeks (Figure S81). Dissolution studies and detailed modeling all showed that this was consistent with an initial adsorption reaction followed by a diffusive penetration of the surface (Brümmer et al., 1988; Barrow et al., 1989). It is not difficult to envisage a slow diffusion process in which metal ions on the surface change places with iron atoms in the bulk of the crystal and so slowly move inwards. Whether this is the mechanism or whether crystal faults such as vacancies or micropores are required is not yet known for metal ions. Such processes are fairly slow and, because they require atoms to jump fairly high-energy barriers, has a large activation energy. There is therefore a large effect of temperature (Figure S81).

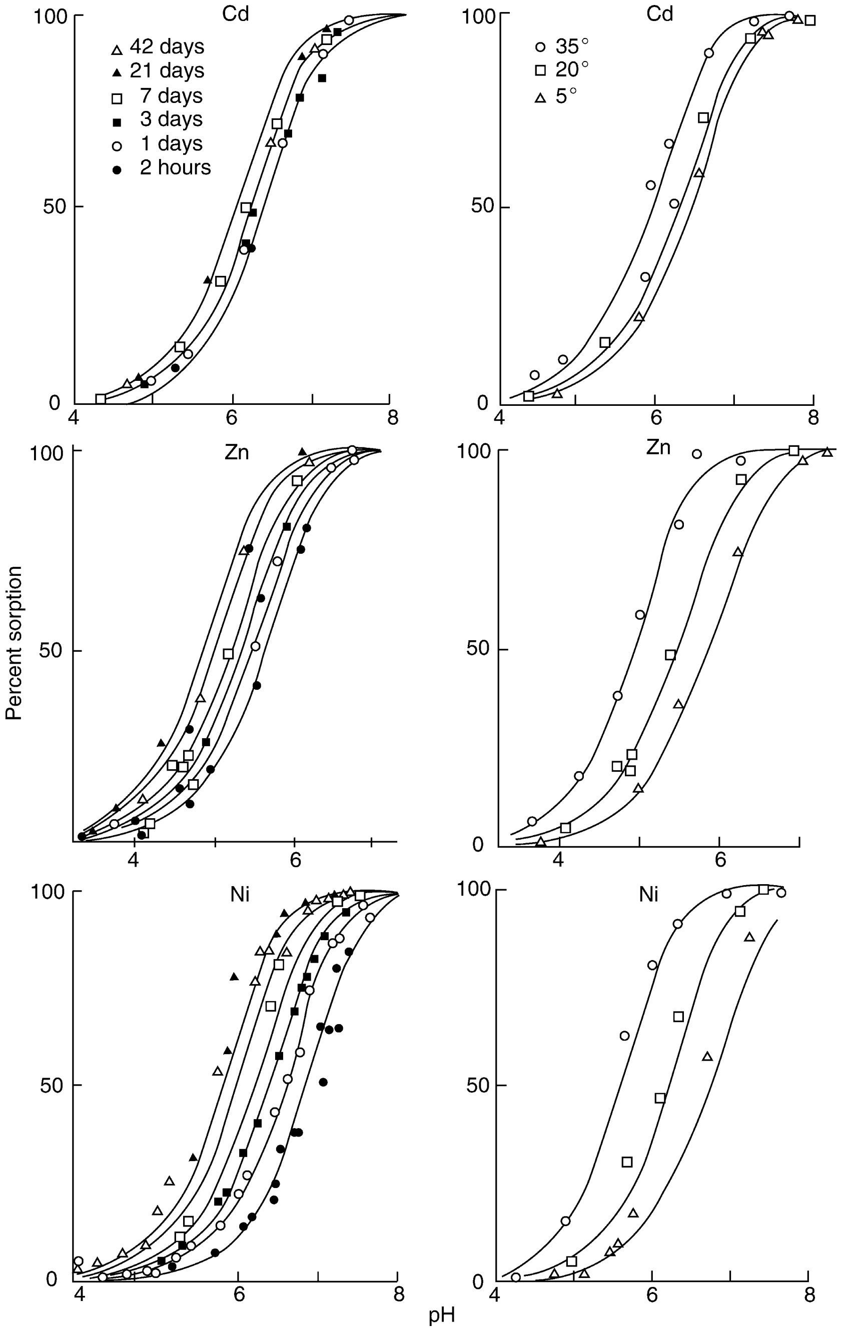


Figure S81 Effect of time, temperature and pH on the sorption of cadmium, zinc and nickel by goethite. The *left hand side* shows the effect of increasing periods at 20 °C; the *right hand side*, the effect the indicated temperatures for 7 days. The *lines* were derived from a model. Because the rate for cadmium was much slower, intermediate lines have been omitted (from Barrow et al., 1989).

For anions, the picture has, until recently, been less clear. However, Strauss et al. (1997a,b) have shown that the extent of the slow reaction between phosphate and goethite depended on the crystallinity of the goethite. For samples, which were well crystallized, there was virtually no slow reaction but for poorly crystallized samples the reaction continued for weeks. The mechanism in this case appears to be slow penetration of the spaces between the crystal domains.

Applying models to soil

It would be simplistic to think that theories developed for model systems could be applied to soils without modification. It is obvious that the metal oxides in soil were formed under impure conditions. The iron oxides, for example, contain variable amounts of aluminum, silicon and even phosphorus. Further, their crystallinity is far from perfect, and more than one kind of variable-charge surface may participate in reaction with a given ion. The most important modification of models is to include a measure of the heterogeneity of the reacting surfaces.

There are two ways in which Equation (10) could be modified to include heterogeneity: we could assume that heterogeneity was either in the values of the electric potential Ψ or in the binding constant K_i. As the terms occur as products, it is mathematically immaterial which assumption is made. There is independent evidence that there is heterogeneity in the charge – for example, positive and negative charges can co-exist in a soil. Hence it is sensible to allocate the heterogeneity to the term for electric potential – but to remember that this is a simplification. The procedure is to assume that there is a distribution of values for Ψ. The normal distribution is both convenient and effective. This distribution of sites is then divided into a number of slices and each slice is assumed to be uniform and characterized by its midpoint. Within each slice, ions are assumed to adsorb, and adsorption is followed by a slow diffusion into the adsorbing particle. The amount of adsorption within each slice is calculated by using the surface activity function, rather than concentration, in a Langmuir Equation and the total adsorption is calculated by summing the adsorption in all the slices. The total amount of penetrated material is similarly obtained by summing the slices. Details of this model and of the appropriate computer programs are given in Barrow (1987).

This model is extraordinarily effective in simulating all of the observed sorption behavior. The remainder of this entry is concerned with demonstrating this.

Simulating sorption curves for soil

The assumption of a normal distribution of values of Ψ produces, on a log scale, the required gentle curve for plots of sorption versus concentration (Figure S82). Further, as the solution concentration becomes very small, the log plots approach unit slope – that is, sorption is linear at low concentrations. Differences in slope are largely explained by differences in the width of the distribution. A narrow distribution, described by a small value for the standard deviation, gives a steep slope. Differences in slope are also partly due to differences in the extent to which sorption affects the charge on the surface. A large change in charge causes a large feedback via the Ψ term (Figure S82).

Simulating the effects of time and temperature for soil

Diffusion is assumed to be very slow so that the depth of penetration is small compared to the reacting area. Hence the amount penetrated might be expected to be proportional to the square root of time. However, this relation should only be expected if the source concentration is constant. As the diffusion proceeds, the concentration in solution decreases. Consequently the concentration of adsorbed reactant decreases and as this is the driving concentration for the diffusion step, diffusion slows. Nevertheless, Equation (7) shows that, when the concentration is held constant, sorption is proportional to a small fractional power of time – rather than to time raised to the power 0.5. There are three reasons for this. One is the assumption of heterogeneity. This gives rise to a range of surface concentrations and so to a range of rates which together sum to give a rate proportional to a lower power of time. A second reason might be called "electrostatic drag". Sorption changes the charge and therefore the value of ψ. This, in turn, decreases the concentration of adsorbed reactant and thus the rate of diffusion. The third reason is that we are not seeing the pure kinetics of diffusion. Diffusion is preceded by an adsorption reaction. This takes the locus of the point describing the progress of sorption to a fairly high value on a plot of log sorption versus log time and subsequent movement cannot possibly show a slope of 0.5.

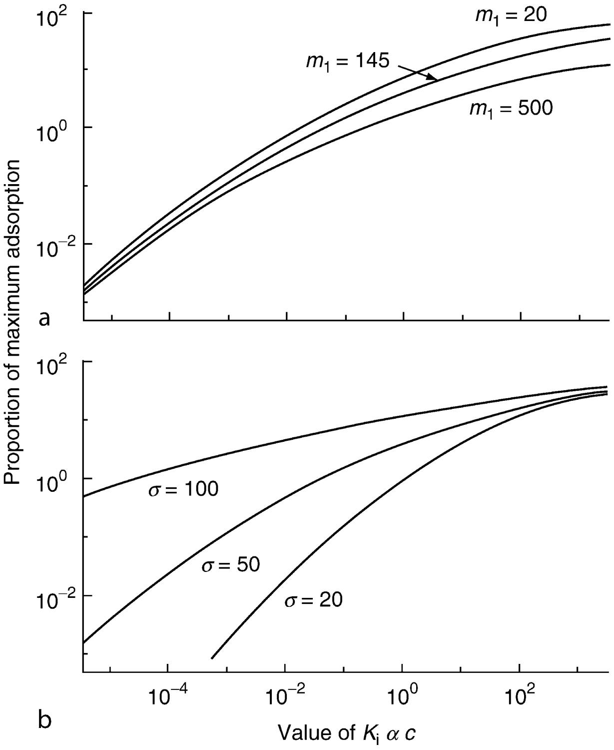


Figure S82 Some sorption curves generated using the model to show the shapes of the curves and the effects of some of the parameters. In the top graph, m_1 is the parameter, which controls the amount of electric feedback as a result of sorption. Large values mimic a large electric feedback and so increase the curvature. The values for σ in the lower graph indicate the standard deviation – that is, the spread of values. Small values of σ give steeper curves (from Barrow, 1987).

There is a large effect of temperature on the rate because the activation energy for diffusion is large. Figure S83 shows that the model can closely simulate the observed effects of both time and temperature on sorption.

Although many reactants show similar effects of time and temperature and can be modeled equally well, it does not follow that the mechanism of diffusion is exactly the same in all cases. It is not difficult to accept that metal atoms could penetrate adsorbing metal oxides or that fluoride could exchange places with hydroxyl groups. The difficulty is with large molecules such as molybdate, phosphate and selenite. It is possible that many oxide particles in soil consist of very small crystals with very thin layers of silicate or phosphate between them. Such a structure could provide a pathway for diffusion.

Explaining the interaction between pH and salt concentration

The interaction between pH and salt occurs *because* there is an initial adsorption reaction on a variable charge surface. An increase in salt concentration increases the number of counter

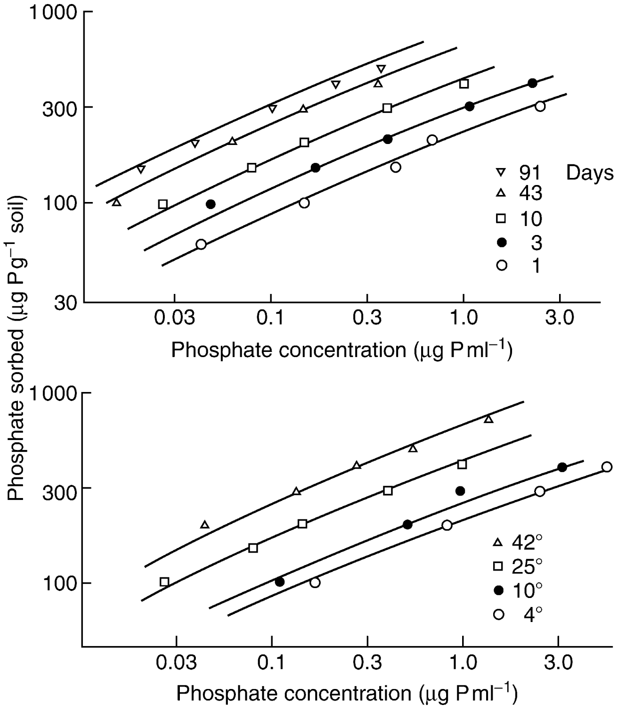


Figure S83 Modeled and observed effects of time and of temperature on phosphate sorption by a soil (redrawn from Barrow, 1983a).

ions close to the surface and therefore changes the relation between potential and distance from the surface. For a given plane of adsorption, it decreases the absolute value of the electric potential. When reaction is with a negatively charged surface, the potential becomes less negative and sorption of anions increases. A convenient – though less precise – way of thinking about this is that an increase in the cation concentration near a negatively charged surface makes it easier for anions to react with the surface. The corollary is, when increasing salt concentration increases sorption of anions, the reacting surface must be negatively charged. By a similar argument, when sorption of anions is decreased by an increase in salt concentration, the reacting surface is positively charged. The results in Figure S79 therefore show that reaction was with a negative surface at medium to high pH and with a positive surface at low pH – that is, it was with a variable charge surface.

If the surface is positively charged at low pH and negatively charged at medium to high pH, it follows that there must be a point of zero charge. In the context of Figure S79 it is more appropriate to speak of a point of zero mean potential in the adsorption plane. This is the mean potential *of the occupied sites* not of the whole soil. Close inspection of Figure S79 will show that this point occurs at a different pH for each reactant. This has implications for the assumption that charge is heterogeneous. It occurs because small amounts of sorption of anions are restricted to the most-positive tail of the distribution. It requires a high pH before the occupied sites in this tail have mean potential of zero. This is discussed further in Barrow and Ellis (1986) and Barrow (1989).

Explaining the effects of pH on cation sorption

In solution, the divalent ions of copper, zinc, cobalt, nickel, cadmium, manganese and mercury hydrolyze to varying extents. We can view this in two ways. One way is to note that the ions tend to be surrounded by six water molecules arranged in an octahedron. One (or more) of these water molecules may lose a proton:

$$\mathrm{M(H_2O)_6^{2+} \rightleftharpoons M(H_2O)_5OH^+ + H^+}$$

In this view, the divalent ions are acids. However, for all except mercury (for which the pK is near 3), they are weak acids with the pK ranging from about 8 to about 10. This means that, at normal soil pH values, the proportion of monovalent ions is very small – but increases ten-fold for each unit increase in pH. We can then argue that disturbance in the octahedral group of water molecules caused by the reaction increases the probability that a collision with a surface site will result in a reaction product. That is, ions, which are prone to hydrolyze, have a large value for the binding constant.

Alternatively, we can view the reaction as an association with hydroxyl ions:

$$\mathrm{M^{2+} + OH^- \rightleftharpoons MOH^+}$$

We then find that the greater the affinity for OH$^-$ ions, the greater the affinity for the surface sites on oxides (Dzombak and Morel, 1990). As the link to the surface site is via an O atom, this relation could reasonably be regarded as causal. These two views are thus merely two ways of describing the same phenomenon.

Similarly, there are two ways of looking at the effects of pH on individual ions. These hinge on whether the adsorbed ion is considered to be present as bound to one or to two surface sites. If it is bound to one site, the mean center of charge is not very close to that of the surface and so the change of electrical potential (Ψ) with changing pH is not very great. However, the concentration of the reacting monovalent ion increases ten-fold per unit increase in pH. These effects are in the same direction and so there is a large increase in sorption with increasing pH. If, on the other hand, the reacting ion is bound to two surface sites, the mean center of charge is closer to the surface. There is therefore a greater change in electric potential with increasing pH and this effect is sufficient to explain the increase in sorption with increasing pH. For much data it is difficult to discriminate between these two explanations. However, it was shown by Barrow and Whelan (1998) that for sorption of Cd, Zn, Ni and Co by soil the effects were too small to be the sorption of monovalent ions and must therefore be due to reaction with divalent ions.

Mercury differs from the other metals because it is a somewhat stronger acid with pK_1 and pK_2 both near 3. Again two explanations can be used for the effects of pH on sorption. Consider the case in which there is a single link to the surface. In the normal range of soil pH, the concentration of $\mathrm{Hg(H_2O)_5OH^+}$ *decreases* ten-fold for each unit increase in pH. When reaction is with a variable charge surface, this decrease is *opposed* by the decrease in the electric potential Ψ. Because a monovalent ion is involved, the α term is more powerful than the Ψ term and the net effect on adsorption is a small decrease with increasing pH (Figure S84). Now consider the case in which there is a double link to the surface.

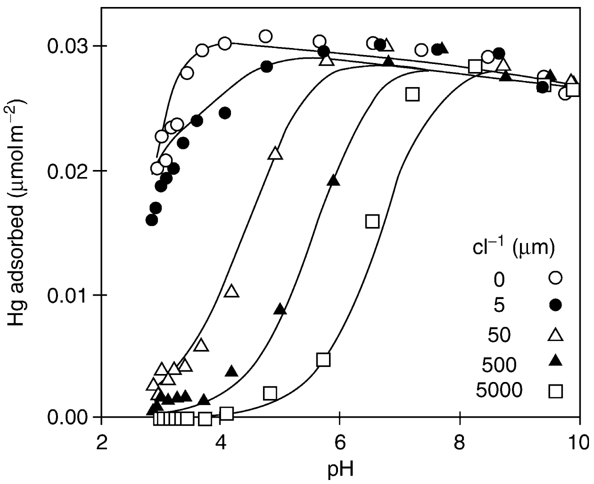


Figure S84 Modeled and observed effects of pH and of chloride concentration on mercury sorption by goethite (from Barrow and Cox, 1992b).

Because the two p*K*s are so close, the concentration of divalent Hg ions decreases almost 100-fold for unit increase in pH. Similarly, this is opposed by the decrease in electric potential but this effect is larger than for the monovalent ions because the mean position of the charge is closer to the surface and because the ion is divalent. Hence this mechanism can also explain the slight decrease in sorption with increasing pH. Chloride ions have a strong affinity for mercury and form complexes especially at low pH. As a result, in the presence of chloride, the concentration of the free mercury ions, and the amount of mercury sorption, often increase with increasing pH. In soil, sorption of mercury is even more complicated because mercury forms complexes with substances in solution giving sigmoid sorption curves (Barrow and Cox, 1992a). Nevertheless, sorption is again explainable for much of the pH range by the proportion present as the monovalent ion.

Explaining the effects of pH on anion sorption

The effects of pH on anion sorption can be explained using the same principles applied to cation adsorption. Again, the factors that matter are the ions present in the solution phase and the change in the potential of the surface with changes in pH. An important feature is that sizes of the ions differ. It ranges from small ions such as F^- to larger oxy-anions such as phosphate. It would be reasonable to assume that the charge on such ions might be sited at different mean distances from the surface. That is, we could allocate a mean position to this charge. Recently, Hiemstra and Van Riemsdijk (1996) have proposed a more sophisticated approach in which the charge on the ion is distributed between two planes – one close to the surface, one a little further away. The outcome is somewhat similar in that this approach, in effect, varies the mean position of the charge. Consider now some important anions starting with fluoride.

The pK_1 of hydrofluoric acid is below the range of soil pH and it might be expected that the main fluoride species present would be F^-. However, fluoride forms strong bonds with aluminum. In the presence of an aluminum oxide, or of soil, below about pH 5.5 most of the fluoride in solution is present as complexes with aluminum. The other important property of the fluoride ion is that it is about the same size as a hydroxyl ion. It can therefore replace a surface hydroxyl so that its adsorption plane is very close to the surface. It therefore experiences a marked change in Ψ with change in pH. Thus, in the absence of a source of aluminum, fluoride sorption at a given total concentration of F in solution decreases markedly with increasing pH but in the presence of a source of aluminum it increases up to about pH 5.5 and then decreases.

Sulfate and selenate are also fully dissociated at soil pH values but both differ from fluoride in that the adsorption plane is somewhat further from the surface. Using the terminology of Hiemstra and Van Riemdijk (1996), the oxygen atoms cause a large proportion of the charge to be distributed to a plane some distance from the surface. Hence they do not experience such a large change in Ψ with increasing pH. Further, complexes with aluminum are not as strong. The net effect is a moderate decrease in sorption with increasing pH.

Boric acid is fairly weak with its pK_1 at about 9. Therefore, in the normal range of soil pH, the proportion present as the monovalent borate ion increases 10-fold for unit increase in pH. The effects of α and of Ψ therefore oppose each other. Because the ion is monovalent and z is therefore unity, the effects of α are slightly more important and sorption increases with increasing pH.

Selenious acid is a diprotic acid with pK_1 at 2.7 and pK_2 at 8.5 in very dilute solution. Hence, in the range of soil pH values, there are two main species present: $HSeO_3^-$ and SeO_3^{2-}. The effects of pH can be readily explained if it is assumed the SeO_3^{2-} species dominates sorption. We can argue that, because it is smaller ion than selenate, the mean position of the charge is closer to the surface – or we can argue that, because it has one fewer O atom, rather more of the charge is distributed to the surface – the outcome is the same: a large decrease in potential with increasing pH. Like the borate ion, its proportion increases ten-fold for each unit increase in pH but the value for z is two. This means that the Ψ term is slightly more important than the α term and sorption decreases.

There are some similarities between mercury and molybdate in that the pK_1 and pK_2 for molybdic acid are close together and below the normal range of soil pH. The concentration of $HMoO_4^-$ therefore decreases 10-fold with unit increase in pH. There does not appear to have been a detailed study on molybdate to assess the relative importance of the $HMoO_4^-$ and the MoO_4^{2-} ions. However, the more rapid decline in sorption with increasing pH than occurs for sulfate suggests that it is necessary to invoke the decreasing concentration of the $HMoO_4^-$ ion with increasing pH, plus the increasingly negative potential, to explain the effects of pH.

The behavior of phosphate has been left until last because it is important to see it in the context of the other reactants – rather than to invent special theories for it. Phosphoric acid is triprotic but the third dissociation is well beyond the range of soil pH. The species of interest are therefore $H_2PO_4^-$ and HPO_4^{2-}. Like selenite, the proportion of the divalent ion increases ten-fold for each unit increase in pH up to the pK_2 – which is about 7 in a soil solution. Figure S79 shows that the behavior of phosphate is similar to that of selenite – and the explanation is analogous. Thus, when phosphate sorption is seen in the context of the other reactants, its behavior is easy to comprehend.

Desorption

It was stated earlier that desorption can be described if the rate of the reaction is taken into account. Of course, the mechanistic model also describes the rate of the reaction – but with a proposed mechanism included in the model. As would be expected, it reproduces the observed desorption (Figure S80). All that is added is the proposed mechanism. Desorption is slow because reverse diffusion is slow. And the longer the forward reaction has continued, the further the reactant has penetrated – and the slower the diffusive return.

Concluding comments

Until fairly recently, sorption of ions by soils seemed to be a confusing assembly of unrelated facts – with differing effects observed under different conditions and few apparent rules. There are two reasons why we are increasingly able to make some order from this confusion. One is that soil scientists have looked at a wide range of reactants – anions, cations, soils, clays, and oxides. As Kipling (almost) said: "*and what should they know of phosphate who only phosphate know.*" The other is that we have followed the common scientific track of looking at simpler systems and then taking the understanding gained to more complex systems. We can understand those complex systems if we assume: that ions react with variable charge surfaces, that the surfaces are heterogeneous, and that the initial adsorption reaction is followed by a diffusive penetration of the surface. We can explain all of the observations and, what is more, we can do this precisely. The ready access to computers means that it is no longer sufficient to express such hypotheses in general terms. They can, and should, be expressed as mathematical models and tested quantitatively against data.

N. J. Barrow

Bibliography

Allen, D.G., Barrow, N.J., and Bolland, M.D.A., 2001. Comparing simple methods for measuring phosphate sorption by soils. *Aust. J. Soil Res.*, **39**: 1433–1422.

Barrow, N.J., 1978. The description of phosphate adsorption curves. *J. Soil Sci.*, **29**: 447–462.

Barrow, N.J., 1979. Three effects of temperature on the reactions between inorganic phosphate and soil. *J. Soil Sci.*, **30**: 271–279.

Barrow, N.J., 1983a. A mechanistic model for describing the sorption and desorption of phosphate by soil. *J. Soil Sci.*, **34**: 733–750.

Barrow, N.J., 1983b. A discussion of the methods for measuring the rate of reaction between soil and phosphate. *Fert. Res.*, **4**: 51–61.

Barrow, N.J., 1984. Modeling the effects of pH on phosphate sorption by soils. *J. Soil Sci.*, **35**: 283–297.

Barrow, N.J., 1985. Reactions of anions and cations with variable-charge soils. *Adv. Agron.*, **38**: 183–230.

Barrow, N.J., 1986. Testing a mechanistic model. I. The effects of time and temperature on the reaction of fluoride and molybdate with a soil. *J.Soil Sci.*, **37**: 267–275.

Barrow, N.J., 1987. *Reactions with Variable-Charge Soils.* Dordrecht: Martinus Nijhoff.

Barrow, N.J., 1989. The reaction of plant nutrients and pollutants with soil. *Aust. J. Soil Res.*, **27**: 475–492.

Barrow, N.J., 1992. A brief description of the effects of temperature on the reaction of inorganic ions with soil. *J. Soil Sci.*, **43**: 305–312.

Barrow, N.J., 1999. The four laws of soil chemistry: the Leeper lecture 1998. *Aust. J. Soil Res.*, **37**: 787–829.

Barrow, N.J., 2000. Towards a single-point method for measuring phosphate sorption by soils. *Aust. J. Soil Res.*, **38**: 1099–1113.

Barrow, N.J., and Bowden, J.W., 1987. A comparison of methods for describing the adsorption of anions on a variable charge mineral surface. *J. Colloid Interface Sci.*, **119**: 236–250.

Barrow, N.J., and Cox, V.C., 1992a. The effects of pH and chloride concentration on mercury sorption. I. By goethite. *J. Soil Sci.*, **43**: 295–304.

Barrow, N.J., and Cox, V.C., 1992b. The effects of pH and chloride concentration on mercury sorption. II. By a soil. *J. Soil Sci.*, **43**: 305–312.

Barrow, N.J., and Ellis, A.S., 1986. Testing a mechanistic model. V. The points of zero salt effect for phosphate retention, for zinc retention and for acid/alkali titration. *J. Soil Sci.*, **37**: 303–310.

Barrow, N.J., and Shaw, T.C., 1975. The slow reactions between soil and anions: 5. Effects of period of prior contact on the desorption of phosphate from soils. *Soil Sci.*, **119**: 311–320.

Barrow, N.J., and Shaw, T.C., 1977. The slow reactions between soil and anions: 6. Effect of time and temperature of contact on fluoride. *Soil Sci.*, **124**: 265–277.

Barrow, N.J., and Shaw, T.C., 1979. Effects of solution: soil ratio and vigour of shaking on the rate of phosphate adsorption by soil. *J. Soil Sci.*, **330**: 67–76.

Barrow, N.J., and Whelan, B.R., 1989. Testing a mechanistic model. VII The effects of pH and of electrolyte concentration on the reaction of selenite and selenate with a soil. *J. Soil Sci.*, **40**: 17–28.

Barrow, N.J., and Whelan, B.R., 1998. Comparing the effects of pH on the sorption of metals by soil, by goethite, and on uptake by plants. *Eur. J. Soil Sci.*, **49**: 683–692.

Barrow, N.J., Madrid, L., and Posner, A.M., 1981. A partial model for the rate of adsorption and desorption of phosphate by goethite. *J. Soil Sci.*, **32**: 399–407.

Barrow, N.J., Gerth, J., and Brümmer, G.W., 1989. Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. II. Modeling the extent and rate of reaction. *J. Soil Sci.*, **40**: 437–450.

Bolan, N.S., and Barrow, N.J., 1984. Modeling the effect of adsorption of phosphate and other ions on the surface charge of variable charge oxides. *J. Soil Sci.*, **35**: 273–281.

Bowden, J.W., Posner, A.M., and Quirk, J.P., 1977. Ionic adsorption on variable charge mineral surfaces. Theoretical charge development and titration curves. *Aust. J. Soil Res.*, **15**: 121–136.

Brümmer, G.W., Gerth, J., and Tiller, K.G., 1988. Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. I Adsorption and diffusion of metals. *J. Soil Sci.*, **40**: 437–450.

Burkitt, L.L., Moody, P.W., Gourley, C.J.P., Hannah, M.C., 2002. A simple phosphorus buffering index of Australian soils. *Aust. J. Soil Res.*, **40**: 497–513.

Dzombak, D.A., and Morel, F.M.M., 1990. Surface Complex Modeling, Hydrous Ferric Oxide. New York: Wiley.

Elprince, A.M., and Sposito, G., 1981. Thermodynamic derivation of equations of the Langmuir type for ion equilibria in soils. *Soil Sci. Soc. Am. J.*, **45**: 277–282.

Gunary, D., 1970. A new adsorption isotherm for phosphate in soil. *J. Soil Sci.*, **21**: 72–77.

Harter, R.D., 1984. Curve-fit errors in Langmuir adsorption maxima. *Soil Sci. Soc. Am. J.*, **48**: 749–752.

Harter, R.D., and Baker, D.E., 1977. Applications and misapplications of the Langmuir equation to soil adsorption phenomena. *Soil Sci. Soc. Am. J.*, **41**: 1077–1080.

Hiemstra, T., and Riemsdijk, Van W.H., 1996. A surface structural approach to ion adsorption: the charge distribution (CD) model. *J. Colloid Interface Sci.*, **179**: 488–508.

Jarvis, S.C., 1981. Copper sorption by soils at low concentration in relation to uptake by plants. *J. Soil Sci.*, **32**: 257–269.

Kinniburgh, D.J., 1986. General purpose adsorption isotherms. *Environ. Sci. Technol.*, **40**: 895–904.

McBain, J.W., 1909. *'Sorption of gases'* Quoted in Glasstone, S., 1959. *Textbook of Physical Chemistry*, 2 nd edn. New Jersey: Van Nostrand.

McLaren, R.G., Williams, J.G., and Swift, R.S., 1983. The adsorption of copper by soil samples from Scotland at low equilibrium solution concentrations. *Geoderma*, **31**: 97–106.

Neal, R.H., and Sposito, G., 1986. Effects of soluble organic matter and sewage sludge amendments on cadmium sorption by soils at low cadmium concentrations. *Soil Sci.*, **142**: 164–172.

Posner, A.M., and Bowden, J.W., 1980. Adsorption isotherms: should they be split? *J. Soil Sci.*, **31**: 1–10.

Ratkowsky, D.A., 1986. A statistical study of seven curves for describing the sorption of phosphate by soil. *J. Soil Sci.*, **37**: 183–189.

Shainberg, I., and Kemper, W.D., 1966. Hydration status of adsorbed cations. *Proc. Soil Sci. Soc. Am.*, **30**: 707–713.

Sibbesen, E., 1981. Some new equations to describe phosphate sorption by soils. *J. Soil Sci.*, **32**: 67–74.

Sposito, G., 1980. Derivation of the Freundlich equation for ion exchange reactions in soils. *Soil Sci. Soc. Am. J.*, **44**: 652–654.
Sposito, G., 1982. On the use of the Langmuir equation in the interpretation of "adsorption" phenomena: II The "two-surface" Langmuir equation. *Soil Sci. Soc. Am. J.*, **46**: 1147–1152.
Sposito, G., 1984. Surface Chemistry of Soil. New York: Oxford University Press.
Strauss, R., Brümmer, G.W., and Barrow, N.J., 1997a. Effects of crystallinity of goethite I. Preparation and properties of goethites of differing crystallinity. *Eur. J. Soil Sci.* **48**: 87–99.
Strauss, R., Brümmer, G.W., and Barrow, N.J., 1997b. Effects of crystallinity of goethite II. Rates of sorption and desorption of phosphate. *Eur. J. Soil Sci.* **48**: 101–114.

Cross-reference

Exchange Phenomena

SPHEROIDAL

The condition of being approximately spherical. A type of weathering by which a block of rock defined in three dimensions by joint, bedding or other planes, is weathered inwards from the defining planes in such a way that the original form of the block becomes gradually spheroidal, with a succession of weathered zones concentric with the center of the spheroid. See Figure S85.

Figure S85 Spheroidal weathering of rock (basalt, Plateau de Gergovie, central France).

STAGNOSOLS

Stagnosols are one of two new Reference Soil Groups (the other being Technosols) officially announced at the 18th World Congress of Soil Science in Philadelphia (IUSS Working Group WRB, 2006). The new group includes soils that were originally part of stagnic units of other Reference Soil Groups (FAO, 2001). Stagnosols have mottles in the topsoil and subsoil, accompanied in some cases by concretions and/or bleaching. These redoximorphic features are evidence of surface-water saturation of a temporary nature, the result of a perched water table. Stagnosols differ from Planosols in that the perched water table does not result from an abrupt textural change.

Connotation. From Latin *stagnare*, to flood.

Synonyms. Commonly called pseudogley in many national classification systems. In the U.S. Soil Taxonomy, many classify as aqualfs, aquults, aquents, aquepts and aquolls.

Definition. Mottling (stagnic color pattern) and/or a bleached horizon make up 50% of the volume within 50 cm of the mineral soil surface; indicating reducing conditions for some time during the year. There is no abrupt textural change below the mottled or bleached horizon.

Parent material. Almost any unconsolidated material such as physically disintegrating bedrock, and from coarse to fine sediments of a variety of origins (glacial, aeolian, water-borne).

Environment. Found in temperate to sub-tropical regions, under humid to perhumid climatic conditions, in depressions where water temporarily pools during wet periods, in a level to gently sloping landscape.

Distribution. There are about 150–200 million ha of Stagnosols on the land surface of the globe, mostly in the humid to perhumid temperate regions of Western and Central Europe, North America, southeast Australia, and Argentina. In these regions they are commonly associated with Luvisols and with silty to clayey Cambisols and Umbrisols. Under similar climatic regimes in subtropical regions, stagnosols are associated with Acrisols and Planosols.

Profile development. Similar to the common soils of humid cool to hot climates, but with pronounced mottling in the upper solum. Bleaching, if present, may extend to the soil surface.

Origin. The distinctive mottling and/or bleaching of the upper solum of a Stagnosol are caused by reduction caused by water saturation, followed by oxidation once the saturated region has drained. The process is cyclic, normally being repeated on a yearly basis. The zone of water-saturation is occasioned by a slowly permeable subsurface horizon rather than an abrupt textural change as in Planosols. A perched water table is the result and below it, the soil is oxidized. The combination of an upper reduced zone (bleached colors and mottles) and a lower oxidized zone (redder and browner colors) constitute "stagnic properties" showing a "stagnic color pattern".

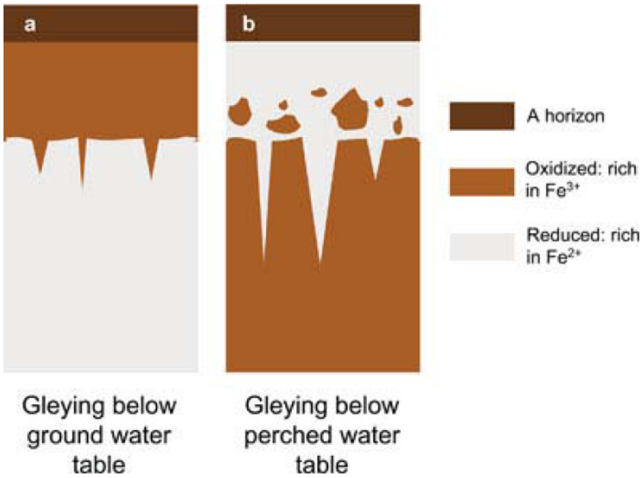


Figure S86 Schematic representation of the difference between gleyic properties (a), and stagnic properties (b). The profiles are about 1 meter in depth (redrawn from FAO, 2001).

They are in contrast to the gleyic pattern, which is associated with movement of the groundwater table, and which has the oxidized part of the soil overlying the reduced (gleyed) part (Figure S86).

Use. Stagnosols are not highly leached, so tend to be inherently fertile. However, during periods of water saturation, the root zone will be deficient in oxygen, so that the agricultural usefulness of the Stagnosols may be limited. Draining, possibly accompanied by deep plowing to loosen up dense subsoil, improves productivity.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

IUSS Working Group WRB, 2006. World reference base for soil resources 2006, 2nd edn. World Soil Resources Reports No. 103. Rome: FAO, 128 pp.

STONY

Said of a soil containing a high proportion of stones, which, if rounded, are taken to be rock fragments between 20 and 60 cm across, and if elongated, rock fragments between 38 and 60 cm in length. Stony soils are difficult and in some cases impossible to till.

STRATIFICATION

The state of being arranged in a succession of layers or strata. Mostly used in this sense in geology, though also used occasionally to describe layering in soil, though if the layering in question is produced by pedogenic processes, horizonation is the appropriate term.

STRUCTURE

The overall architecture of a soil defined by the assemblage of structural units, which it contains. The way the soil is organized in terms of the physically definable parts within it. Compare *Texture*.

SUBSOIL

A term used imprecisely to mean any part of the soil below the surface layer or layers. May be used more precisely to refer to the solum below the A horizon.

SULFUR TRANSFORMATIONS AND FLUXES

Importance of sulfur

Sulfur is an important macronutrient necessary for plant growth. Deficiencies of this element have been found throughout the world, especially in those regions distant from atmospheric sources of sulfur with marine or anthropogenic origins. For agronomic systems, deficiencies vary among crops with legumes and crucifers having notably high sulfur requirements. Deficiencies may be exacerbated with the application of low sulfur, but high nitrogen and phosphorus fertilizers (Duke and Reisenauer, 1986). For forests, sulfur availability in soil does not generally limit production. Deficiencies have, however, been found, especially where atmospheric inputs are low or where there is excess nitrogen. Examples of such forests include *Pinus radiata* in Australia and *Pseudotsuga menziesii* (Douglas-fir) fertilized with nitrogen along the Pacific Coast of North America (Mitchell et al., 1992a).

Since the mid-1970s there has been increasing attention on sulfur due to its major role in contributing to "acidic deposition." This source of sulfur, which is primarily derived from the combustion of fossil fuels and smelting of ores, may result in inputs that ranged from more than 120 kg S ha^{-1} yr^{-1} at highly polluted sites in Europe (Erkenberg, 1989) to less than 1 kg S ha^{-1} yr^{-1} in remote sites such as Australia (Mitchell et al., 1992a). This atmospheric sulfur enters the soil as sulfur dioxide and sulfate both of which may acidify the soil either directly from the hydrogen ions derived from H_2SO_4 or as SO_4^{2-} acting as a counter anion. The leaching of sulfate may result in the depletion of nutrient cations (e.g., Ca^{2+}, Mg^{2+} and K^+) or the release of acidic cations (H^+ and Al^{+n}), the latter of which can be toxic to the biota of soils and drainage waters (Reuss and Johnson, 1986).

Forms of sulfur

Organic sulfur

Organic sulfur forms predominate in most soils and there is often a direct correspondence between organic carbon and total sulfur concentration with an average C:S ratio of about 108:1 (Stevenson, 1986). The relative composition and distribution of sulfur forms are depicted for selected soils in Figure S87. Soil organic sulfur consists of two major classes: carbon-bonded sulfur and ester sulfate. These classes are the major sulfur constituents for grassland, agronomic and forested soils and, if mineralized, provide an important source of sulfate for uptake by higher plants (Freney and Williams, 1983). Carbon-bonded sulfur enters the soil from plants as litter and roots while animal sources including excreta are important sources of ester sulfates (Fitzgerald, 1978). Both types of organic sulfur are also formed in situ by soil biota during decomposition and humification.

Carbon-bonded sulfur in soil contains amino acids, sulfolipids and sulfonic acids as well as many poorly defined compounds. Some of these compounds are formed and stabilized by humification. The chemical forms of sulfur in humus are largely unknown, but may include both aliphatic and aromatic structures. Both nitrogen and sulfur amino acids have been detected as constituents of humic substances, and these amino acids compose a substantial portion of soil sulfur. It seems likely that plant products such as thiols (–SH) and acyl

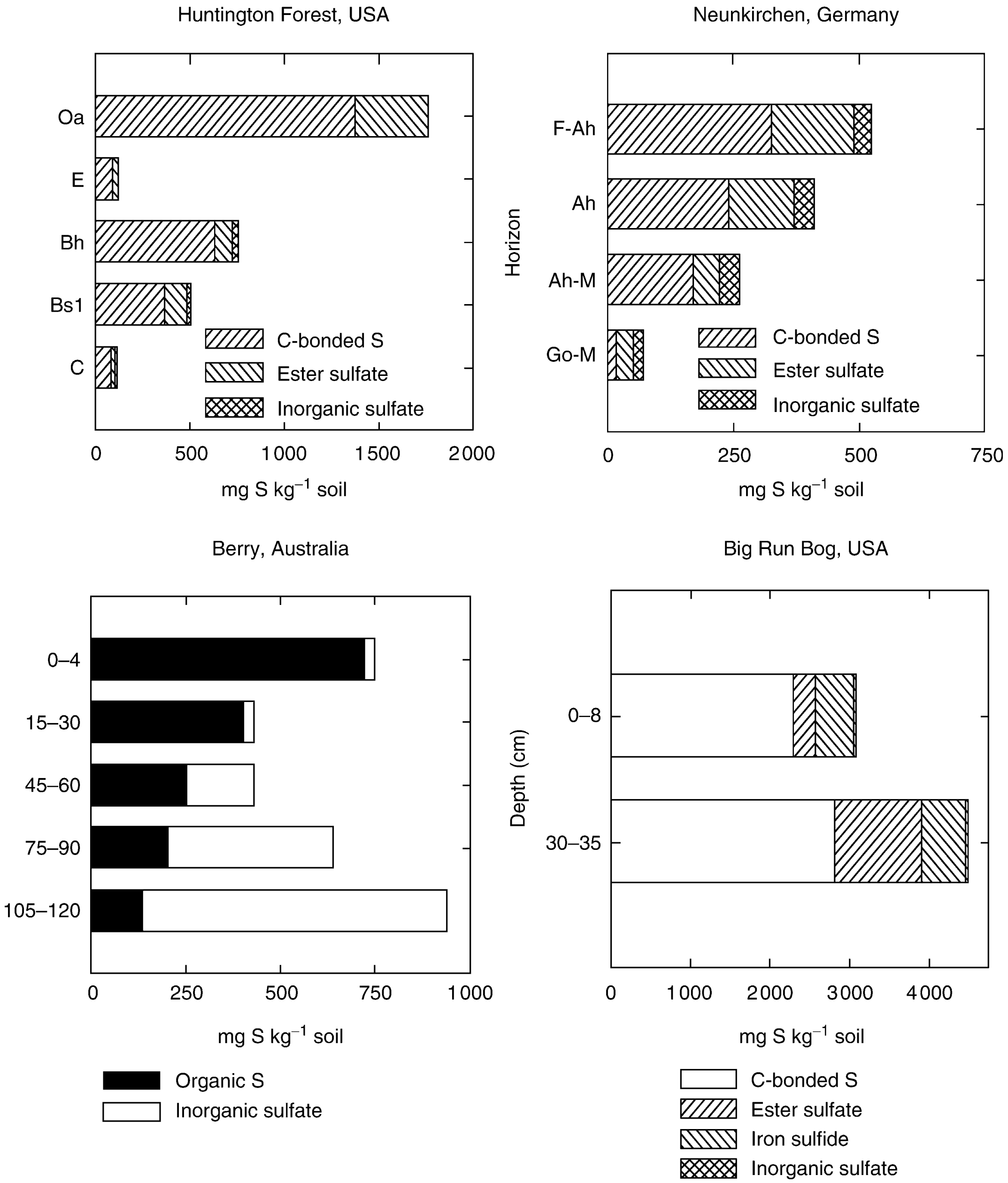


Figure S87 Sulfur forms and distribution in four soils. Data for the Huntington Forest and Neunkirchen from Mitchell et al. (1992a); Berry from Freney and Williams (1983); and Big Run Bog from Wieder et al. (1987).

thiols (R–C–SR′) would also be incorporated into organic matter during humification by polymerization processes.

Compounds included in the operationally-defined ester sulfate class are those that contain the C–O–S linkage (ester sulfate) and the C–N–S linkage (sulfamate) along with some organic sulfites. The accurate quantification of these operationally-defined classes is highly dependent on complete recovery of inorganic sulfate (Alewell and Matzner, 1996) and accurate determinations of the HI-reducible sulfur component (Freney, 1961). The C–O–S linkage is found in greatest quantity, with the other forms rarely being important. Ester sulfate can originate from animals (e.g., chondroitin sulfate), microorganisms (e.g., choline sulfate) and plants (e.g., sulfated thioglycosides) (Fitzgerald, 1978).

Organic sulfur pools have also been classified with respect to lability since only a small portion of soil sulfur appears to be actively involved in sulfur transformations. One of the most important labile sulfur fractions is microbial biomass that may contribute ~10 mg S $\mathrm{kg^{-1}}$ soil (Nakas, 1986). This microbial pool has been mostly studied in agronomic soils where biotic processes may be particularly important in regulating sulfur availability for plant uptake (Schoenau and Germida, 1992).

Inorganic sulfur

Sulfate, the predominate form of inorganic sulfur, is derived from wet and dry deposition, mineral weathering, and catabolism of organic sulfur. Most of the stable sulfate minerals in soil contain aluminum, iron or calcium. These may include jurbanite ($AlOHSO_4$), basaluminite ($Al_4(OH)_{10}SO_4$), alunite ($KAl_3(SO_4)_2(OH)_6$), and gypsum ($CaSO_4 \cdot H_2O$). Under xeric conditions, some forms such as gypsum may accumulate, while in acid sulfate soils aluminum-sulfate forms such as jurbanite and basaluminite may be found (Mitchell et al., 1992a). The actual detection of these aluminum-sulfate minerals in forest soils has, however, been subject to considerable debate (Alewell et al., 1996; Lükewille et al., 1995).

Reduced inorganic sulfur compounds including iron sulfides are generally considered to be unimportant in soils in which oxygen is not limiting. Even for wetland soils, organic sulfur constituents generally dominate due to high concentrations of organic carbon (e.g., Big Run Bog; Figure S87). However, the relative importance of iron sulfide compounds, including pyrite, generally increases under high sulfate concentrations such as for those wetland soils with marine or brackish water influences (Giblin and Wieder, 1992).

Transformation and fluxes

There has been considerable attention on the relative importance of abiotic versus biotic processes in regulating sulfur transformations and fluxes as depicted in Figure S88. The relative importance of these processes varies greatly in soils, but overall biotic processes are most important for those plant–soil systems that have small atmospheric sulfur inputs, but high requirements for sulfur, whereas abiotic processes are more predominant for those systems with high sulfur inputs and substantial fluxes of drainage water. Analyses using stable sulfur isotopes have suggested that in soils with atmospheric inputs ≤ 10 kg S ha^{-1} yr^{-1} that most of the deposited sulfur is cycled through plant and microbial biomass (Mayer et al., 1997; Novak et al., 2001).

Mineralization and immobilization

Sulfur mineralization (the transformation of organic sulfur to sulfate) and immobilization (the transformation of sulfate to organic sulfur) occur concomitantly in soil. The transformation rates, pools of sulfur involved, and net alterations in pools with respect to sulfur input/output budgets have been evaluated by both laboratory and field experiments including the use of radioactive (Dhamala and Mitchell, 1992) and stable sulfur (Mitchell et al., 1998; Alewell et al., 1999) isotopes. For forest soils much of the work has been done in temperate regions of North America (Mitchell et al., 1992a,b) while for agronomic important soils considerable work has also been done in Australia and New Zealand (McLachlan, 1975). From these studies some generalizations can be made. Sulfate can be directly incorporated into ester sulfate or carbon-bonded sulfur. These immobilization processes are microbially mediated and regulated by various environmental factors including substrate availability and physical factors such as temperature and moisture. Although both ester sulfate and carbon-bonded sulfur can be mineralized, the former pool is generally more labile. The overall stability of the organic sulfur fractions has been demonstrated in forest soils using field experiments. Even after acidification, substantial additions of sulfate or disturbance, there were only minor changes in the organic sulfur pools, but significant increases in adsorbed inorganic sulfate (Mitchell et al., 1989, 1994).

Various conceptual and mathematical models have been developed to evaluate how these processes might affect soil sulfur pools and sulfate retention. Mineralization of sulfur is generally modeled as a first order reaction rate with the reaction

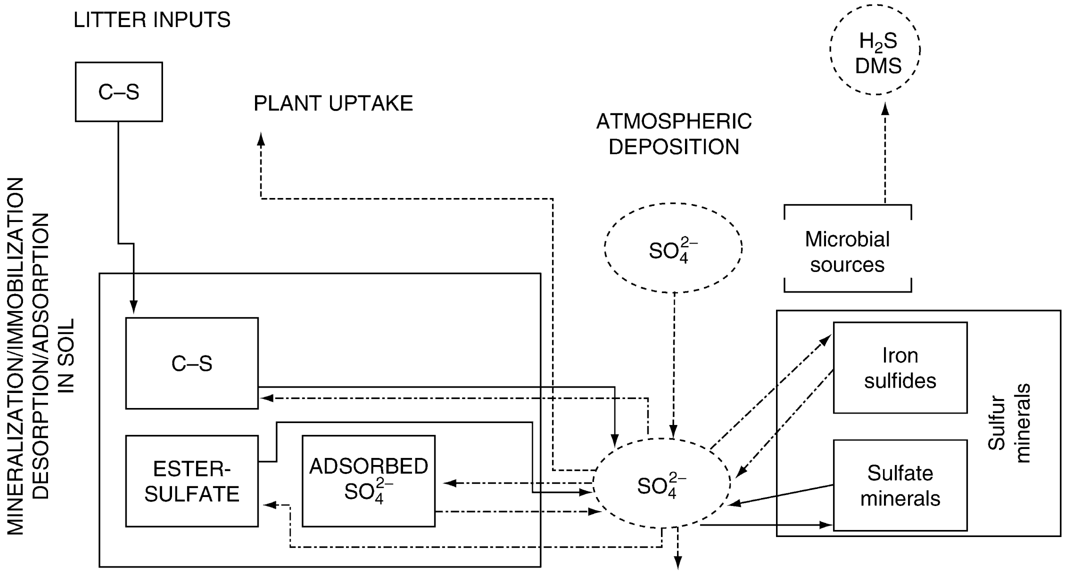


Figure S88 Major sulfur fluxes and transformations in soils.

constant sometimes being a function of parameters that affect microbial activity (Schoenau and Germida, 1992; Gbondo-Tugbawa et al., 2002). The processes that regulate the mineralization of carbon-bonded sulfur and ester sulfates are distinct. As depicted in Figure S89, mineralization of carbon-bonded sulfur is closely linked with carbon catabolism while ester sulfate dynamics is dependent upon sulfohydrolases some of which are extracellular.

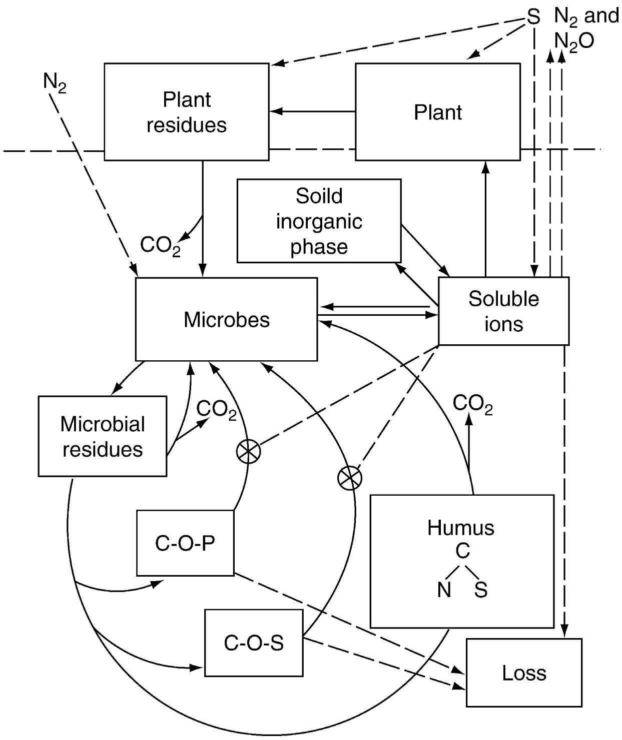


Figure S89 Conceptual model of organic sulfur transformations showing differences between carbon-bonded sulfur and ester sulfate dynamics from McGill and Cole (1981).

Adsorption/desorption and mineral formation/dissolution

The ability of soils to retain sulfate by adsorption or mineral formation is well recognized. The mechanisms are chemically complex for sulfate adsorption as shown in Figure S90. Adsorption of sulfate is generally considered to take place by two mechanisms. Sulfate retention has generally been shown to be pH dependent suggesting a non-specific adsorption mechanism where the negative charge of adsorbed sulfate onto aluminum or iron hydroxide surfaces that may be balanced by displacement of OH^-. The other mechanism may result in "irreversible" adsorption of sulfate along with accompanying cations and has been designated "selective" or "specific" adsorption. The multiple negative charge and the bridging that can occur due to SO_4^{2-} being divalent are important for its co-adsorption with cations. At very low pH, sulfate adsorption may result in a dehydration reaction and thus there is no generation of OH^-.

In addition to the mechanism of inorganic surface adsorption, mineral formation may explain some sulfate retention in soils, particularly when pH is low and aluminum high (Nordstrom, 1982). There is little evidence, however, that sulfate minerals play a major role in controlling sulfate concentrations in solution for most forest soils (Alewell et al., 1996; Lükewille et al., 1995). The reaction of gibbsite with sulfate may also result in the precipitation of jurbanite or basaluminite and the displacement of equivalent quantities of OH^- as also occurs with sulfate adsorption:

$$\mathrm{Al(OH)_3} + \mathrm{SO_4^{2-}} \rightleftharpoons \mathrm{Al(OH)SO_4} + 2\mathrm{OH^-} \tag{1}$$

$$4\mathrm{Al(OH)_3} + \mathrm{SO_4^{2-}} \rightleftharpoons \mathrm{Al_4(OH)_{10}SO_4} + 2\mathrm{OH^-} \tag{2}$$

Factors affecting sulfate adsorption

Several factors enhance sulfate adsorption including: (1) decreasing soil pH; (2) increasing clay content or the quantity

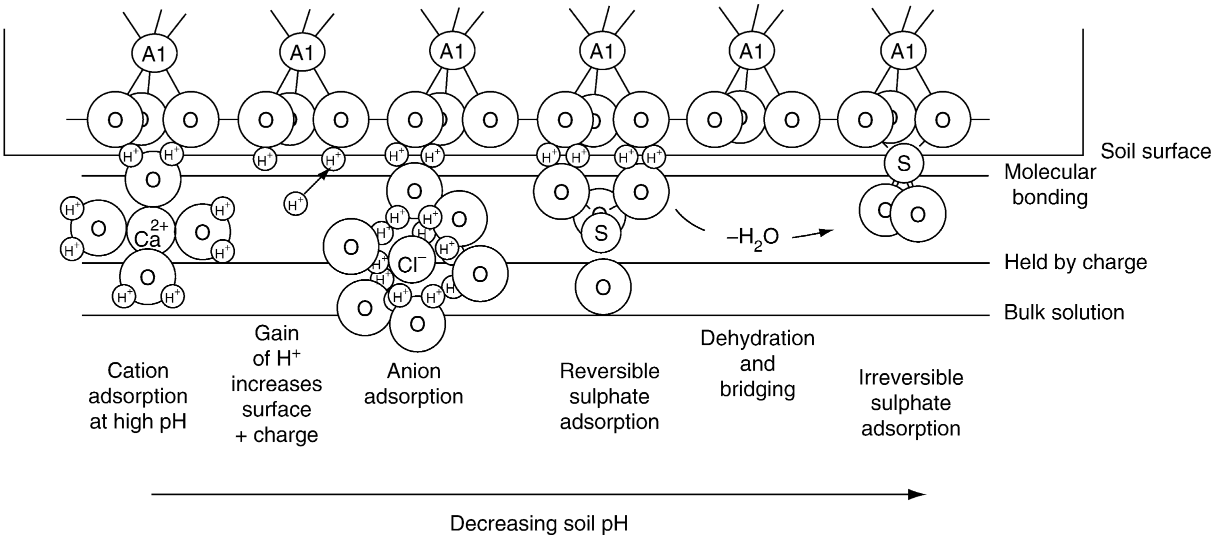


Figure S90 Schematic diagram of sulfate adsorption mechanisms (from Mitchell et al., 1992a).

of aluminum and iron oxides; and (3) decreasing organic matter. The relative importance of each of these factors varies with soil type. Adsorption of sulfate generally increases with decreasing soil pH. If soil is acidified by naturally formed organic acids or strong mineral acids of anthropogenic origin (i.e., acidic deposition), sulfate adsorption potential will likely increase. In the case of organic acids, this effect can be complicated by the blockage of organic ligands on exchange sites that are commonly sesquioxides of aluminum and iron. When some soils are acidified, there may be a pH level below which sulfate adsorption decreases due to solubilization of aluminum or iron. The effect of pH on sulfate adsorption is a function of the actual mechanisms and these vary among soils. For example, when anion adsorption is due to exchange, adsorption of sulfate would increase by H^+ addition. The amphoteric nature of the anion exchange capacity necessitates increased sulfate adsorption with decreasing pH. As H^+ is incorporated onto the surface, the mineral surface becomes positively charged and thus can retain additional anions. In the case of multivalent anions such SO_4^{2-}, a bridge can form between the anion and the surface, and there is a potential for covalent bonds to form by loss of H_2O. Anions that form covalent bonds are tightly held and may change the original surface from an anion to a cation exchanger (Mitchell et al., 1992a).

The most commonly utilized model for describing adsorption is based on the Langmuir (1918) Equation typically written as follows:

$$\frac{C}{Ss} = \frac{1}{Mb} + \frac{C}{M} \tag{3}$$

where

- C is the concentration of SO_4^{2-} in solution;
- M is the adsorption capacity;
- b is a coefficient related to the bonding energy of SO_4^{2-} adsorption; and
- Ss is amount of SO_4^{2-} adsorbed per unit area.

When C/Ss is plotted as a function of C, then $1/Ss$ is the slope and $1/Mb$ the intercept. Examples of isopleths of a high and low sulfate adsorbing soils are shown in Figure S91. The use of this equation has been criticized, because such a plot will usually result in an apparent significant relationship between C/Ss versus C, because C is a variable on both axes. A modification of the Langmuir Equation has been used to estimate sulfate adsorption in forest soils. Use of the initial mass of sulfate added, rather than the final concentration, has resulted in improved predictions of sorption (Nodvin et al., 1986). Other equations, which have been utilized, include the Freundlich Equation and the Temkin Equation.

Reversibility of sulfate adsorption

The degree to which sulfate adsorption is reversible is important for projecting the recovery of acidified surface waters and soils following decreases in atmospheric deposition of sulfate (Reuss and Johnson, 1986; Harrison et al., 1989; Johnson and Mitchell, 1998). Reductions of sulfate in forest soil leachates in response to decreases in sulfate inputs will be prolonged if sulfate desorbs (Figure S92). Sulfur emissions reached a maximum in the contiguous United States around 1970 (Butler and Likens, 1991; Husar et al., 1991) and in Europe around 1980 (Christophersen et al., 1990; Matzner and Meiwes, 1994) and subsequently have been decreasing.

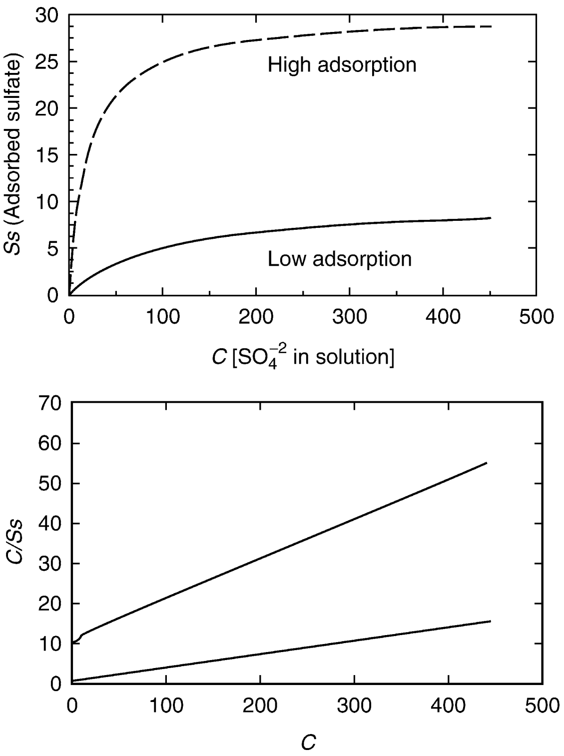


Figure S91 Langmuir adsorption isopleths of a low and high sulfate adsorbing soils.

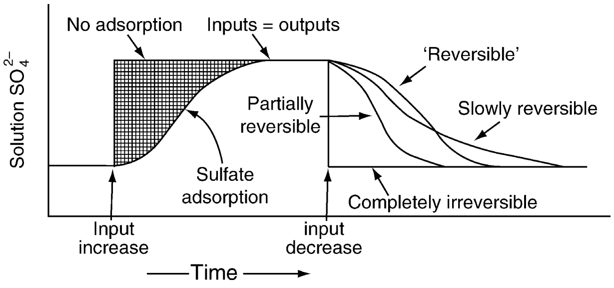


Figure S92 Reversibility of sulfate adsorption (from Harrison et al., 1989).

These decreases in sulfur emission have been reflected in decreases in sulfate concentrations of surfaces waters in the Northeast U.S. (Driscoll et al., 1995; Likens et al., 2002), eastern Canada (Dillon and LaZerte, 1992) and Europe (Allot et al., 1992). How these changes in emissions and hence sulfur inputs affect the soil sulfur cycle in these regions has been shown to vary among sites. Some sites have shown a rapid response due to limited sulfate desorption (Wright et al., 1988; van Dijk et al., 1992) while others have exhibited a delay due to high rates of sulfate release (Dillon and LaZerte, 1992; Alewell et al., 2001). The degree of the reversibility of adsorbed sulfate affects the recovery of surface waters, which had previously been acidified (Reuss and Johnson, 1986; Johnson and Mitchell, 1998).

Because sorption reactions are kinetic, there is increased adsorption or desorption with increasing time of equilibration between the exchanger and solution. Many researchers consider most sulfate adsorption reactions to be reversible given sufficient time for desorption to occur (Barrow and Shaw, 1977), but it is important to recognize that the residence time of solutes in forest soils may range from minutes to days. Especially under conditions of high flow, solute concentrations may not reflect equilibrium conditions such as those predicted by adsorption isopleths. The results of sulfate adsorption reversibility experiments in the laboratory are as varied as the observations of sulfate adsorption, and this may be a reflection of the many factors that influence this processes including the actual experimental procedure including time, intensity of shaking and the actual extractant used for desorbing sulfate (Mitchell et al., 1992a).

Losses of sulfur from soil

The major pathways of sulfur movement through the soil are shown in Figure S88. The relative importance of these pathways varies among ecosystems in which the soil is located.

Gaseous losses

A wide range of sulfur gases (i.e., H_2S, COS, DMS, CS_2 and DMDS) may be volatilized from soils. There is wide variation in these loss rates among inland soils with an estimated average rate of 1.2 nmol m^{-2} min^{-1} (0.02 kg ha^{-1} yr^{-1}) which is a very small loss compared with other sulfur fluxes in the soil (Andrea and Jaeschke, 1992). Thus, these gaseous losses have little importance in evaluating sulfur transformations in the soil except as they may contribute to biogenic atmospheric sulfur.

Plant uptake

Sulfur is taken up by plants as sulfate which can either be reduced and converted to carbon-bonded sulfur constituents or remain as inorganic sulfate. In those ecosystems where sulfur availability is low, the cycling of sulfur through vegetation may play an important role in regulating other sulfur fluxes. For forests, total sulfur requirements are generally less than 15 kg S ha^{-1} yr^{-1} and thus for sites with very high atmospheric inputs of sulfur, the cycling of sulfur through the vegetation is not important in affecting sulfate leaching (Mitchell et al., 1992a). For agronomic systems, some crops may contain high amounts of sulfur and if harvested may result in substantial loss of sulfur (Table S24). If these crops are grown in regions with low sulfur availability, this removal may deplete the reserves of this element and result in nutrient deficiencies (Duke and Reisenauer, 1986).

Table S24 Sulfur content of selected crops at harvest (from Duke and Reisenauer, 1986)

Crop	Component	Content (kg ha^{-1})
Alfalfa	Hay	45
Cabbage	Head	73
Mixed grasses	Hay	52
Sugar cane	Tops	40
Sugar beet	Tops	41

Leaching

The importance of sulfur loss via leaching depends on the concentration of sulfate in soil water and the rate of drainage water loss. For forest ecosystems the movement of sulfate through drainage waters is often an important component of the sulfur cycle. An examination of sulfur inputs versus sulfate leaching losses from forest ecosystems (Figure S93) shows that loss

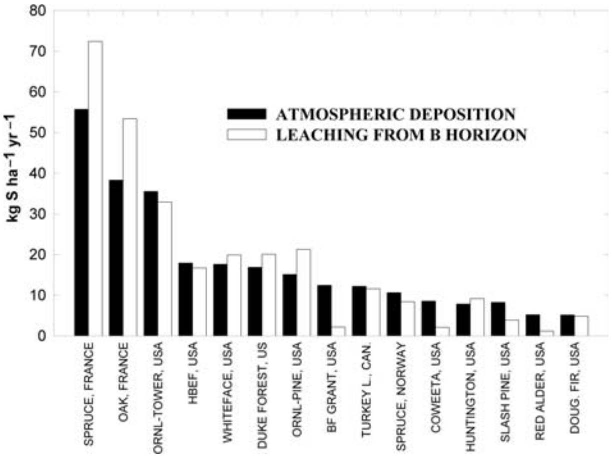


Figure S93 Sulfate fluxes in selected forested ecosystems. Data for sites from Mitchell et al. (1992a,b).

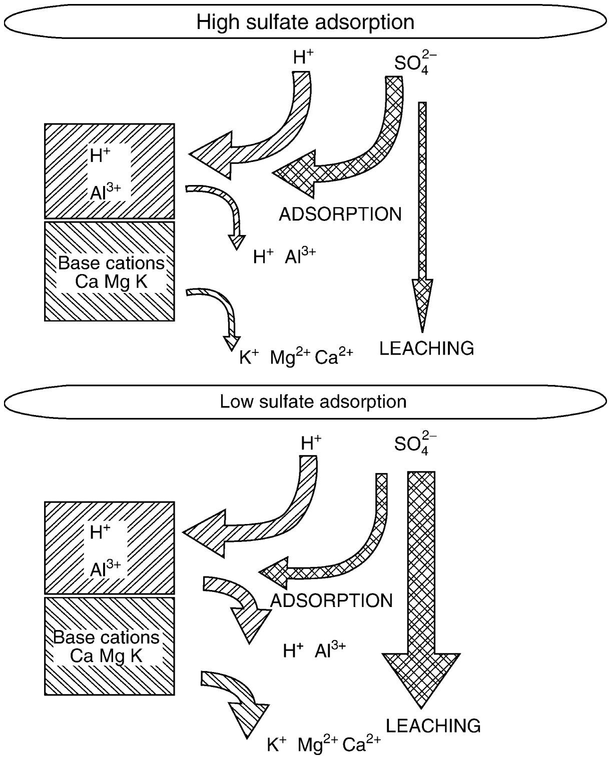


Figure S94 Effect of high and low SO_4^{2-} retention on cation losses from soil.

rates of sulfate may equal or even exceed current atmospheric inputs. Some forests, however, do exhibit net sulfur retention, which may be due to either abiotic or biotic processes. Generally, the loss of sulfur via leaching is not important with respect to sulfur nutrition, but it can affect other elements, especially cations.

Relationship to cations

If the sulfate is not retained by biological or chemical processes as it is leached through soil, there is concomitant movement of cations. The associated cations depend upon the relative importance of acidic (H^+, $Al^{+n)}$ and basic cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) within the exchange complex (Figure S94). The relative importance of various cations, which are released in solution, depends on their relative proportions on the exchange complex as well as selectivity coefficients of the exchange reactions. Sulfate in solution serves as an anion for which basic cations, including important plant nutrients (calcium, magnesium, potassium), or acidic cations are needed to maintain charge neutrality. High sulfate leaching rates may result in the depletion of these nutrient cations or contribute to the release of toxic, acidic cations.

Acknowledgments

M. J. Mitchell is grateful for the support from the United States Environmental Protection Agency, National Science Foundation, and the New York State Energy and Research Development Authority in supporting research on this topic. C. Alewell acknowledges the support of the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG).

M. J. Mitchell and C. Alewell

Bibliography

Alewell, C., 2001. Predicting reversibility of acidification: the European sulphur story. *Water Air Soil Pollut.*, **130**: 1271–1276.

Alewell, C., and Matzner, E., 1996. Water, $NaHCO_3^-$, $NaH_2PO_4^-$ and NaCl-extractable SO_4^{2-} in acid forest soils. *J. Soil Sci. Plant Nutr.*, **159**: 235–240.

Alewell, C., Manderscheid, B., Lükewille, A., Koeppe, P., and Prenzel, J., 1996. Describing SO_4^{2-} dynamics in the Solling roof project with two different modelling approaches. *Water Air Soil Pollut.*, **85**: 1810–1806.

Alewell, C., Mitchell, M.J., Likens, G., and Krouse, R., 1999. Sources of stream sulfate at the Hubbard Brook Experimental Forest: long-term analysis using stable isotopes. *Biogeochemistry*, **44**: 281–299.

Allot, T.E.H., Harriman, R., and Battarbee, R.W., 1992. Reversibility of lake acidification at the Round Loch of Glenhead, Galloway, Scotland. *Environ. Pollut.*, **77**: 219–225.

Andrea, M.O., and Jaeschke, W.A., 1992. Exchange of sulphur between biosphere and atmosphere over temperate and tropical regions. In Howarth, R.W., Stewart, J.W.B., and Ivanov, M.V., eds., *Sulphur Cycling on the Continents: Wetlands, Terrestrial Ecosystems and Associated Water Bodies.* SCOPE 48. Chichester: Wiley, pp. 27–61.

Barrow, N.J., and Shaw, T.C., 1977. The slow reactions between soil and anions: 7: effect of time and temperature on contact between an adsorbing soil and sulphate. *Soil Sci.*, **124**: 347–354.

Butler, T.J., and Likens, G.E., 1991. The impact of changing regional emissions on precipitation chemistry in the eastern United States. *Atm. Environ.*, **25A**: 305–315.

Christophersen, N., Robson, A., Neal, C., Whitehead, P.G., Vigerust, B., and Henriksen, A., 1990. Evidence for long-term deterioration of streamwater chemistry and soil acidification at the Birkenes catchment, southern Norway. *J. Hydrol.*, **116**: 63–76.

Dhamala, B.R., and Mitchell, M.J., 1992. Utilization of ^{35}S in analyzing sulfur transformations and fluxes in forest soils. In Hendry, M.J., and Krouse, H.R., eds., *Workshop Proceedings on Sulphur Transformations in Soil Ecosystems (5–7 November 1992),* National Hydrology Research Symposium No. 11. Saskatchewan, Saskatoon, pp. 297–314.

van Dijk, H.F.G., Boxman, A.W., and Roelofs, J.G.M., 1992. Effects of a decrease in atmospheric deposition of nitrogen and sulfur on the mineral balance and vitality of a Scots pine stand in the Netherlands. *For. Ecol. Manag.*, **51**: 207–215.

Dillon, P.J., and LaZerte, B.D., 1992. Response of Plastic Lake catchment, Ontario, to reduced sulphur deposition. *Environ. Pollut.*, **77**: 211–217.

Driscoll, C.T., Postek, R.M., Kretser, W., and Raynal, D.J., 1995. Long-term trends in the chemistry of precipitation and lake water in the Adirondack region of New York, USA. *Water Air Soil Pollut.*, **85**: 583–588.

Duke, S.H., and Reisenauer, H.M., 1986. Roles and requirements of sulfur in plant nutrition. In Tabatabai, M.A., ed., *Sulfur in Agriculture,* Agronomy Monograph no. 27, Wisconsin, Madison, pp. 123–168.

Erkenberg, A., 1989. Sulphur status of selected European forest soils. In Klimo, E., and Materna, J., eds., Proc. Workshop on Verification of Hypothesis on the Mechanisms of Damage and Possibilities of Recovery of Forest Ecosystems. Univ. of Agriculture Brno, pp. 225–236.

Fitzgerald, J.W., 1978. Naturally occurring organosulfur compounds in soil. In Nriagu, J.O., ed., *Sulfur in the Environment. Part II. Ecological Impacts.* New York: Wiley, pp. 391–443.

Freney, J.R., 1961. Some observations on the nature of organic sulfur compounds in soils. *Aust. J. Agric. Res.*, **12**: 424–432.

Freney, J.R., and Williams, C.H., 1983. The sulfur cycle in soil. In Ivanov, M.V., and Freney, J.R., eds., *The Global Biogeochemical Sulphur Cycle.* New York: Wiley, pp. 129–201.

Gbondo-Tugbawa, S.S., Driscoll, C.T., Mitchell, M.J., Aber J.D., and Likens, G.E., 2002. A model to simulate the response of a northern hardwood forest ecosystem to changes in S deposition. *Ecol. Appl.*, **12**: 8–23.

Giblin, A.E., and Wieder, R.K., 1992. Sulphur cycling in marine and freshwater wetlands. In Howarth, R.W., Stewart, J.W.B., and Ivanov, M.V., eds., *Sulphur Cycling on the Continents: Wetlands, Terrestrial Ecosystems and Associated Water Bodies.* Chichester: Wiley, pp. 85–124. SCOPE 48.

Harrison, R.B., Johnson, D.W., and Todd, D.E., 1989. Sulfate adsorption and desorption in a variety of forest soils. *J. Environ. Qual.*, **18**: 419–426.

Husar, R.B., Sullivan, T.J., and Charles, D.F., 1991. Historical trends in atmospheric sulfur deposition and methods for assessing long-term trends in surface water chemistry. In Charles, D.F., ed., *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies.* New York: Springer, pp. 65–82.

Johnson, D.W., and Mitchell, M.J., 1998. Responses of forest ecosystems to changing sulfur inputs. In Maynard, D., ed., *Sulfur in the Environment*. New York: Marcel Dekker, pp. 219–262.

Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum. *J. Am. Chem. Soc.*, **40**: 1361–1382.

Likens, G.E., Driscoll, C.T., Buso, D.C., Mitchell, M.J., Lovett, G.M., Bailey, S.W., Siccama, T.G., Reiners, W.A., and Alewell, C., 2002. The biogeochemistry of sulfur at Hubbard Brook. *Biogeochemistry*, **60**: 235–316.

Lükewille, A., Malessa, V., and Alewell, C., 1996. Measured and modelled retention of inorganic sulfur in soils and bedrock (Harz Mountains, Germany). *Water Air Soil Pollut.*, **85**: 683–688.

Matzner, E., and Meiwes, K.J., 1994. Long-term development of element fluxes with bulk precipitation and throughfall in two German forests. *J. Environ. Qual.*, **23**: 162–166.

Mayer, B., Prietzel, J., and Krouse, H.R., 2001. The influence sulfur deposition raes on sulfate retention patterns and mechanisms in aerated forest soils. *Appl. Geochem.* **16**: 1003–1019.

McLachlan, K.D. ed., 1975. *Sulphur in Australasian Agriculture.* Sydney: Sydney University Press, p. 261.

McGill, W.B., and Cole, C.V., 1981. Comparative aspects of cycling of organic C, N, S and P through soil organic matter. *Geoderma*, **26**: 267–286.

Mitchell, M.J., Driscoll, C.T., Fuller, R.D., David, M.B., and Likens, G.E., 1989. Effect of whole-tree harvesting on the sulfur dynamics of a forest soil. *Soil Sci. Soc. Am. J.*, **53**: 933–940.

Mitchell, M.J., David, M.B., and Harrison, R.B., 1992a. Sulphur dynamics of forest ecosystems. In Howarth, R.W., Stewart, J.W.B., and Ivanov, M.V., eds., *Sulphur Cycling on the Continents: Wetlands, Terrestrial*

Ecosystems and Associated Water Bodies. SCOPE 48. Chichester: Wiley, pp. 215–254.

Mitchell, M.J., Harrison, R.B., Fitzgerald, J.W., Johnson, D.W., Lindberg, S.E., Zhang, Y., and Autry, A., 1992b. Sulfur distribution and cycling in forest ecosystems. In Johnson, D.W., and Lindberg, S.E., eds., *Atmospheric Deposition and Nutrient Cycling in Forest Ecosystems,* Ecological Series 91, New York: Springer, pp. 90–128.

Mitchell, M.J., David, M.B., Fernandez, I.J., Fuller, R.D., Nadelhoffer, K., Rustad, L.E., and Stam, A.C., 1994. Response of buried mineral soil-bags to three years of experimental acidification of a forest ecosystem. *Soil Sci. Soc. Am. J.*, **58**: 556–563.

Mitchell, M.J., Krouse, H.R., Mayer, B., Stam, A.C., and Zhang, Y., 1998. Use of stable isotopes in evaluating biogeochemistry of forest ecosystems. In Kendall, C., and McDonnell, J., eds., *Isotope Tracers in Catchment Hydrology.* Amsterdam, The Netherlands: Elsevier, pp. 489–518.

Nakas, J.P., 1986. Role of microflora in terrestrial sulfur cycling. In Mitchell, M.J., and Nakas, J.P., eds., *Microfloral and Faunal Interactions in Natural and Agro-Ecosystems.* Dordrecht: Martinus-Nijhoff/Dr W. Junk Publ., pp. 285–316.

Nodvin, S.C., Driscoll, C.T., and Likens, G.E., 1986. Simple partitioning of anions and dissolved organic carbon in a forest soil. *Soil Sci.*, **142**: 27–35.

Nordstrom, S.A., 1982. The effect of sulfate on aluminum concentrations in natural waters: stability relations in the system Al_2O_3–SO_3–H_2O at 298 K. *Geochim. Cosmochim. Acta*, **46**: 681–692.

Novak, M., Bottrell, S.H., and Prechova, E., 2001. Sulfur isotope inventories of atmospheric deposition, spruce forest floor and living Sphagnum along a NW–SE transect across Europe. *Biogeochemistry*, **53**: 23–50.

Reuss, J.O., and Johnson, D.W., 1986. *Acid Deposition and the Acidification of Soil and Water.* New York: Springer. p. 119.

Schoenau, J.J., and Germida, J.J., 1992. Sulphur cycling in upland agricultural systems. In Howarth, R.W., Stewart, J.W.B., and Ivanov, M.V., eds., *Sulphur Cycling on the Continents: Wetlands, Terrestrial Ecosystems and Associated Water Bodies.* SCOPE 48. Chichester: Wiley, pp. 261–277.

Stevenson, F.J., 1986. *Cycles of Soil Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients.* New York: Wiley, p. 380.

Wieder, R.K., Lang, G.E., and Granus, V.A., 1987. Sulphur transformations in sphagnum-derived peat during incubation. *Soil Biol. Biochem.*, **19**: 101–106.

Wright, R.F., Lotse, E., and Semb, A., 1988. Reversibility of acidification shown by whole-catchment experiments. *Nature*, **334**: 670–675.

SUPERGENE

Used especially of ore deposits enriched by weathering processes and altered by the transfer of materials in aqueous solution, percolating downwards from the zone of weathering. The term was coined by the Russian geochemist Fersman, who considered the supergene zone to be the region of the earth where chemical elements migrate at low temperatures and pressures in the processes *inter alia* of weathering and soil formation. According to Perel'man (1967, p. 1) the supergene zone may extend for several thousand meters below the surface.

Bibliography

Perel'man, A.I., 1967. *Geochemistry of Epigenesis*. Translated from Russian by Kohanowski, N.N., Foreword by Fairbridge, R.W. New York, Plenum Press, 266 pp.

SURFACE SOIL WATER CONTENT

See *Water Budget in Soil*.

SURFICIAL

Surficial deposits are those that blanket or mantle a land surface, and include an active soil layer if it is present. In cartography, maps described as 'Surficial Geology Maps', show Pleistocene deposits, but not soils, which are mapped seperately.

SUSTAINABLE AGRICULTURE

In theory, an agriculture that leaves an agroecosystem completely functional after a harvest, and able to sustain a succession of harvests indefinitely. Such a system has never been achieved, though the agriculture developed in Europe in the eighteenth century, and based on a four-fold rotation, came close. Current agriculture as practiced in the industrialized world is heavily dependant on the energy of fossil fuels, and for that reason (if for no other) is inherently unsustainable.

SWAMP

A wetland similar to marsh though with a well developed tree or shrub layer, permitted by seasonally low water levels. Trees or shrubs also inhibit water flow, which may lead to the development of acidity.

Cross-reference

Wetland

T

TABLELAND

Elevated land defined by steep slopes around a flat surface of considerable extent: a plateau rather than the more restricted version, a mesa.

TAIGA

The belt of coniferous forest south of the tundra, encircling the North Pole in Eurasia and North America. The characteristic soil-forming process of the taiga (or boreal forest) is podzolization.

Bibliography

Day, Trevor., 2006. Taiga. New York: Chelsea House. 220 pp.

Cross-references

Biomes and their Soils
Podzols

TAILINGS

The fine crushed material, from which an ore mineral has been extracted at a mine, and which is deposited as a slurry into a tailings pit or pond. Tailings may be sulfide bearing in metal and coal mining, and if the water table in the pit is allowed to drop, will oxidize and cause problems of acid mine drainage. Drainage away from the mining district is a potential problem for floodplains and their soils downstream (Walton-Day et al., 1999).

Bibliography

Walton-Day, K., Rossi, F.J., Gerner, L.J., Evans, J.B., Yager, T.J., Ranville, J.F., and Smith K., 1999. Effects of fluvial tailings deposits on soils and surface- and groundwater quality, and implications for remediation – Upper Arkansas River, Colorado, 1992–1996. U.S. Geological Survey, Water-Resources Investigations Report. Volume: 99–4273.

Cross-reference

Redox Reactions and Diagrams in Soil

TECHNOSOLS

Technosols are one of two new Reference Soil Groups (the other being Stagnosols) officially announced at the 18th World Congress of Soil Science in Philadelphia (IUSS Working Group WRB, 2006). The group brings together soils originally considered among the Regosols (FAO, 2001), but which have been modified by the technical processes that are usual in urban and industrial (including mining) environments, and which commonly add extraneous artifacts to the soil.

Connotation. Technosols are soils that are strongly influenced by human-made material; from the Greek *technikos*, skillfully made.

Synonyms. Technosols are often referred to as urban or mine soils. They appear principally as arents (truncated anthropic soils, refuse anthropic soils, mixed anthropic soils, fill anthropic soils) in the U.S. Soil Taxonomy, though any class of soil may be modified by the qualifier “anthropic” provided it has an anthropic epipedon. In the new Russian system Technosols would classify as technogenic superficial formations.

Definition. Soils modified by human activities (other than farming) and by human additions (artifacts), in the artificial environments associated with urbanization (roads and parking lots for example) and industrialization. Artifacts must make up at least 20 percent or more in the upper 100 cm of the soil, or, if shallower, down to a continuous rock or a cemented

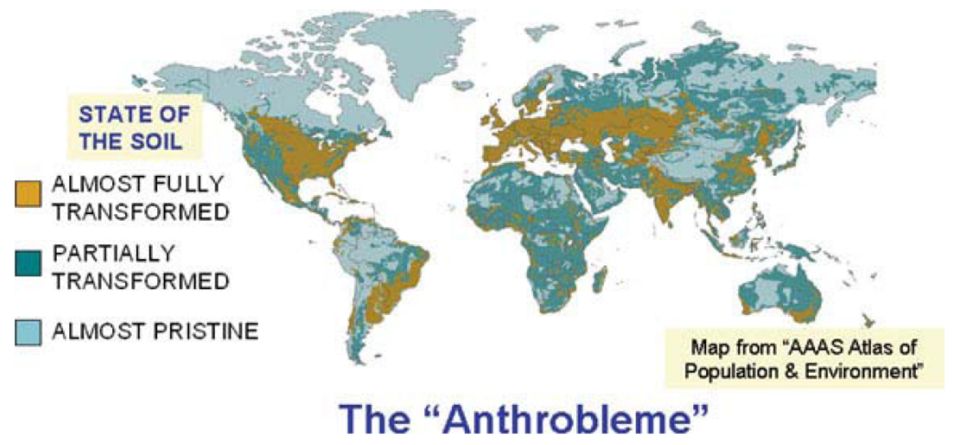


Figure T1 The region of the Earth's land surface that has been most modified by human activities, has been called the anthrobleme, or human scar, (Chesworth, 2006). The greatest modifications affect about a third of all soils, and largely comprise soils of the grassland and temperate forest biomes.

or indurated layer. For present purposes the term artifact is taken to include all human-created materials that differ in significant ways from the natural materials routinely present in soils before the development of human civilization in the last 10 to 13 000 years (that is, since Neolithic times). This would include soils developed from waste dumps such as landfills or mine tailings (with associated soils downstream, affected by acid mine drainage), and soils on cinder or ash piles, and soils containing artificial surfaces (geomembranes, road-beds and other human-made surfaces).

Parent material. Any pre-existing land-surface that has been significantly modified by any human activity other than agriculture. The pre-existing surface may be a natural soil, modified by extractions (quarrying for example) or additions (for example by dumping on the surface or by burial at depth). Alternatively it may be a completely artificial material upon which soil forming processes have acted.

Environment. The human environment generally, which is virtually the whole land surface. It is concentrated to a greater or lesser degree to about 60% of the land, and especially those parts associated with the main population centers.

Distribution. Mostly in or near centers of population, and associated with urban and industrial activities (Figure T1). Technosols may also be widely scattered at distance from such centers, for example along roads.

Profile development. Where the Technosol has developed on a pre-existing soil, the original profile development may still be present, more or less modified depending on the intensity of the human activity that created it. On artificial surfaces, profile development is minimal or non-existent, except on archeological remains from Medieval or earlier times, where such features, as clay-translocation may be apparent.

Origin. In most Technosols, pedogenesis, as the term is normally understood, is virtually non-existent. The critical soil-forming activity in this case (i.e., human actions that modify a land surface or deposit) is not commonly accepted as such. The most obvious ones are the excavation and translocation of a natural soil, or the dumping or burial of artificial materials. Of course, the localities where the effect of the normally accepted soil forming processes of weathering, leaching, eluviation and so on, have the highest probability of having brought about demonstrable changes to an anthropic site, are the oldest archeological sites. That would include the centers of urbanization in Mesopotamia, Egypt, the Mediterranean, the Indus valley, China, and in Central and Andean America.

Use. The physical and chemical properties of a Technosol depend greatly on the human activity that created the soil, and the nature of any artificial materials that may have been added. Contamination by toxic substances, from domestic or industrial sources, is more likely than for other Referrence Soil Groups. Restoration, if desired, may involve expensive procedures of removal and replacement of contaminated material (in effect the replacement of one Technosol by a new one), or by burial of the Technosol by a layer of uncontaminated soil to permit the regeneration of the biomass. In this latter case, the new layer of soil becomes the upper horizon of the Technosol.

Ward Chesworth and Otto Spaargaren

Bibliography

Chesworth, W., 2006. The enemy within, Chapter 3. In Lavigne. D.M., ed., *Gaining Ground.* Guelph, Canada; Limerick, Ireland: published by IFAW/University of Limerick, pp. 31–42.
FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.
IUSS Working Group WRB, 2006. World reference base for soil resources 2006, 2nd edn. World Soil Resources Reports No. 103. Rome: FAO, 128 pp.

Cross-references

Anthrosols
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Profile, Physical Modification

TEMPERATURE REGIME

Soil Taxonomy uses temperature classes at the family level of the classification. These are based on the mean annual soil temperature, and the difference between mean temperatures in summer and winter. The terms used outside of the tropics are shown in Table T1.

Table T1 Temperature classes (°C) in soil taxonomy (outside the tropics)

Pergelic	0	Permafrost present (except when dry)
Cryic	0 to 8	Summer soil T < about 15 °C
Frigid	0 to 8	Summer soil T > about 15 °C
Mesic	8 to 15	
Thermic	15 to 22	
Hyperthermic	22	

Zonation along these lines may be related to latitude or altitude.

For the tropics, where mean temperatures normally show a seasonal variation of less than 5 °C, the prefix "iso" is added to the last four: isofrigid, isomesic, isothermic and isohyperthermic. In the tropics the zonation is commonly related to altitude.

TENSIOMETER

An instrument for measuring the surface tension of a liquid, including soil water. Widely used to indicate when irrigation is required in arable agriculture.

TERRACE

A raised, elongated, level stretch of land that marks a break in sloping land. A downslope, or riser defines one side of the terrace, and an upslope the other. Terraces are formed naturally, particularly along a water course, but are also constructed artificially along contours (contour terracing) to create a level surface for cultivation on a hillside, to control erosion, develop a depth of soil, manage water, and prevent frosts (Doolittle, 2000, chapter 8).

Bibliography

Doolittle, William E. 2000. *Cultivated Landscapes of Native North America.* Oxford: Oxford University Press. 574 pp.

TERRAIN

A tract of land considered in terms of its physical features. Sometimes spelled terrane, though in this spelling the word also has a special meaning in plate tectonics where it connotes a unit of the lithosphere with an internally consistent structure.

TERRIC

Unconsolidated mineral soil. Where an unconsolidated mineral layer underlies an organic soil, it is referred to as a terric layer.

TEXTURE

Texture refers to the relative amounts of the different particle size fractions or separates in the soil (see Figure T2).

Cross-reference

Particle Size Distribution

THERMAL REGIME

Ordinarily the *thermal regime* of the soil is referred to as the regular pattern of soil temperature fluctuations in the soil, without relating it to the source of energy that controls that regime. To describe better the thermal regime of the soil, it is helpful to introduce the concept of the soil surface as an active surface with respect to radiation, heat, and mass exchange with the soil proper underneath it and the atmosphere above it.

At the soil surface, solar radiation is intercepted, transformed, and redistributed between the atmosphere and the soil. The energy balance for the soil surface is presented schematically in Figure T3. Most of the incoming radiation is dissipated through reflection, long wave back radiation, soil water evaporation, sensible heat transfer to the atmosphere as convection and conduction, while only a relatively small amount of energy dissipates into the soil proper as the soil heat flux.

The flux of heat into and out of the soil is a process of thermal energy transfer in the soil, which determines the thermal regime of the soil, of which the fundamental index is the soil temperature. Thus the thermal regime of a soil is characterized by giving the temperature distribution with respect to depth, time, and season for a given soil at a given location.

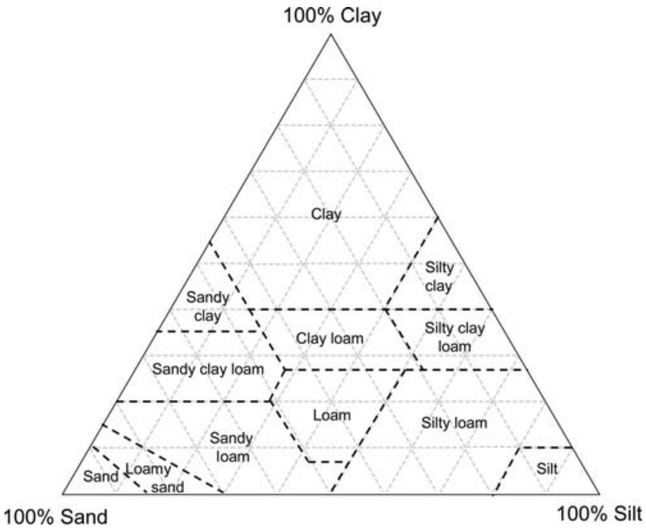


Figure T2 Relative amounts of the different particle size fractions or separates in the soil USDA.

Soil temperature profiles

Soil temperature profiles depend on the heat flux density and the soil thermal properties, namely, the *thermal conductivity* (*q.v.*) and *heat capacity* (*q.v.*) of the soil.

Global pattern

Data presented by Houghton (1954) show the global radiation to be the highest and the albedo the lowest for lower latitudes as compared to corresponding values for higher latitudes (Figure T4). These differences in solar energy intercepted at the soil surface are responsible for most of the differences between soil temperature profiles and thus to the different thermal regimes at different locations. Baver, Gardner, and Gardner (1972) have presented approximations of soil temperatures for summer and winter periods for the northern hemisphere for different soil depths and latitudes (Figure T5). It is interesting to note that (*a*) soil temperatures below 10 cm depth are about the same for all soil depths for 20° N or S during the summer, but at 10 and 30 cm depth are somewhat higher at 40° N than at 40° S and (*b*) soil temperatures increase at all depths from the higher latitudes toward the equator, yet are somewhat lower at 40° N than at 40° S. These observations are very general, yet they serve well to show the global pattern.

Local pattern of temperature profiles

It is obvious that on the global pattern soil temperatures taken by averaging the pattern over large areas of different exposures, coverage and thermal properties do not show the diversity in soil temperature profiles caused by the local conditions. The local pattern of soil temperature profiles is divided into the diurnal pattern and the seasonal or annual pattern.

The diurnal patterns of soil temperature are affected by the soil thermal properties, the soil cover, and the energy balance at the soil surface. Data collected by Yakuwa (1945), and given in Figure T6 show that in early morning the temperature is lowest at the soil surface and higher at deeper zones of the soil. After sunrise the soil surface starts to warm up, reaches a maximum when the sun reaches its highest point (local noontime), and subsequently drops down once again. The pattern of the temperature that changes at the surface with respect to time has a wave form, similar to a sinusoidal curve. Below the soil surface the temperature waves of different soil levels show that as depth increases, the differences between maximal and minimal temperatures decrease, yet this occurrence is delayed the deeper the level of measurement is. If we define the temperature wave amplitude as the half span of temperature change between the maximum and minimum at a given soil level, then the temperature amplitudes decrease with soil depth. Moreover, these temperature amplitudes are different for different soils, as can be seen from data presented by Baver et al. (1972), and given in Table T2. The temperature amplitudes at the soil surfaces and at deeper layers depend on the thermal balance of the soil surface and the soil thermal properties, which affect the heat flux dissipation at the soil surface into the soil profile.

The seasonal soil temperature profile varies similarly to the diurnal variations. For the northern hemisphere the maximum temperature will be reached during the summer months of June and July (January and February in the southern hemisphere) in similarity to midday, and the minimum temperature will be reached during the winter months of December and January (June and July in the southern hemisphere) in similarity to the nocturnal temperature in the diurnal pattern. Baver et al. (1972)

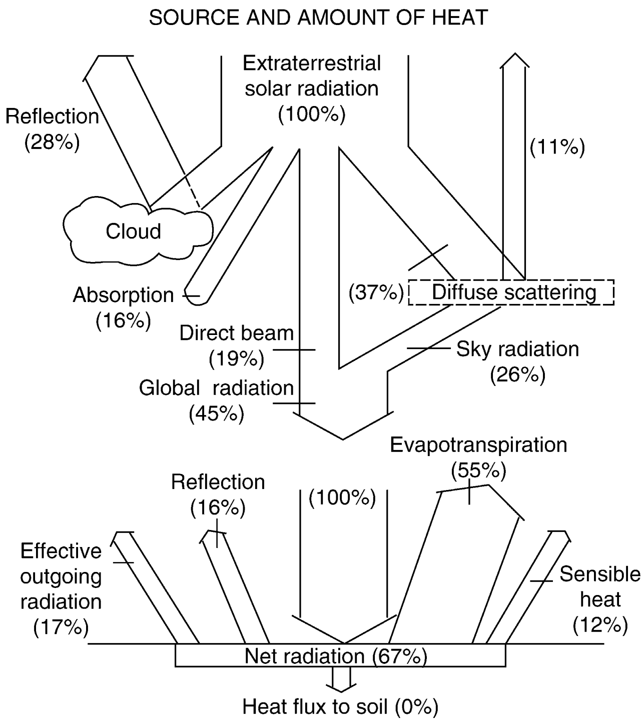


Figure T3 Daytime heat balances (after Baver et al., 1972).

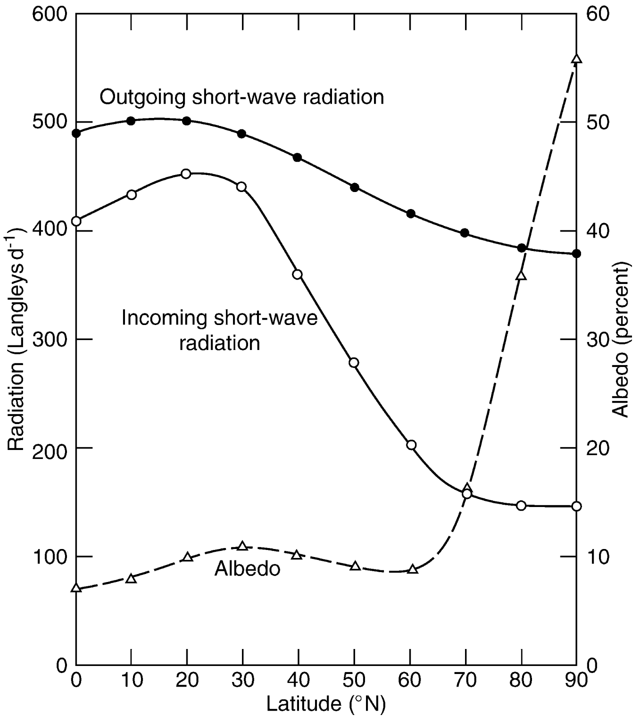


Figure T4 Radiation distribution in the northern hemisphere in relation to latitude (after Houghton, 1954, and Baver et al., 1972).

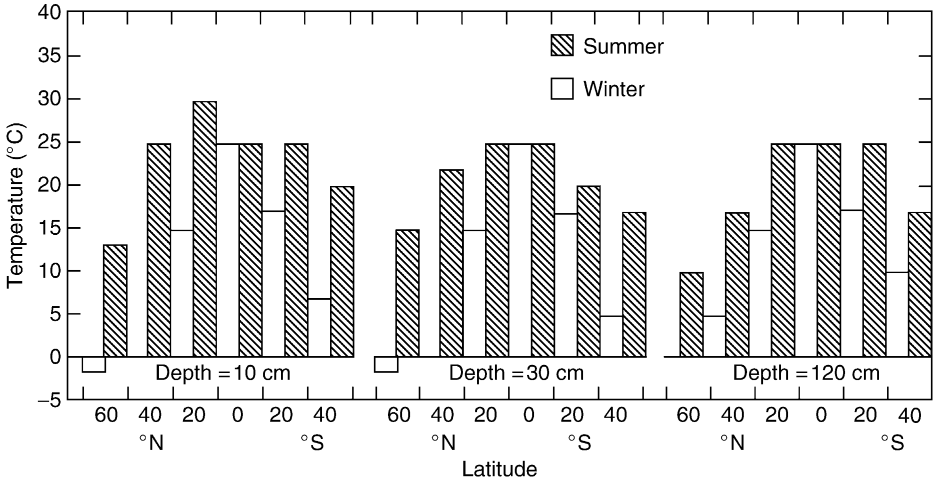


Figure T5 Variations in soil temperature with latitude in the Western Hemisphere (after Baver et al., 1972).

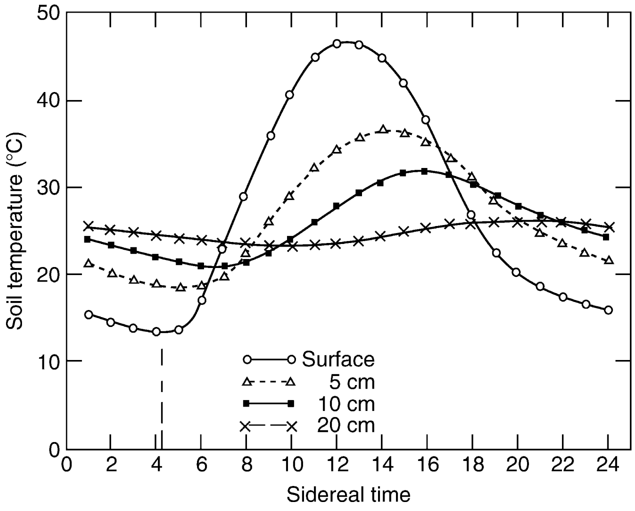


Figure T6 Diurnal variations in temperature in a loam soil (after Yakuwa, 1945).

Table T2 Effect of soil type on soil temperature amplitudes (in °C) at different depths (after Baver et al., 1972)

Soil depth (cm)	Sand	Loam	Clay	Peat
0	40.0	33.6	21.5	23.2
5	19.4	18.5	13.7	13.9
10	12.3	10.7	7.7	5.4
20	4.8	3.0	2.2	0.7
30	1.6	0.7	0.6	0.3
Depth at which temperature amplitude is 0.1 °C (cm)	56.9	46.6	46.8	39.5

used temperature data published by Smith (1932) to show the monthly variation of temperatures in relation to depth. These data also show clearly that the annual temperature amplitudes decrease with depth, and their maximum is delayed the deeper the level of measurement, in resemblance to the diurnal temperature wave changes.

Soil heat flux

The diurnal and annual patterns of soil temperature distributions illustrate the fact that heat is continuously moving into or out of the soil and that thermal energy is continuously redistributed within the soil. Heat is flowing from the warmer regions into the cooler regions of the soil. The diurnal temperature pattern given in Figure T6 shows that during the daytime from some time after sunrise until early afternoon.

There is a warming tendency from the soil surface to a depth of 10 cm, yet during the night-time there is a cooling tendency of the same layers. During the day, heat flows from the surface toward the deeper layers as long as the surface is warmer than the deeper layers, while the reverse occurs at night. The amount and the rate of heat being redistributed within the soil depend on the thermal energy balance, namely, on the soil heat flux at the soil surface and the soil heat capacity and its thermal properties. Table T3 gives examples of annual soil heat fluxes at different latitudes of the northern hemisphere. These data show that there are smaller variations between maximal gain or loss of heat as given by the soil heat flux densities, the nearer the site is to the equator, and that the net heat balance is not zero; there are years when the annual heat flux shows a total gain or loss of heat in or from the soil profile.

Heat conduction

To analyze or estimate the thermal regime of a soil, the soil temperature profiles and the heat flux densities should be analyzed mathematically as a process of heat conduction. This process can be described by *Fourier's Law* of heat conduction given in Equation (1):

$$G = -\lambda \frac{\partial T}{\partial Z} \qquad (1)$$

where G is the heat flux density defined as the quantity of heat transferred during a unit of time across a unit of surface area perpendicular to axis Z. The proportionality factor λ depends on the soil and is termed the *thermal conductivity* (*q.v.*) of the

Table T3 Annual soil heat flux density at the soil surface (cal cm^{-2} month^{-1}) for four different stations (after Van Wijk and deVries, 1963)

Station	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Total
Sodankila (67° N 27° E) 1915–1916	−119	−132	−210	+664	1716	1209	1018	80	−338	−808	−742	−649	+1689
Potsdam (52° N 13° E) 1903	−248	−96	88	321	536	568	384	112	−120	−332	−504	−528	+181
Djakarta (6° S 107° E) 1922	10	38	−5	4	4	−35	20	43	33	10	10	−17	+75
Ikengueng (42° N 108° E) 1931–1932	−224	−119	−20	310	595	606	494	130	−190	−494	−639	−628	−249

Negative values show heat loss from the soil profile.

soil. The term $\partial T/\partial Z$ is called the *temperature gradient*, which is the differential quotient of the temperature T as a function of distance along axis Z in the direction of the larger value of T. If Z is measured in centimeters T in degrees Celsius, and G in cal cm^{-2} s^{-1}, λ is expressed by cal cm^{-1} s^{-1} °C^{-1}. The negative sign indicates that heat flow direction is opposed to the direction of temperature increase. Equation (1) describes the heat conduction process for a specific medium provided several assumptions are kept, e.g., (*a*) the heat flow is unidirectional (in the vertical direction); (*b*) no heat is generated or converted into other forms, like latent heat of vaporization, in the medium; (*c*) the medium is rigid, and no changes in respect to space either as a whole or its constituents occur; and (*d*) the thermal properties of the medium are the same in respect to the various axes, that is, the medium is isotropic.

Since soil is a composite medium, strictly speaking, Equation (1) cannot be applied to soils, but for all practical purposes if an appropriate mean value of λ can be specified, it can be used. The average property of λ depends on the soil constituents, i.e., its mineralogical composition, bulk density, texture, structure, water and air contents, organic matter, and temperature. The λ dependence on these factors will be considered in a subsequent section dealing with thermal conductivity.

Usually the soil's water contents, air contents, and bulk densities change with depth and time; thus the thermal conductivity changes accordingly with depth and time. If the temperature distribution around a soil volume of given λ does not vary with time, then the heat flux G is independent of time; such a situation is called a *stationary state*, or sometimes a *steady-state* condition. If the temperature varies with respect to position within the soil and time, then we have a *nonsteady state condition*, or *transitory state*. This is the common case under natural conditions; thus since Equation (1) cannot describe a transitory state, another equation should be derived to account for the change of temperature with time and depth.

According to the principle of energy conservation, heat should also be conserved. Taking a slab of soil of unit cross-section at depth Z and height dz, a balance of heat flux can be made. Let us denote G_z as the heat flux density at depth z entering the slab, and $G_{z+\mathrm{d}z}$ the heat flux at depth $z + \mathrm{d}z$ leaving the slab; then the difference between G_z and $G_{z+\mathrm{d}z}$ will equal the differential $-\partial G/\partial z\omega \mathrm{d}z$ of heat flux density for the slab or the amount of heat stored in the slab. This is given in Equation (2), which is called the *equation of continuity*, and is an expression for the principle of energy conservation. Equation (2) equates the differential of the heat flux density and the heat storage as expressed by the temperature change, where C represents the *volumetric heat capacity*, defined as the amount required to raise the temperature of a unit volume of the soil by one degree [i.e., it is a unit that equals (cal cm^{-3} of soil)], and t is time.

$$-\frac{\partial G}{\partial z} = C\frac{\partial T}{\partial t} \tag{2}$$

Substituting Equation (1) into Equation (2) gives the generalized heat flow equation

$$C\frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(\lambda\frac{\partial T}{\partial z}\right) \tag{3}$$

In case the soil is homogeneous and isotropic, λ and C are independent of z, and Equation (3) becomes Equation (4), where $\alpha = \lambda/c$ is called the *thermal diffusivity* of the soil and has the dimensions of unit area per unit time (cm^2 s^{-1}).

$$\frac{\partial T}{\partial t} = \frac{\lambda}{c}\frac{\partial^2 T}{\partial z^2} = \alpha\frac{\partial^2 T}{\partial z^2} \tag{4}$$

For a given soil, of which the thermal properties are known, Equation (4) will yield the temperature profiles at any time provided conditions of soil heat flux density at the boundaries of the soil or temperature variations of time dependent are given or assumed.

Since the global radiation fluxes intercepted at the soil surface are of a periodic nature, the soil surface temperature and the soil heat flux density fluctuations have a periodic nature. Their periodic nature cannot, however, be described by simple sine or cosine functions. The soil temperature distribution with respect to depth and time can be described by a general periodic function given by Equation (5)

$$T(z,t) = T_{\mathrm{A}}(z) + \sum_{k=1}^{\infty} T^*_{0,k}\exp\left(-\frac{zk}{\sqrt{2\alpha/\omega}}\right) \sin\left(k\omega t - z\sqrt{k\frac{\omega}{2\alpha}} + \psi_{\mathrm{k}}\right) \tag{5}$$

where $T_{\mathrm{A}}(z)$ and T^*_0 are the average mean temperature as a function of depth and the temperature amplitude at the soil surface ($z = 0$), respectively, ψ_k is the phase constant, and ω is the radial frequency. The radial frequency is defined as $\omega = 2\Pi/P$, where P is the period duration, for example, ω equals $2\Pi/86\,400 = 7.27 \times 10^{-5}$ (s^{-1}) for a diurnal variation and 1.99×10^{-7} (s^{-1}) for an annual variation, and k signifies the harmonics of the variations. Equation (5) is simplified if k is assumed to equal 1 and a value called the *damping depth*,

$$D = \sqrt{\frac{2\alpha}{\omega}} = \sqrt{\frac{2\lambda}{c\omega}}$$

is introduced, as given in Equation (6) where ψ is the phase constant.

$$T(z,t) = T_{\mathrm{a}}(z) + T_0^* \exp\left(-\frac{z}{D}\right) \sin(\omega t - z/D + \psi) \qquad (6)$$

The decrease in temperature amplitude with depth and the shift of phase when it occurs, by a factor $-z/D$ are typical of the propagation of periodic temperature variations in a soil and are found also when λ and C change with depth, but then the damping depth D changes with depth. The damping depth is the depth at which the amplitude decreases to 1/e or 0.37 of its initial value (e is the base of natural logarithms). The physical cause for the damping depth and the reduction of the temperature wave variation with depth is the fact that the soil layers have heat capacity, and thus some heat is either stored or released in the layers when the temperature increases or decreases, respectively. The damping depth is also a function of the temperature variation period, by definition, since it includes the radial frequency. If the diurnal damping depth of the soil is taken as a unit, then the annual damping depth is larger by $\sqrt{(365/1)} \approx 19.1$ times than the diurnal damping depth.

Heat flux densities

The harmonic heat flux density $G(z,t)$ can now be obtained by using the derivative of Equation (6) with respect to z and substituting it into Equation (1); the result is given in Equation (7). Usually the term

$$G(z,t) = -\lambda \frac{\partial}{\partial z}[T_0(z)] + T_0^* \sqrt{\lambda c \omega} \exp\left(-\frac{z}{D}\right) \sin(\omega t - z/D + \psi + \pi/4) \qquad (7)$$

is small and can be neglected. The sine function argument in Equation (7) when compared with that in Equation (6) is advanced by π/4, which means that the heat flux wave precedes the temperature wave by π/4, which is 3 h for a diurnal fluctuation and about 6 weeks for the annual variation (i.e., the time of maximum temperature at a certain depth will occur about 3 h later than that at which the heat flux density will reach its maximum at the same depth). The amount of heat released or stored in the soil or at a given depth is obtained directly by integrating Equation (7) with respect to time intervals and the soil layer depths under consideration.

Modification of the soil thermal regime

The thermal regime of a soil can be modified through changing the energy balance at the soil surfaces by one of the following ways: vegetative cover, various mulches, or changing the thermal properties of the soil surface through *tillage* (*q.v.*) or *irrigation* (*q.v.*).

Vegetative covers change the energy balance by changing the reflectivity, decreasing the amount of global radiation to the soil surface beneath it, and decreasing the heat losses or gains by acting as an insulator. A vegetative cover acts as an insulator above the base soil, which during summer reduces the energy interception at the soil surface and consequently the soil heat flux, as compared with bare soil, thus reducing the soil surface temperature amplitudes and the rate at which the soil warms up. During winter the same cover insulates the soil and decreases heat loss from the cover as compared with bare soil. The vegetative cover also reduces the diurnal variations for a covered soil.

Mulches can affect the thermal regime of the soil by their color, transparency, or thermal conductance. Light colored or transparent mulches will increase the reflection of the global radiation during the periods of low interception angle (i.e., morning or late afternoon hours), while at midday they will transmit the solar energy through them to the soil surface underneath and intercept the outgoing long-wave radiation, thus producing a greenhouse effect of heating up the soil. Mulches having a low thermal conductivity will act as insulators and thus will consequently decrease the heat gain or loss from the soil.

Changes in soil thermal properties

Changing the soil thermal properties can be achieved by changing the soil's water content, its bulk density, or both. Changes such as an increase in soil water content increase the soil's heat capacity and its thermal conductance (i.e., after irrigation or after the winter); therefore the diurnal and annual variations are reduced. That is, the rate of the soil warming is reduced during the morning on a daily basis, or during the spring on an annual basis (Table T4). Decreasing the soil water content, as by *soil drainage* (*q.v.*) or *evaporation* (*q.v.*), will decrease the soil's heat capacity and will raise the soil surface temperature.

Tillage operations usually produce a loose surface layer that acts as a mulch having a lower heat capacity and thermal conductivity as compared to a nontilled soil under equal conditions. Because of its thermal properties, the tilled layer is warmer by day and colder by night, which makes it more vulnerable to radiative frost. The diurnal and annual temperature amplitudes in the tilled layer are larger than those for a nontilled soil. Table T4 gives thermal properties of various soils under different conditions. Tilled soils may be looked upon as being nonhomogeneous soils from the soil structural point of view, and as such it is possible to treat them theoretically as soils made up of two distinct layers as reported in a review

Table T4 Thermal properties of tilled and untilled soils

Soil type	Volumetric water content (cm^3 H_2O/cm^3 soil)	Thermal conductivity λ (cal^{-1} s^{-1} $°C^{-1}$)	Volumetric heat capacity (cal cm^{-3} $°C^{-1}$)	Damping depth (cm)	Source
Sand	0.0	0.7×10^{-3}	0.3	8.0	Van Wijk and Derksen, 1963
	0.2	4.2×10^{-3}	0.5	15.2	(Table 4.2)
Clay	0.2	0.7×10^{-3}	0.3	7.4	Van Wijk and Derksen, 1963
	0.4	3.8×10^{-3}	0.7	12.2	(Table 4.2)
Nontilled sandy soil	0.175	3.4×10^{-3}	0.44	14.6	Van Wijk and Derksen, 1963 (Table 6.2)
Tilled sandy soil	0.125	1.7×10^{-3}	0.31	12.3	Van Wijk and Derksen, 1963 (Table 6.2)

by Van Wijk and Derksen (1963). However, soils are normally nonhomogeneous in their texture, structure, and water content distributions, and hence their thermal properties will vary with depth and time. Under these circumstances simple analysis cannot be performed, and theoretical models become very cumbersome and complicated. Such analytical attempts were made by Lettau (1954, 1962) and more recently, using digital computers, by Wierenga and de Wit (1970).

Amos Hadas

Bibliography

Baver, L.D., Gardner, H.R., and Gardner, W.R., 1972. *Soil Physics*, 4th edn. New York: Wiley, 498 pp.

Houghton, H.G., 1954. On the annual heat balance of the northern hemisphere. *J. Meteorol.*, **11**: 1–9.

Lettau, H.H., 1954. Improved models of thermal diffusion in the soil. *Trans. Am. Geophys. Un.*, **35**: 121–132.

Lettau, H.H., 1962. A theoretical model of thermal diffusion in nonhomogeneous conductors Gerland. *Betr. Geophys.*, **71**: 257–271.

Smith, A., 1932. Seasonal subsoil temperature variations. *J. Agric. Res.*, **44**: 421–428.

Wierenga, P.J., and de Wit, C.T., 1970. Simulation of heat transfer in soils. *Soil Sci. Soc. Am. Proc.*, **32**: 326–328.

Van Wijk, W.R., and Derksen, W.J., 1963. Sinusoidal temperature variation in a layered soil. In Van Wijk, W.R., ed., *Physics of Plant Environment*. Amsterdam: North Holland, pp. 171–209.

Van Wijk, W.R., and de Vries, D.A., 1963. Periodic temperature variation in a layered soil. In Van Wijk, W.R., ed., *Physics of Plant Environment*. Amsterdam: North Holland, pp. 102–143.

Yakuwa, R., 1945. Uber die Bodentemperaturen in dem verschiedenen Bodenarten in Hokkaido. *Geophys Mag. (Tokyo)*, **14**: 1–12.

Cross-references

Conductivity, Thermal
Energy Balance
Evaporation
Heat Capacity
Irrigation
Soil Drainage
Soil Water
Thermodynamics of Soil Water
Tillage

THERMODYNAMICS OF SOIL WATER

The word thermodynamics is derived from θερμοσ (heat) and δυναμις (force, power).

It presents the science of all forms of energy and mass, including entropic ("waste") heat contained in the mass at ambient temperature. The origin of the word suggests that this branch of science deals with both the statics (equilibrium) and the dynamics (non-equilibrium) of energy and mass. Statics ("classical thermodynamics") deals with the state of a system in which no heat or mass transfer occurs (this state is extremely rare in natural soils). It formulates the distribution of the different forms of energy (energy balance) when the system is in equilibrium. Dynamics ("non-equilibrium thermodynamics") deals with transport processes of mass and heat. It formulates the loss of energy (entropy production) in systems in which energy and mass transfer occurs.

"Soil water" is often used interchangeably with the term "soil moisture".

Here we distinguish between the two terms: "soil water" indicating the chemical component H_2O in the soil and "soil moisture" meaning the soil solution. Thermodynamics distinguishes the different chemical components in the system. It deals with the interaction between and transfer of these components and heat.

Equilibrium (classical) thermodynamics of soil water

The birth and early development of thermodynamics is rather confusing. The founders tried to deal with such things as the effectiveness of steam engines (S. Carnot). R. Meyer, who was the first (1842) to publish the equivalence of work and heat, based his conclusion on his observations of the degree of "redness" of human blood. No wonder that thermodynamics had a shaky start. The first mathematical formulation of the "First Law of Thermodynamics" (the law of conservation of energy) came from Helmholtz and Joule in 1847. All these scientists were dealing with systems, in which "action" or transfer occurred. Yet the system had to be at equilibrium and the "changes" had to be infinitesimal small and "reversible" (meaning that the changes can be reversed without any loss of useful energy).

One would expect the First Law of thermodynamics to equate integral values of the different forms of energy. Yet the equations always come in differential form first. At first only "closed" systems were considered, implying that no mass could move into or out of the "system". It was not until J. Willard Gibbs published his two great treatises "*The Equilibrium of Heterogeneous Substances*" (Transactions of the Connecticut Academy, 1876 and 1878), that the "system" was opened up and many of the mysteries of the previous 40 years were clarified. The Transactions of the Connecticut Academy were not widely read in Europe and it was not until C. N. Lewis published his famous book in 1923, twenty years after Gibbs' death, that his works became widely known. In the year of his retirement, Gibbs remarked that during the 30 years of his teaching at Yale University, he estimated that only half a dozen of his students had benefited from his lectures.

We start with the integrated Gibbs Equation:

$$E = U + \Psi = TS - PV + \Sigma_i \mu_i m_i + \Sigma_i \psi m_i \quad (1)$$

where E is the energy of the system, U is the "internal" energy, and Ψ is the energy derived from external force fields.

U consists of three "blobs" of different forms of energy. The first one (TS) is the entropic energy (heat in the system at the ambient temperature, T). The second one ($-PV$) is the energy the system has lost in order to create a volume, V, for itself to exist at the ambient pressure, P. The third one is the sum of the chemical energy of each component (i) in the system, with m_i being the mass of component i and μ_i being the chemical potential of component i. When the mass of component i is electrically charged, the chemical potential is replaced by the electro-chemical potential.

Ψ is derived from external force fields, such as gravity or an electrical or magnetic field. In the gravity field $\Psi = ghm$, g being the gravitational acceleration and h the height above a reference level. If other forms of energy (such as kinetic energy or viscous stress energy) play a role in the transformations of energy, they should be added to Equation (1). Although kinetic and viscous stress energy play a dominant role in energy transformations in the soil solution on the Navier-Stokes scale, on the Darcy scale they are almost always negligible, and will therefore be ignored here.

The “free” energy, G, was defined by Gibbs as

$$G \equiv U - TS + PV = \sum\nolimits_i \mu_i m_i \tag{2}$$

Thus, μ_i is the specific (per unit mass) Gibbs free energy of constituent i.

The first expressions of the First Law were all in differential form, even after Gibbs “opened up” the system:

$$\mathrm{d}U = T\,\mathrm{d}S - P\mathrm{d}V + \sum\nolimits_i \mu_i\,\mathrm{d}m_i \tag{3}$$

This is the differential form of the Gibbs Equation. It is not trivial, because if one carries out the complete differentiation of Equation (1), one finds that, after subtraction of Equation (3) there is a “left-over”:

$$S\,\mathrm{d}T - V\mathrm{d}P + \sum\nolimits_i m_i\,\mathrm{d}\mu_i = 0 \tag{4}$$

This “left-over” is known as the Gibbs-Duhem Equation. From Equation (4) it follows that

$$\mathrm{d}\mu_{\mathrm{W}} = Sm_{\mathrm{w}}^{-1}\,\mathrm{d}T - Vm_{\mathrm{w}}^{-1}\,\mathrm{d}P + \sum\nolimits_{(k \neq w)} m_k m_{\mathrm{w}}^{-1}\,\mathrm{d}\mu_{\mathrm{k}} \tag{5}$$

This is the central equation in classical thermodynamics of soil water. It dictates how the chemical potential (specific Gibbs free energy) of water in the soil changes with temperature, pressure and the composition of the soil solution. The guiding principle is now, that when the system is in equilibrium, $\mathrm{d}\mu_{\mathrm{w}} = 0$, or, the specific Gibbs free energy of water is the same everywhere. Or, as far as water is concerned, there is no transport and no entropy production. In short: the water is at rest. There inverse statement: “when $\mathrm{d}\mu_{\mathrm{w}} = 0$, the water is at rest” is not necessarily true and is not a fundamental principle of thermodynamics. It is possible that the last two terms of the RHS of Equation (5) (temporarily) balance each other, making $\mathrm{d}\mu_{\mathrm{w}} = 0$, but both water and the solute are on the move, and entropy is being produced. This is possible when “leaky” semi-permeable membranes are present. Heavy clay soils are excellent examples of “leaky” semi-permeable membranes.

Thus, the concept of the “total” potential of soil water (the sum of all the component potentials) is not very useful. When the whole system is at rest (complete equilibrium), the total potential of the water is equal everywhere in the system. But, when the total potential of the water is equal everywhere, the water is not necessarily at rest. The gradient of the total potential is not the appropriate driving force in the flux equation of water, the Darcy Equation. This will become clearer in the section on non-equilibrium thermodynamics.

The apprentice in thermodynamics often asks him/herself: “What is the practical use of all this?” Thermodynamics is still not a coherent, comprehensive science. Developments are still happening haphazardly. Some scientists such as Clifford Truesdell have complained bitterly about the inconsistencies and the lack of mathematical rigor, using words like “*thermodynamics was approached through detours in the fog of word-play* …”.

Only two of the many practically useful results will be discussed here.

The tensiometer (and the pressure membrane apparatus)

Early scientists, working on the thermodynamics of soil moisture, such as L. A. Richards, G. H. Bolt and M. J. Frissel, of course realized that water in the soil is present as part of the soil solution. The soil solution contains dissolved salts and ions. In addition, it contains counter-ions, a surplus of cations acting to counter-balance the surplus of electrons present in the lattices of clay particles. This “electrical double layer” acts as an osmometer and the counter-ions cause a volume element of the solution, close to a clay surface, to carry a volume charge. In the presence of an electrical field this gives the soil solution an additional form of energy. In addition to the above, there are microforce fields acting on the solution in close proximity of solid surfaces (London-Van der Waals forces). All this implies that Equation (5) should contain a few more terms if the thermodynamic system were to be chosen as an element of the soil solution on the Navier-Stokes scale. If, however, the thermodynamic system is chosen on the Darcy scale, these terms do not require individual attention.

The first requirement in Soil Physics is to formulate the hydrostatics of soil water. This requires the establishment of the characteristic relationships for the water at rest. There are no “membranes” in nature or in the laboratory that are semi-permeable to heat. Thus, when a system is brought to equilibrium the temperature will be the same everywhere. The energy level in the external force fields, such as gravity, can easily be dealt with separately. In order to measure the energy level of soil water derived from internal force fields (menisci, electrical double layers, London-Van der Waals forces), it is now advantageous to bring the soil solution in equilibrium with a compartment containing a solution that reflects the composition of the soil solution. In contrast, one may also bring the soil solution in equilibrium with a compartment containing pure water. This is possible by using a membrane that is “perfectly” semi-permeable to all dissolved materials in the soil solution. By using a perfect osmometer and measuring the hydrostatic pressure in the osmometer, one measures the energy level of the soil water resulting from all internal force fields plus all dissolved materials (the total osmotic pressure of the soil solution). In the former case, using a perfectly “leaky” membrane, such as the cintered ceramic cup (tensiometer cup) or a Visking membrane in a pressure plate apparatus, the solution inside the compartment (tensiometer cup) reflects the composition of the “free salts” in the soil solution and will show the “equilibrium” solution. By measuring the hydrostatic pressure in the tensiometer, one measures the energy level of all internal force fields (including electrical double layers), but excluding the effect of the free salt. This energy level is called the matric potential. The counter-ions cannot equilibrate in the tensiometer cup. They act as internal mini-osmometers and can be considered part of the matrix (the solid phase of the soil). Because most soils are “leaky” in terms of membrane properties, the water in the soil moves as a solution. It is therefore that the gradient of the matric potential is the principal driving force on the soil water (in addition to the force of the gravitational field). The semi-permeable properties of clay soils, causing osmotic pressure differences to drive the water, will be dealt with in the section “Non-equilibrium thermodynamics” (see below). The action of osmotic pressure gradients will then be formulated as “capillary” osmosis and the semi-permeable properties of the soil will be evaluated by a “reflection coefficient”.

The Maxwell relations and their use in the hydrostatics of swelling soils

Complaints about the lack of mathematical rigor in thermodynamics find their origin in the birthplace of thermodynamics: a closed pot on a bench in a chemistry laboratory. Temperature and pressure were allowed to change in steps, ΔT and ΔP, but only in small steps, δT and δP. Entropy production was not allowed and therefore the steps had to be infinitesimal small, $\mathrm{d}T$ and $\mathrm{d}P$. This began to look like differentials. In differential form, the Gibbs Equation can be subjected to cross-differentiation. This leads to the Maxwell relations. Many such Maxwell relations can be formulated. Many more can be found after performing Legendre transforms on the Gibbs free energy. Most of these Maxwell relations are pretty useless, but occasionally one finds a gem.

As an example we present here a Maxwell relation for shrinking soils. For many decades soil scientists have searched for an expression for the differential of the matric potential (tensiometer pressure), p, with respect to the differential of the load (or overburden) pressure, P. Here, both the dependent and the independent variable are intensive variables. The appropriate Maxwell relation shows that the sought-after expression is the differential of the void ratio (volume of voids per volume of solids), with respect to the differential of the moisture ratio (volume of water per volume of solids), at constant load pressure, P. Here, both the dependent and the independent variable are extensive variables.

Thus:

$$\begin{aligned} &\mathrm{d}p(\mathrm{d}P)^{-1} \text{ at constant } m_{\mathrm{w}}(m_{\mathrm{solids}})^{-1} \\ &\quad = \mathrm{d}e(\mathrm{d}\vartheta)^{-1} \text{at constant } P \end{aligned} \tag{6}$$

where e is the void ratio and curly *theta* is the moisture ratio.

This means that one can predict the change in the tensiometer reading upon loading from the slopes of the shrinkage lines for different values of P. Because the shrinkage lines for different values of P are nearly parallel, one only needs to measure the unloaded shrinkage line in order to predict how the tensiometer reading changes upon loading (Groenevelt and Grant, 2001).

Non-equilibrium thermodynamics of soil water

The thermodynamic "system" is now chosen to be a unit volume element in the soil solution. All the extensive variables are expressed per unit volume. Subsequently, each of the terms of the differential form of the Gibbs Equation (Equation (3)) is written as a differential with respect to time.

The mathematical sloppiness of classical thermodynamics disappears once the terms of the differential form of the Gibbs Equations are transformed into proper time differentials and one enters the realm of non-equilibrium thermodynamics.

Next, for each of the terms separately, an appropriate conservation (continuity) equation is constructed. The general form of such a conservation equation shows that the change of the content of the entity of concern, with time, is equal to the negative of the divergence of the flux of that entity (inflow minus outflow), plus or minus one or more source or sink terms. Thus, for the entropic energy term one writes:

$$\mathrm{d}(SV^{-1})\mathrm{d}t^{-1} = -\mathrm{div}\, j_{\mathrm{s}} + \sigma \tag{7}$$

where SV^{-1} is the entropy per unit volume of solution; j_{s} is the flux of entropy and σ is the entropy production term. This latter term plays a central role in non-equilibrium thermodynamics. If all the processes and forms of energy are accounted for, and nothing is counted twice, and all algebra is carried out correctly, then the entropy production term is non-negative. As the absolute temperature is always positive, the energy dissipation term, $T\sigma$, must also be non-negative. When σ, and thus $T\sigma$, is zero, the system is at equilibrium and nothing moves. If anything moves, then entropy is produced, and σ and $T\sigma$ are positive. Energy is being dissipated. That is, energy is transformed from useful energy to waste energy (= heat at the ambient temperature). This is the "Second Law of Thermodynamics".

As the first term on the RHS of Equation (3) is already multiplied by T, one finds, after replacing the time differentials of the different terms in Equation (3) by the RHS of their appropriate conservation equations, the product $T\sigma$ as the source term of entropy conservation equation. After all the appropriate substitutions are made, the term $T\sigma$ is singled out (written explicitly) and the equation is then called "the (energy) dissipation function".

On the RHS of the dissipation function one usually finds the sum of a number of products of fluxes and forces. One may reshuffle these forces and the fluxes, under the strict principles that the rules of algebra are carried out correctly and that nothing is forgotten or counted double.

The resulting complete expression for the energy dissipation is then the sum of products of fluxes and conjugated forces.

$$T\sigma = -j_{\mathrm{q}}\,\mathrm{grad}\,T - j^{\mathrm{V}}\mathrm{grad}\,H - j^{\mathrm{D}}\mathrm{grad}\,\pi - j^{\mathrm{E}}\mathrm{grad}\,E \tag{8}$$

where j_{q} is the caloric (Fourier) heat flux; j^{V} is the (Darcy) flux of the soil solution; j^{D} is the (Fick) diffusion flux and j^{E} is the electric current (usually indicated by capital I); grad π is the gradient of the osmotic pressure and grad E is the gradient of the electrostatic potential.

One recognizes the primary forms of dissipation, viz. the dissipation of heat energy, pressure energy, mixing/unmixing energy, and electrical energy.

If one now constructs simple linear homogeneous transport equations relating a flux to its conjugated flux (the one that is occurring in the same product), one gets, respectively, the transport equations of Fourier (1822), Darcy (1856), Fick (1855) and Ohm (1827).

Physics and chemistry have long recognized that "coupled" transport can occur. Examples of such coupled transport processes are osmosis, electro-osmosis, thermo-osmosis, the Peltier effect, etc. A coupled transport process takes place when a flux arises due to a non-conjugated force (that is a force that occurs in a product other than the one in which the flux of concern occurs).

Non-equilibrium thermodynamics now postulates that each flux, occurring in the energy dissipation function is a linear, homogeneous (no intercept) function of all forces occurring in the same equation for the total energy dissipation. Thus:

$$\begin{aligned} j_{\mathrm{q}} &= -L_{\mathrm{TT}}\,\mathrm{grad}\,T - L_{\mathrm{TV}}\,\mathrm{grad}\,H - L_{\mathrm{TD}}\,\mathrm{grad}\,\pi \\ &\quad - L_{\mathrm{TE}}\,\mathrm{grad}\,E \end{aligned} \tag{9}$$

$$\begin{aligned} j^{\mathrm{V}} &= -L_{\mathrm{VT}}\,\mathrm{grad}\,T - L_{\mathrm{VV}}\,\mathrm{grad}\,H - L_{\mathrm{VD}}\,\mathrm{grad}\,\pi \\ &\quad - L_{\mathrm{VE}}\,\mathrm{grad}\,E \end{aligned} \tag{10}$$

$$\begin{aligned} j^{\mathrm{D}} &= -L_{\mathrm{DT}}\,\mathrm{grad}\,T - L_{\mathrm{DV}}\,\mathrm{grad}\,H - L_{\mathrm{DD}}\,\mathrm{grad}\,\pi \\ &\quad - L_{\mathrm{DE}}\,\mathrm{grad}\,E \end{aligned} \tag{11}$$

$$\begin{aligned} j^{\mathrm{E}} &= -L_{\mathrm{ET}}\,\mathrm{grad}\,T - L_{\mathrm{EV}}\,\mathrm{grad}\,H - L_{\mathrm{ED}}\,\mathrm{grad}\,\pi \\ &\quad - L_{\mathrm{EE}}\,\mathrm{grad}\,E \end{aligned} \tag{12}$$

The diagonal (backward slash) terms of the right hand sides of Equations (9) to (12), with the L_{KK} coefficients, represent the "straight", well-known transport processes, and are known as the "laws" of Fourier (1822), Darcy (1856), Fick (1855), and Ohm (1827), respectively. All other (off-diagonal) terms represent coupling processes, and their coefficients, L_{KM}, are known as coupling coefficients. They come in pairs of twins, and are located symmetrically across the diagonal. They represent all possible coupling phenomena that can occur, in this case in the presence of the four driving forces occurring in this scheme.

If the energy dissipation equation is complete and all algebra has been carried out correctly, then the two twin (cross) coefficients are equal:

$$L_{\mathrm{KM}} = L_{\mathrm{KM}} \tag{13}$$

Thus the matrix of coefficients in Equations (9) to (12) is symmetrical. In the above matrix there are six of these pairs of equal twins. These equalities are known as the *Onsager Reciprocal Relations* (ORRs).

The fundamental value of the procedure outlined above is that all possible forms of energy dissipation are accounted for, even if they have never been observed.

For Soil Physics they are extremely important and useful. Often, one of the cross coefficients is much more difficult to measure than the other. So, the ORR provides a route around the difficulty. If both cross coefficients can be measured, then the observed equality is a warranty of the correctness of the observations.

After the merciless denigration of the Onsager Reciprocal Relations by Truesdell, soil physicists should rise up and except the validity and the great practical usefulness of ORRs. The framework of the matrix of coefficients in the Equations (9) to (12), is comparable, in nature but not quite in stature, to the periodic system as proposed by Mendeleev. For his systematic framework Onsager received the Nobel Prize in Chemistry (1968), but Mendeleev never received that prize. The first such prize in chemistry was awarded to Jacobus van't Hoff, even though Mendeleev was still alive. The refusal by the Nobel Committee to award the price to Mendeleev continued until he died in 1907.

The framework makes it possible, in case the measurement of a certain coefficient is difficult or expensive, to measure its twin, which often appears to be easier or cheaper to measure.

When building models for transport processes in clay soils, e.g., based on electrical double layer theory, one can use these ORRs to verify the correctness of the model: if the cross-coefficients are not equal, the researcher can be assured that somewhere he/she made a mistake.

The actual occurrence of a coupled transport process always relies on some kind of a selection mechanism, such as a mechanism that can select between molecules of different chemical nature, e.g., water and salts, or a mechanism that can select between "hot" and "cold" molecules, e.g., a liquid/gas interface. It should be noted that convection (advection) is never a selection mechanism.

The coupled transport processes are discussed here in pairs of twin phenomena, and indicated by their (equal) coefficients:

- L_{VT} (thermo-osmosis) and L_{TV} (reverse thermo-osmosis or thermo-filtration)
  Both these phenomena are very common in soils. The transport of water due to a temperature gradient and the transport of heat due to a water potential gradient are very important transport processes, which are occurring, constantly in natural soils. In unsaturated soil they are due to evaporation and condensation (the selection mechanism here is the heat of vaporization/condensation). In saturated soils the magnitude of these phenomena is very small (the selection mechanism is now the heat of wetting). In frozen soils they are caused by freezing and melting (the selection mechanism here is the heat of freezing/melting and solidification/sublimation). These phenomena as well as the values of the two coefficients are discussed in the literature by Kay and Groenevelt. Presently, the most widely used theory to describe simultaneous heat and mass transfer in soils is still the mechanical theory of Philip and de Vries, stemming from the year 1957. That theory is not based on thermodynamics, but on mechanical considerations. The consequence is that the Onsager reciprocity is lost. An interesting comparison between the mechanistic and the thermodynamic theory has been presented by Raats. Recently, the mechanistic theory has been revised by Miller, who, in great detail, built mechanical models for the two cross coefficients, and came to the conclusion that they "*are identical in accord with Onsager's reciprocity principle*". It is of interest to note that Miller concludes his paper with, quote: "*Raats's (1975, p. 942) summary statement has a familiar ring: 'The main point is that for Onsager reciprocal relations to have any meaning they should be based on physical considerations.'* Raats' statement is truly remarkable, because thermodynamics are based on energy dissipation, always leading to the ORR, whereas the physical model of Philip and de Vries did not lead to the equality of the cross coefficients. His statement has a Truesdellian ring. What Raats is trying to say is: "If one wishes to take advantage of the Onsager Reciprocal Relations, they are for the taking, but, if one does not, so what?"
- L_{VD} (osmosis, also called capillary osmosis) and L_{DV} (reverse osmosis or salt sieving)
  These phenomena are very common in soils. The magnitude is directly related to the clay content of the soil. (The selection mechanism lies with the electrical double layer). Clay particles expel negative ions and therefore, they expel dissociated salts (negative adsorption). The longstanding conflict as to whether the osmotic pressure (potential) should be added to the hydraulic potential of water to produce the "total" potential of water, the gradient of which then serves as the driving force on the water is here resolved. As the value of L_{VD} is almost always smaller then the value of L_{VV} (except for a perfectly semi-permeable membrane), the concept of the "total" potential is useless. The negative of the ratio L_{VD} over L_{VV} is known as the *reflection coefficient*.
- L_{VE} (electro-osmosis) and L_{EV} (reverse electro-osmosis or streaming current)
  These electrokinetic phenomena also find their cause in the existence of electrical double layers. The most commonly observed result of the effects is the streaming potential in clay soils.
- L_{TD} and L_{DT} (thermo-diffusive processes)
  In the literature these phenomena are known as, respectively, the Dufour (1872) effect and the Soret (1880) effect. The magnitude of these phenomena in soils is small, but their occurrence is quite probable.

- L_{TE} and L_{ET} (thermo-electric processes)
  In the literature these phenomena are known as, respectively, the Peltier (1834) effect and the Seebeck (1826) effect. The magnitude of these phenomena in soils is small, but their occurrence is quite likely.
- L_{DE} (electrophoresis, or sedimentation potential) and L_{ED} (diffusion current, or sedimentation current)
  These phenomena, together with osmosis and reverse osmosis, electro-osmosis and streaming current are extensively discussed in the literature by Elrick and Groenevelt.

They calculated the magnitude of all six coefficients on the basis of electrical double layer theory. A comprehensive review of all electrokinetic phenomena in different branches of science and in industry was presented by Rastogi et al. (1993).

Modern development

The branch of science called "Non-equilibrium Thermodynamics" is now split into two sub-branches. The first one, dealt with above, is now called "Linear Non-equilibrium Thermodynamics". Indeed all transport equations presented above are linear. This sub-branch of science deals with processes that are "not far from equilibrium". The second sub-branch is now called "Nonlinear Non-equilibrium Thermodynamics" (Stratonovich, 1992). Its great proponent is Ilya Prigogine, who received the Nobel Prize in Chemistry for his work in 1977. This sub-branch of science deals with "violent" processes ("far away from equilibrium"), such as Liesegang rings and atom bombs. The natural transport processes in the soil are never "violent", and, as long as Darcy's Law (one of the primary energy dissipating processes) holds, all coupling processes fall in the park of "not far from equilibrium". However, if there are cases where Darcy's Law breaks down and turns into the non-linear Forchheimer Equation (that is when the water in the soil becomes turbulent), soil physicists may have to turn their attention to this latest branch of thermodynamics.

Pieter H. Groenevelt

Bibliography

Bolt, G.H., and Frissel, M.J., 1960. Thermodynamics of soil moisture. *Neth. J. Agric. Sci.*, **8**: 57–78.

Gibbs, J.W., 1961. *The scientific papers of J. Willard Gibbs*, *Vol. I. Thermodynamics.* New York: Dover, 434 pp.

Glansdorff, P., and Prigogine, I., 1971. *Thermodynamic Theory of Structure, Stability and Fluctuations.* London: Wiley.

Groenevelt, P.H., 1971. Onsager's reciprocal relations. *Search*, **2**: 264–267.

Groenevelt, P.H., 1979. Transport Processes. In Fairbridge, R.W., and Finkl, C.W., eds., *The Encyclopedia of Soil Science*, Part 1, pp. 578–581.

Groenevelt, P.H., and Bolt, G.H., 1969. Non-equilibrium thermodynamics of the soil-water system. *J. Hydrol.*, **7**: 358–388.

Groenevelt, P.H., and Bolt, G.H., 1972. Water retention in soil. *Soil Sci.*, **113**: 238–245.

Groenevelt, P.H., and Elrick, D.E., 1976. Coupling phenomena in saturated homo-ionic montmorillonite; II. Theoretical. *Soil Sci. Soc. Am. J.* **40**: 820–823.

Groenevelt, P.H., and Grant, C.D., 2001. Re-evaluation of the structural properties of some British swelling soils. *Eur. J. Soil Sci.*, **52**: 469–477.

Groenevelt, P.H., and Grant, C.D., 2002. Curvature of shrinkage lines in relation to the consistency and structure of a Norwegian clay soil. *Geoderma*, **106**: 235–245.

Groenevelt, P.H., and Kay, B.D., 1974. On the interaction of water and heat transport in frozen and unfrozen soils: II. The liquid phase. *Soil Sci. Soc. Am. Proc.*, **38**: 400–404.

Groenevelt, P.H., Grant, C.D., and Semetsa, S., 2001. A new procedure to determine soil water availability. *Aust. J. Soil Res.*, **39**: 577–598.

Katchalsky, A., and Curran, P.F., 1965. *Non-Equilibrium Thermodynamics in Biophysics.* Cambridge: Harvard University Press.

Kay, B.D., and Groenevelt, P.H., 1974. On the interaction between water and heat transport in frozen and unfrozen soils: I. Basic theory: The vapor phase. *Soil Sci. Soc. Am. Proc.*, **38**: 395–400.

Miller, R.D., 1998. Capillary thermomechanics in serially porous media with implications for randomly porous media. *Water Resources Res.*, **34**: 1361–1371.

Philip, J.R., and de Vries, D.A., 1957. Moisture movement in porous materials under temperature gradients. *Eos Trans. AGU*, **38**: 222–232.

Pippard, A.B., 1964. *The Elements of Classical Thermodynamics*. Cambridge: Cambridge University Press.

Raats, P.A.C., 1975. Transformation of fluxes and forces describing the simultaneous transport of water and heat in unsaturated porous media. *Water Resources Res.*, **11**: 938–942.

Rastogi, R.P., Srivastava, R.C., and Singh, S.N., 1993. Nonequilibrium thermodynamics of electrokinetic phenomena. *Chem. Rev.*, **93**: 1945–1990.

Stratonovich, R.L., 1992. *Nonlinear Nonequilibrium Thermodynamics I.* Berlin: Springer, p. 361.

Truesdell, C., 1968. In Parkus, H., and Sedov, L.I., eds., *Irreversible Aspects of Continuum mechanics and Transfer of Physical Characteristics in Moving Fluids.* Vienna: Springer, P. 373.

Cross-references

Flow Theory
Permeability
Water Movement
Wetting Front

THERMOGENIC

Used of soils in which a relatively high temperature (as in tropical and sub-tropical climatic regimes) has been responsible for prominent characteristics of the soil. May also be used of soils buried beneath, and weakly metamorphosed by volcanic deposits, as in the illustration of a baked paleosol from central France (Figure T7).

Figure T7 Baked soil from the slopes of the extinct Cantal volcano, Col d'Aulac, central France. The overlying rock is a columnar basalt originally emplaced as a lava flow. Credit: Pierre Larroque.

Bibliography

Chesworth, W., Dejou, J., de Kimpe, C., Macias Vasquez, F., Cantagrel, J-M., Larroque, P., Garcia Paz, C., Rodeja Garcia, E., and Quantin, P., 1985. Etude de paléosols rouges developpés sur les basaltes miocenes du Massif Central francais. Cahiers O.R.S.T.O.M., sèr. Pedologie, **20**: 189–208.

THERMOSEQUENCE

A sequence of soils in which the dominant factor accounting for any physical, chemical and biological differences has been the local variation of temperature under which under which the sequence has developed. Not easily distinguishable from climosequence.

Cross-reference

Factors of Soil Formation

THIONIC OR SULFIDIC SOILS

Definition and classification

Thionic soils (FAO, 2001), re-labelled sulfidic soils in IUSS Working Group WRB (2006), are characterized by the presence of either a sulfuric or thionic horizon or sulfidic materials. Sulfidic material or deposit is understood to be that material containing high levels of reduced forms of S (in general >0.75%), a low content of calcium carbonate (3 times less than S by weight) and pH in H_2O (1:1) >4.0. Identification of these soils can be carried out by oxidation of soil samples with hydrogen peroxide. If after this treatment the pH decreases by 0.5 units or more, the presence of a layer of sulfidic material in the soil is assumed. These materials contain reduced forms of S, and occur in soils subjected to prolonged periods of flooding, which result in anoxic conditions (Figure T8).

In contrast, the sulfuric or thionic horizon is formed when sulfidic material becomes exposed to oxidizing conditions. The oxidation of sulfidic material involves an acidifying process, so that in the sulfidic horizon the pH_{H2O} may reach values lower than 4.0, and mottled areas or layers of yellow or yellowish brown color may occur due respectively to the presence of jarosite or schwertmanite. For this to occur, the acid released by the oxidation of the reduced forms of S (mainly pyrite) overcome the neutralizing capacity of the soil, resulting in an hyperacid soil with free inorganic acids. The presence of high levels of calcium carbonate may neutralize this acidity, thereby avoiding the formation of a sulfidic horizon.

In the criteria of the World Reference Base for Soil Resources (IUSS-ISRI-FAO, 2006), the term Thionic is added to describe those groups of soils that possess sulfidic material or a thionic horizon. This is a very important edaphic feature for the WRB and the qualifier thionic occupies the top position in the ranking of the suffix qualifiers of Fluvisols, Gleysols and Histosols. Podzols with horizons of thionic nature have also recently been found in sandy deposits on the coast of São Paulo (Brazil) (Restinga ecosystem) and thus inclusion of the qualifier thionic in the Podzol group has been proposed (Haenel et al., 2004). As regards Soil Taxonomy (Soil Survey Staff, 1999) the thionic character of the soils is incorporated at the Great Group level, when it is manifested within the upper 50 cm and at the Subgroup level when manifested at lower depths. However, unlike the WRB, Soil Taxonomy distinguishes between soils containing sulfidic material and those with a sulfuric horizon. Thus in the entisols, suborder aquents, only the presence of sulfidic material is recognized. If this is found within the upper 50 cm, the soil belongs to the Great Group sulfaquents, whereas if it occurs lower in the soil, the thionic character is included at the Subgroup level (sulfic endoaquents, sulfic fluvaquents, sulfic hydraquents). When a sulfuric horizon develops in a soil, it is then considered within the order of the Inceptisols, and appears within the Great Group of the sulfaquents if the sulfuric horizon appears within the upper 50 cm. If the horizon is present at a greater depth or the soil only contains sulfidic material this is described at the Subgroup level (sulfic cryaquepts, sulfic endoaquepts). Other soils such as Histosols or gelisols may also contain thionic material. In the Histosols this is included as a criterion at the Great Group level, differentiating between the presence of sulfidic material (sulfosaprist, sulfohemist) and a sulfuric horizon (sulfihemist, sulfisaprist). In the gelisols this is applied at a lower taxonomic level (sulfuric aqueothels, sulfuric aquiturbels).

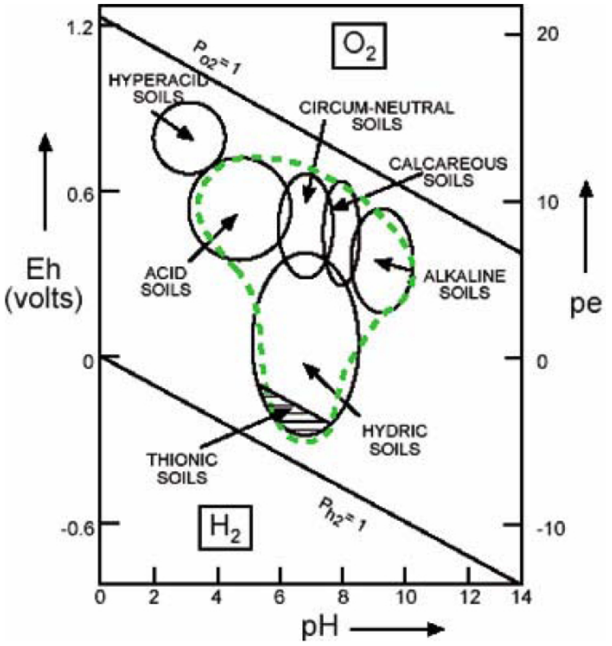


Figure T8 Eh-pH conditions of thionic or sulfidic soils. The formation of sulfidic material requires strongly reducing conditions and slight

Process of formation

The synthesis and accumulation of sulfidic material occur under anoxic conditions, in which the metabolism of organic matter is carried out via sulfate-reducing bacteria. This requires the simultaneous presence of a high content of sulfate, reactive Fe oxyhydroxides and labile organic matter. Thionic or sulfidic soils are therefore usually associated with saline or brackish coastal environments, such as salt marshes or mangrove swamps.

Prolonged flooding prevents the diffusion of oxygen in the part of the soil saturated with water. More specifically, the rate of diffusion of oxygen in a slow moving aqueous environment is of the order of 10 000 times slower than in a gaseous environment. As a result, the molecular oxygen in the edaphic system is used up rapidly, thereby obliging microorganisms to use other substances or elements as oxidants. The energy yield from the oxidation of organic matter depends on the type of oxidant used by the microorganisms, according to Reactions (1) to (5).

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$
$$\Delta G^0 = -479\ \mathrm{kJ\ mol^{-1}} \tag{1}$$

$$5CH_2O + 4NO_3^- \rightarrow CO_2 + 2N_2 + 4HCO_3^- + 3H_2O$$
$$\Delta G^0 = -453\ \mathrm{kJ\ mol^{-1}} \tag{2}$$

$$CH_2O + 2MnO_2 + 3CO_2 + H_2O \rightarrow 2Mn^{2+} + 4HCO_3^-$$
$$\Delta G^0 = -349\ \mathrm{kJ\ mol^{-1}} \tag{3}$$

$$CH_2O + 4Fe(OH)_3 + 7CO_2 \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O$$
$$\Delta G^0 = -114\ \mathrm{kJ\ mol^{-1}} \tag{4}$$

$$CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$$
$$\Delta G^0 = -77\ \mathrm{kJ\ mol^{-1}} \tag{5}$$

Aerobic oxidation is clearly the most energetically favorable process, whereas sulfate reduction is the least favorable. The different oxidants are therefore used sequentially so that sulfate reduction is initiated in the soil after other oxidants such as nitrates and the most bioavailable forms of Mn and Fe oxides have been used up. Sulfate reduction is carried out by microorganisms that are strict anaerobes (*Desulfovibrio* spp.), and may occur within a wide range of pH (4.2 to 10) and Eh (−500 to 110 mV). However, it appears that the optimal pH is close to neutral and optimal values of Eh occur between −150 and 75 mV (Figure T8).

Sulfate reduction involves the release of sulfide into the interstitial water (Reaction (5)). The formation and accumulation of sulfidic material in the soil occurs as a consequence of the reaction of sulfide with different forms of Fe. The reactions result in the formation of Fe sulfides (mackinawite, greigite, pyrite) and elemental sulfur, which are the main constituents of sulfidic material.

Characterization of the main iron sulfide minerals

Various Fe sulfides (amorphous Fe, mackinawite, greigite and pyrite) as well as elemental sulfur are included in sulfidic material.

Mackinawite (FeS)

Mackinawite (FeS) is an iron sulfide of tetragonal structure, which is deficient in sulfur and has a composition that ranges between $FeS_{0.9}$ and $FeS_{0.95}$. Mackinawite, along with greigite, is considered as a metastable Fe sulfide that is a precursor of pyrite. Some authors place its stability field below the limit of stability of pyrite, requiring strongly reducing (Eh < −250) and alkaline environments (Figure T9) (Butler and Rickard, 2000).

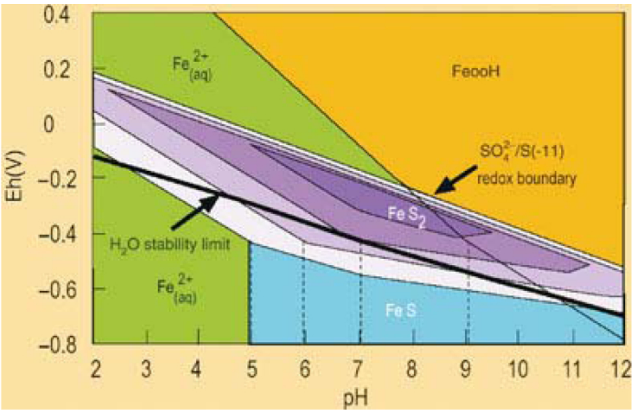


Figure T9 Eh-pH diagram for the Fe–S–H_2O system at 25 °C (modified from Butler and Rickard, 2000). The formation of pyrite is kinetically related to the degree of supersaturation ($IAP \gg K_{sp}$). The diagram represents the increase in the stability field of pyrite as the total concentration of sulfide and Fe in the interstitial water increases. It can be observed that the stability field of pyrite is located very close to the $SO_4^{2-}/S(-II)$ boundary (suboxic environments) and basically expands towards acidic conditions. Strongly reduced and alkaline conditions appear to favor the stability of Fe^{II} monosulfide.

$$HS^- + Fe^{2+} \rightarrow Fe(SH_2) \rightarrow FeS + H_2 \tag{6}$$

$$6FeOOH + 9H_2S \rightarrow 6FeS + 3S^0 + 12H_2O \tag{7}$$

$$FeS + S^0 \rightarrow FeS_2 \tag{8}$$

Greigite (Fe_3S_4)

Greigite constitutes a magnetic thiospinel iron sulfide, containing Fe and S in different oxidation states [Fe^{3+} (Fe^{3+}, Fe^{2+}) (S^0, S^{2-})], which indicates that its formation from mackinawite requires the presence of an oxidant (O_2, S^0, Fe oxides). It has generally been observed that in soils with a stable presence of Fe sulfides, the ion activity product (IAP) is supersaturated at the surface with respect to greigite, whereas at depth – where the environment becomes anoxic – it is supersaturated with respect to Fe monosulfides (Figure T10). Greigite is also considered as another precursor of pyrite, according to Reactions (9) and (10).

$$3FeS + S^0 \rightarrow Fe_3S_4 \tag{9}$$

$$Fe_3S_4 + 2S^0 \rightarrow 3FeS_2 \tag{10}$$

The presence of mackinawite and greigite can be recognized because they confer the soils with a bluish black color (5BG 2/1, according to the Munsell Soil Color Chart). They can also be identified by adding a dilute solution of hydrochloric acid. These Fe sulfides are soluble in acid environments and release hydrogen sulfide (H_2S), which is easily identifiable by its characteristic odor. Mackinawite, greigite and amorphous FeS are considered to be the main components of the so-called AVS (acid volatile sulfide) fraction.

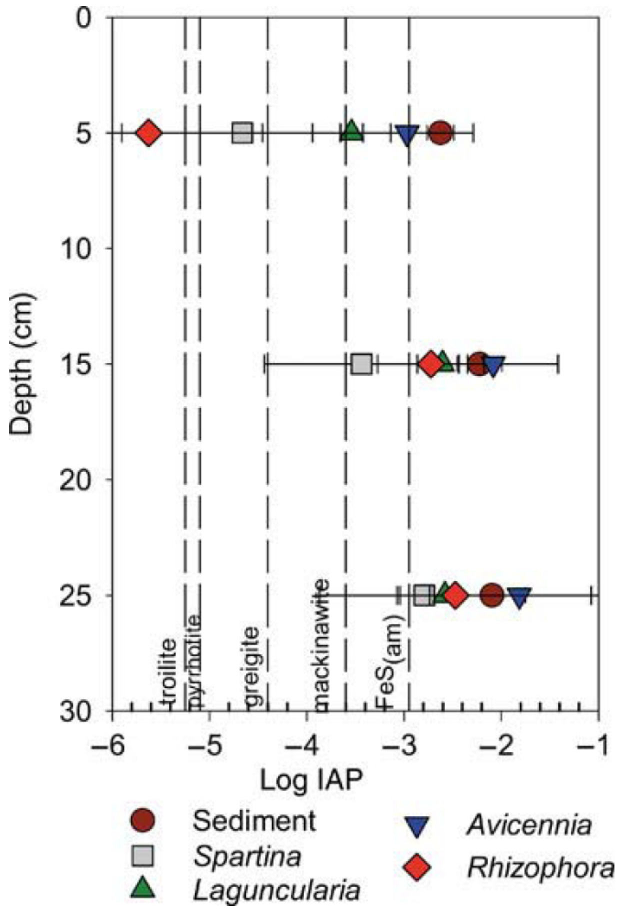


Figure T10 Comparison between *IAP*s and sulfide solubility products for different soils from a Brazilian mangrove swamp (*vertical dashed lines*, based on data from Davison, 1991). The results show that the interstitial water is saturated by different Fe sulfides. The different soils show a similar situation at depth – the interstitial water is basically saturated by amorphous FeS and mackinawite. The differences in the uppermost layer of the soil should be interpreted as the result of the combined effects of the plants and physiographic position on the geochemical conditions of the soil. The formation of greigite (Fe_3S_4) appears to be favored at the surface, where the degree of aeration is greater and the conditions more acidic (Otero et al., 2007).

Pyrite (FeS_2)

Pyrite is the most thermodynamically stable of the Fe sulfides (Berner, 1967) and the most common form of sulfur in both sediments and rocks, usually representing more than 90% of the sulfidic material. The reaction $FeS + S^0 \rightarrow FeS_2$ has been proposed by different authors as a possible route of synthesis (Goldhaber and Kaplan, 1974; Berner, 1970). However, it is generally accepted that the solid-solid reaction is too slow a process (years) to explain satisfactorily the rapid formation of this mineral in soils and recent sediments. Other pathways have been suggested in recent studies.

1. Polysulfide pathway:
   The presence of polysulfides in the interstitial water of soils and sediments has been demonstrated in various studies. The formation of pyrite from polysulfides is rapid (hours) and does not necessarily require an intermediate stage

$$Fe^{2+} + S_5^{2-} + HS^- \rightarrow FeS_2 + S_4^{2-} + H^+ \qquad (11)$$

   This mechanism satisfactorily explains the rapid accumulation of sulfidic material in suboxic environments such as tidal environments (salt marshes or mangrove swamps). It has been observed that when a solution is supersaturated with Fe monosulfides and pyrite, the former are precipitated, even though supersaturation of pyrite exceeds that of FeS. This basically occurs when the pH of the solution is slightly alkaline. However, at pH $\sim$ 6.5, or low concentrations of sulfide, the solution remains unsaturated by monosulfides of Fe and supersaturated by pyrite, and the latter is precipitated. In salt marshes and mangrove swamps the effect of the tide and the plants present contributes to the partial oxidation of the soil, favoring the formation of polysulfides, as well as eliminating part of the alkalinity generated by the processes of sulfate reduction, so that the soil solution is slightly acidic (Pons et al., 1982; Goldhaber and Kaplan, 1974; Howarth, 1979).
2. The H_2S pathway:
   This route explains the formation of pyrite in anoxic environments, with Fe^{II} monosulfides as precursors and H_2S acting as an oxidant (Reaction 12) (Rickard, 1997; Rickard and Luther, 1997). It has been established in recent studies that this process can occur at ambient temperatures and as the pK_1 of H_2S is 6.98, the process is favored under acid to weakly alkaline conditions (Butler and Rickard, 2000). Such conditions are common in saltmarsh soils containing sulfidic material (Otero and Macías, 2002, 2003).

$$FeS + H_2S \rightarrow FeS_2 + H_2 \qquad (12)$$

   This second route helps to explain the low concentrations of the AVS fraction and the rapid formation of pyrite in strictly anoxic environments.

Environmental implications

Pyrite oxidation. Formation of acid sulfate soils

Sulfidic material is stable as long as the initial conditions of its formation, i.e., anoxic conditions, are maintained. However, when the material comes into contact with aerobic conditions, the process of oxidation is initiated. The mechanism of pyrite oxidation is complex and has been the object of many investigations (Nordstrom, 1974; Stumm and Morgan, 1996). In a preliminary stage, pyrite is oxidized by molecular oxygen (Reaction 13) – each mole of pyrite generating two moles of sulfidic acid and the precipitation of a Fe hydroxide.

$$\begin{aligned} &4FeS_2 + 15O_2 + 14H_2O \\ &\rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ \qquad (13) \end{aligned}$$

However, some authors consider that this inorganic reaction is too slow a process to account for pyrite oxidation and that under natural conditions it may be catalyzed by microorganisms of the genus *Metallogenium* or even *Thiobacillus*. The result of this is decrease in pH to values of around 4.5. When this occurs, the oxidation of pyrite may be initiated, even in the absence of oxygen, with Fe^{3+} acting as oxidant, according to Reaction (14).

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (14)$$

The process requires acidic conditions that favor the dissolution of the Fe hydroxide formed in the first stage of oxidation. The oxidation of pyrite with Fe^{3+} releases 16 moles of protons for each mole of pyrite oxidized, which causes strong acidification of the environment. At this stage values of $pH < 3.5$ are reached, which correspond to the optimal conditions for growth of some species as *Acidithiobacillus ferroxidans* (fomerly known as *Thiobacillus ferroxidans*). This chemolithotrophic species is able to transform CO_2 into organic matter by using Fe^{2+} to reduce CO_2, thereby generating Fe^{3+}. In this way is helps to increase the concentration of Fe^{3+} in the environment and accelerates the oxidation of pyrite by the order of 5 to 6 times (Nordstrom, 1982). Despite this, the involvement of *A. ferroxidans* is not limited to this indirect action, but it also appears to act directly on the surface of the pyrite crystals, catalyzing the oxidation of pyrite S. The new geochemical conditions generated are characterized by extreme acidity and a solution with a high ionic charge (especially of sulphate and Fe), and the soils are thus denominated "*acid sulfate soils*". These conditions favor the precipitation of different Fe and Al sulfates, although jarosite and schwermanite are the most characteristic minerals in these soils.

Trace metal–sulfide interactions and the relationship with bioavailability

Di Toro and co-workers (1990, 1992) established the importance of the AVS fraction in the control of the bioavailability of divalent trace metals. According to this model, even though the molar concentration of divalent metals (ΣCu, Ni, Ag, Hg, . . .) is lower that the molar concentration of the AVS fraction ($SEM/AVS < 1$; SEM: simultaneously extractable metals), these metals would not be toxic because the concentration in the interstitial water would be very low, as it is controlled by the formation of the corresponding metal sulfide, according to Reaction (15).

$$FeS + Me^{2+} \rightarrow MeS + Fe^{2+} \quad (15)$$

This hypothesis has been confirmed by the results of numerous laboratory experiments. Thus when the sum of the molar concentration of the divalent metals (extracted 1 or 3 M HCl) rises above the molar concentration of AVS, there is a sharp increase in the mortality of different invertebrates (DiToro et al., 1990, 1992). However, this model has been questioned in later studies. The high spatial and seasonal variability and variability at depth shown by the AVS fraction in soils and sediments suggests that the model would not apply to natural conditions (Otero et al., 2000; Morse and Rickard, 2004).

Furthermore, recent studies have shown that the pyrite fraction may incorporate large quantities of certain elements that are toxic for the biota (e.g., Hg, Cu, As, . . .) (Huerta-Díaz and Morse, 1994; Otero et al., 2000; Otero and Macías, 2002). The high stability of pyrite compared with that of the AVS fraction suggests that pyritization of trace metals may be an important sink for these metals. However, it has been established in recent studies that the fate of this fraction is also tied to seasonal changes in thionic or sulfidic soils. Moreover, Otero et al. (2000) established that the *Nereis diversicolor* preferentially assimilated those metals associated with the pyrite fraction. The oxidation of soils due to the activity of this species favors oxidation of pyrite and the release of associated metals.

Xosé L. Otero, T. O. Ferreira, P. Vidal, F. Macías, and
W. Chesworth

Bibliography

Berner, R.A., 1967. Termodynamic stability of sedimentary iron sulfides. *Am. J. Sci.*, **265**: 773–785.

Berner, R.A., 1970. Sedimentary pyrite formation. *Am. J. Sci.*, **268**: 1–23.

Davinson, W., 1991. The solubility of iron sulphides in synthectic and natural waters at ambient temperature. *Aquat. Sci.*, **53**: 309–329.

DiToro, D.M., Mahony, J.D., Hansen, D.J., Scott, K.J., Hicks, M.B., Mays, S.M., and Redmond, M.S., 1990. Toxicity of cadmium in sediments: the role of acid volatile sulfide. *Environ. Toxicol. Chem.*, **9**: 1489–1504.

DiToro D.M., Mahony J.D., Hansen D.J., Scott, K.J., Carlson A.R., and Ankley, G.T., 1992. Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environ. Sci. Technol.*, **26**: 96–101.

Goldhaber, M.B., and Kaplan, I.R., 1974. The sufur cycle. In Goldberg, E.D., ed. *The Sea,* Vol. 5. *Marine Chemistry.* New York: Wiley-Intersciece, pp. 527–655.

Howarth, R.W., 1979. Pyrite: its rapid formation in a salt marsh and its importance in ecosystem metabolism. *Science*, **203**: 49–51.

Huerta-Díaz, M.A., and Morse, J.W., 1992. Pyritization of trace metals in anoxic marine sediments. *Geochim. Cosmochim. Acta*, **56**: 2681–2702.

IUSS Working Group WRB, 2006. World reference base for soil resources 2006, 2nd edn. World Soil Resources Reports No. 103. Rome: FAO, 128 pp.

Morse, J.W., and Rickard, D., 2004. Chemical dynamics of sedimentary acid volatile sulfide. *Environ. Sci. Technol.*, 131A–135A.

Nordstrom, D.K., 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In Kittrick, J.A., Fanning, D.S., and Hossner, L.R., eds., *Acid Sulfate Weathering.* Madison, WI: Soil Science Society of America Special Publication No. 10, pp. 1–18.

Otero, X.L., Sánchez, J.M., and Macías, F., 2000. Bioaccumulation of heavy metals in thionic fluvisols by a marine polychaete (*Nereis diversicolor*): the role of metal sulfide. *J. Environ. Qual.*, **29**: 1133–1141.

Otero, X.L., and Macías, F., 2003. Spatial variation in pyritization of trace metals in salt marsh soils. *Biogeochemistry*, **62**: 59–86.

Otero, X.L., and Macías, F., 2003. Spatial variation in pyitization of trace metals in salt-marsh soils. *Biogeochemistry*, **61**: 247–268.

Otero, X.L., Ferreira T.O., Vidal-Torrado, P., and Macías, F., 2006. Spatial variation in pore water geochemistry on a mangrove system in the island of Pai Matos (Cananeia-Brazil). *Applied Geochemistry*, **21**: 2171–2186.

Pons, L.J., Van Breemen, and Driessen, P.M., 1982. Physiography of coastal sediments and development of potential soil acidity. In Kittrick, J.A., Fanning, D.S., and Hossner, L.R., eds., *Acid Sulfate Weathering.* Madison, WI: Soil Science Society of America Special Publication No. 10, pp. 37–53.

Rickard, D., 1997. Kinetics of pyrite formation by the H_2S oxidation of iron(II) monosulfide in aqueous solutions between 25 and 125 °C: the rate equation. *Geochim. Cosmochim. Acta*, **61**: 115–134.

Rickard, D., and Luther, G.W., III, 1997. Kinetics of pyrite formation by the H_2S oxidation of iron(II) monosulfide in aqueous solutions between 25 and 125 °C: the mechanism. *Geochim. Cosmochim. Acta*, **61**: 135–147.

Soil Survey Staff, 1999. Soil taxonomy. A basic system of soil classification for making and interpreting soil survey. 2nd edition. United States Department of agriculture. Natural Resources Conservation service. Washington DC. USA.

Stumm, W., and Morgan, J.J., 1996. *Aquatic Chemistry.* 3rd edn. New York: Wiley. 1022 pp.

Cross-references

Biomes and their Soils
Fluvisols
Geography of Soils
Hydric Soils
Redoximorphic Features
Redox Reactions and Diagrams in Soil

THIXOTROPY, THIXOTROPISM

Thixotropy is an isothermal, reversible, time-dependent process whereby a material stiffens under conditions of constant composition and volume while at rest and softens or liquefies under transitory stress (Freundlich, 1935; Mitchell, 1961; Gaucher, 1968). This process is characteristic of gels that liquefy under vibration and then solidify again when left standing. It is displayed strongly by clays such as bentonites when holding large amounts of exchangeable sodium, a hydrophilic ion (Russell, 1973).

Strength properties

Thixotropic behavior is exhibited by some soils high in crystalline clay minerals and by others in which the clay fraction is amorphous. The clay minerals, responsible for the plasticity and cohesion of soils, occur as very small, thin, plate-like particles (less than 2 μm in size). Among the three major groups of crystalline clay minerals, montmorillonite exhibits a high strength gain due to its thixotropic properties. Kaolinite, on the other hand, gains little or no strength from thixotropy, whereas illite is intermediate between the other two. Kaolinite can be made more thixotropic by the addition of a dispersing agent to prevent the *flocculation* (*q.v.*) that commonly prevails in natural specimens. Amorphous clay fractions can be similar in chemical composition to crystalline clay minerals, although some are essentially gels of hydrous iron and aluminum oxides. Soils that are high in amorphous clays also exhibit thixotropy to a high degree.

Although dilute suspensions of colloidal particles may exhibit thixotropism, the agronomist is concerned primarily with the age hardening that occurs in concentrated suspensions such as very soft clays between the plastic limit and the liquid limit (see *Soil engineering*). Some very soft clays stiffen and gain strength when allowed to remain undisturbed after being remolded while in a concentrated suspension. Other clays such as montmorillonites, however, gain considerable strength with time after being compacted at water contents somewhat less than 100%. This age hardening after remolding is quite different from the gain in strength produced by changing the volume of the clay by driving off a part of the pore water during consolidation (Lee, 1968). The gain in strength due to thixotropy occurs without removing any of the pore water and without volume change.

Thixotropic soils

Thixotropic clays are soils that tend to liquefy when disturbed. The sensitivity of clay, a measure of its tendency toward liquefaction, is determined by the relation

$$\text{sensitivity} = \frac{\text{strength of undisturbed material}}{\text{strength of remolded material}}$$

where the sensitivity is the ratio of undisturbed to remolded strength (Peck et al., 1974). Sensitivity values for most soils range between 1 and 8. Natural soils having values greater than 4 are known as *sensitive clays*. *Extrasensitive clays* have values greater than 8. If the sensitivity is greater than 16, such clays are described as *quick clays* (Skempton and Northey, 1952). Most clay soils are naturally sensitive to some extent because their strength decreases when they are remolded. Extrasensitive or thixotropic clays become quick when there is a loss of strength (see vol. XIII: *Quick Sand-Quick Clay*). These clays have a rather open structure with a random orientation (see *Structure*), but because the clay minerals are plate-shaped rather than rounded, the volume of voids is usually much greater than the volume of solid material. When the structure is broken by disturbance, the particles are set free in their surrounding pore water and the mass becomes a viscous liquid because the water cannot escape from the mixture (Fahn et al., 1953; Seed and Chan, 1957). Once the structure is destroyed by shock or distortion, it cannot be reformed artificially, although the strength of the remolded material may be increased by drying or by chemical changes (Ingles and Metcalf, 1973) (see *Soil engineering*).

Hazards

Thixotropic soils can be very troublesome in agricultural operations or in construction of roads and other works. They also create natural hazards on hillslopes because they are subject to mass movements in the form of earth flows (Sharpe, 1960). Substantial downslope movement over time is a normal feature of landscapes such as the Appalachian region of Pennsylvania and West Virginia. Earth movements may be rapid in the form of slides as well as the slower flows. The bearing capacities of thixotropic soils is low and deteriorates rapidly under traffic. Thus, for example, the soils will support a tractor on the first pass, may on the second, but not on the third. Because they can liquefy when subject to vibration, thixotropic soils pose major problems in construction of highways and other works. They had best be avoided or removed, if either is feasible. Because they do pose serious problems, identification of bodies of thixotropic soils in early stages of planning construction projects or land-use programs is necessary.

Charles W. Finkl, Jr.

Bibliography

Fahn, R., Weiss, A., and Hofman, H., 1953. Thixotropy in clays. *Berichte der Deutsche Keramischen Gessellschaft*, **30**: 21.

Freundlich, H., 1935. *Thixotropy.* Paris: Hermann et Cie, 50 pp.

Gaucher, G., 1968. *Trait de Pedologie: Agricole Le Sol.* Paris: Dunod, 578 pp.

Ingles, O.G., and Metcalf, J.B., 1973. *Soil Stabilization*. New York: Wiley, 374 pp.

Kerr, P.F., 1963. Quick clay. *Sci. Am.*, **209**(5): 132–142.

Knight, K., 1963. The origin and occurrence of collapsing soils, *Proc. 3rd Reg. Conf. Afr. Soil Mech. Found. Eng.*, **1**: 127–130.

Lee, I.K., 1968. *Soil Mechanics.* Sydney: Butterworths, 625 pp.

Mitchell, J.K., 1961. Fundamental aspects of thixotropy in soils. *Trans. Am. Soc. Civil Eng.*, **126**: 1586–1620.

Peck, R.B., Hanson, W.E., and Thornburn, T.H. (eds.), 1974. *Foundation Engineering.* New York: Wiley, 514 pp.

Rosenqvist, Th., 1959. Physico-chemical properties of soils: Soil-water systems. *J. Soil Mech. Found. Div., ASCE*, **85**(SM2): 31–53.

Russell, E.J., 1973. *Soil Conditions and Plant Growth.* London: Longmans, 849 pp.

Seed, H.B., 1968. Landslides during earthquakes due to soil liquefaction, *Proc. Am. Soc. Civil Eng.*, **94**(SM5): Proc. Paper 6110, 1053–1122.

Seed, H.B., and Chan, C.K., 1957. Thixotropic characteristics of compacted clays. *Proc. Am. Soc. Civil Eng.*, **83(SM4)**: Proc. Paper 1427, 1–34.

Sharpe, C.F.S., 1960. *Landslides and Related Phenomena.* Paterson, NJ: Pageant Books, 137 pp.

Skempton, A.W., and Northey, R.D., 1952. The sensitivity of clays. *Geotechnique*, **3**(1): 30–52.

Cross-references

Aggregate Stability to Drying and Wetting
Flocculation
Soil Engineering
Structure

TILL

A clay rich, unstratified deposit, left behind by continental glaciers, commonly with embedded pieces of gravel and rock sized particles (boulder clay), and relatively uncongenial to arable agriculture. An older term drift, comprises all loose materials covering formerly glaciated land, and as well as till, includes the stratified deposits of outwash plains, eskers, kames, varves, glaciofluvial materials and others. Indurated till is termed tillite.

Bibliography

Martini, I.P., Brookfield, M.E., and Sadura, S., 2001. Principles of Glacial Geomorphology and Geology. Upper Saddle River, NJ: Prentice-Hall, 381 pp.

Cross-reference

Ice Erosion

TILLAGE

One of humankind’s first steps towards civilization came when a stick was first used to till and manage the soil. The first power to operate tillage tools came from human muscles, then from domesticated animals, and most recently from mechanical machines which operate using mostly energy stored in fossil fuel sources. With development of soil tillage and selection of high-yielding grain plants the nomadic life styles of the hunter and herder were transformed to a settled agriculture with stabilized food production, which provided the foundation for modern civilizations. Soil tillage management systems evolved to meet the changing needs of societies for food and fiber. Today, tillage management systems continue to evolve to achieve the sometimes conflicting goals of maintaining crop production while conserving soil resources and environmental quality for future generations. Conservation tillage management systems emphasize the use of crop residue cover on the soil surface to maintain productivity and conserve soil and environmental resources.

In a general sense, *tillage* is the manipulation, usually mechanical, of soil properties for any purpose; but in modern agriculture it is usually restricted to modifying soil conditions for the production of food, fiber, and energy crops (Soil Science Society of America, 1987). More specifically, *tillage* is “the operation of implements through the soil to prepare seedbeds and rootbeds, control weeds and brush, aerate the soil, and cause faster breakdown of organic matter and minerals to release plant foods” (Soil Conservation Society of America, 1982).

Historically, soil tillage has played a central role in agricultural productivity. Tillage with primary and secondary implements loosens and granulates the soil, which is often compacted naturally or by machinery traffic, to prepare a seedbed for germination and growth of crop plants. For wetland crops such as rice (*Oriza sativa*), tillage is used to puddle the soil and make it impermeable to the movement of water. However, for most dryland crops tillage is used to enhance infiltration of water into soil early in the season to store needed water for crop growth. Zonal soil tillage during the growing season, with secondary tillage implements such as disks, cultivators, harrows, rod-weeders, rotary hoes, etc. controls the growth of weeds, which compete with crop plants for needed water and nutrients. Tillage also aids incorporation and decomposition of crop residues, which in some cases controls insects and crop plant disease. An additional benefit of tillage, long recognized by farmers, is increased soil nutrient supply to crop plants resulting from enhanced mineralization of soil organic reserves. Soil tillage practices also influence soil temperature, soil erosion, water infiltration, and susceptibility to compression. Design of soil opening implements for placement of seed, fertilizers, manure, and lime has evolved considerably from the initial use of a stick to place seed in the ground. So has our understanding that soil openers also provide a channel for preferential flow of water and chemicals to groundwater and a pathway for evaporative loss of soil water.

Our tillage management philosophy has changed considerably over the past century from one of maximum pulverization of soil to produce crop plants to one involving reduced or minimum soil tillage to maintain soil productivity while conserving soil and environmental resources (Pereira, 1975). New knowledge has allowed us to use tillage for specific goals of soil management; sometimes a specific goal dominates over others and often the goal has a specific time frame related to crop development, weather, and climate.

Tillage traditions

Some ancient civilizations developed agricultural crop production systems, which were in balance with nature. Rice (*Oriza sativa*) production systems in eastern Asia are an example of stable production systems, which have existed for thousands of years with only slight changes. In other parts of the world, human cultures and new crop production systems flourished for a short time and then disintegrated (Lowdermilk, 1953). For example, in the Middle East, in an area that is presently Iraq, a large population of 16 million people was once supported by an elaborate system of agriculture, which eventually failed. Speculations as to the causes of failure include climate change, excessive soil erosion and/or loss of an adequate supply of water. Now that region, agriculturally, supports only a few million persons.

Soils in the western hemisphere were essentially unused for crop production until the 1600s, except for small isolated areas in Mexico and South America. Agricultural development in North America during the early colonial period resulted in clearing of large areas of forest in the eastern part of the continent. In the American climate of hotter summers and extremes in rainfall, the traditions of tillage brought from Europe resulted in tremendous losses of topsoil through erosion. Early conservationists warned of the dangers to soil productivity posed by indiscriminate tillage and plowing (McDonald, 1941). However, uncleared land was abundant and as soil productivity declined many early settlers abandoned their farms and moved to virgin land in the western wilderness. The soil resources of the Midwest and Great Plains were virtually untouched until the early to mid-1800s. Great Plains and midwest corn belt soils were converted from native vegetation to cultivated cropland in a very short time mainly through developments in mechanization and a tremendous increase in power made available for tillage. Over two decades at the turn of the century, a conversion was made from animal power to mechanical power.

Use of mechanical energy to till and mix plant residue into soil rapidly accelerated the rate of change from native to cultivated conditions in North America as compared to changes occurring for agriculture developing earlier in other parts of the world. The incorporation and repeated fragmentation of soil and plant residues by tillage accelerated oxidation of soil organic matter and residues resulting in release of plant available nutrients. The native fertility of most forest and grassland soils in North America which were cleared of native vegetation and tilled, most commonly with the moldboard plow, declined significantly as soil organic matter was mined by crop removal without the subsequent addition of nutrient replacements. Within the lifetimes of many of these pioneer farmers, soil organic matter levels declined to 40 to 60% of their original levels, soil productivity declined, erosion losses of surface soil increased, and net mineralization of soil organic matter fell below that needed for sustained grain crop production. With increasing time of cultivation, the relative amount of plant-available N recycled from plant roots and residues increases and N supply from the humus fraction declines (Figure T11). To maintain grain yields with continuous tillage, supplemental N inputs from fertilizers, animal manures, and legumes are required. Depending on the type of soil, the release of nutrients is generally sufficient to meet crop nutrient requirements for several years or more after beginning tillage of a native soil condition. Fenster and Peterson (1979) reported little response to fertilizer during the first 30 to 40 years of wheat production on native soil in west central Great Plains. A similar trend was observed for soils in the corn belt where there was a sharp increase in fertilizer use in the late 1950s was stimulated in part by decline in the soil's capacity to supply available plant nutrients which was associated with decreased use of legume green manure crops and increased prevalence of high yielding grain crops in cropping systems (Power and Papendick, 1985).

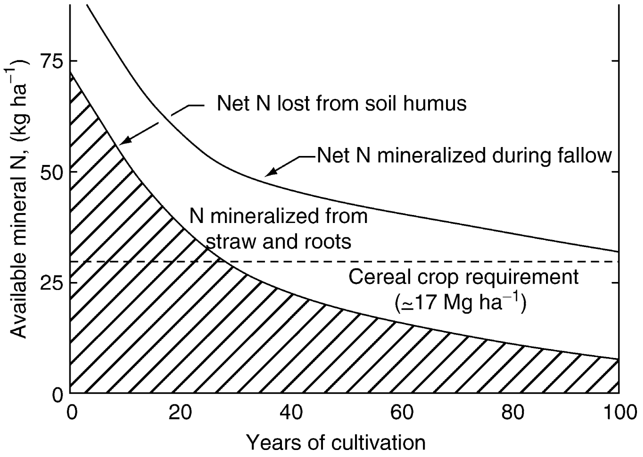


Figure T11 Influence of cultivation and time on relative mineralization from soil humus and wheat residue (from Doran and Smith, 1987 after Campbell et al., 1976).

The long-term cost of inversion tillage practices is acceleration of soil erosion, the oxidation of soil organic matter, and depletion of native soil fertility reserves. In North America, this was graphically demonstrated by the alarming soil erosion loss resulting from decreased soil organic matter, reduced plant and residue cover on the soil, and drought conditions which occurred during the 'dust bowl' of the 1930s.

Conservation tillage

Concern over soil erosion losses, economics of crop production, and increasing pressure to farm land too steep or too dry for conventional tillage practices led to the development of reduced tillage and residue management systems which conserve crop residues on the soil surface. Prior to the 1960s these conservation tillage systems generally involved some form of reduced or subsurface tillage (McCalla and Army, 1961; Triplett, 1982). The introduction of selective herbicides in the 1950s, however, ushered forth the era of weed control without tillage.

Within the past two decades the merits of reduced and no-tillage management systems have been recognized both in the United States (Allmaras et al., 1991; Phillips and Phillips, 1984; Sprague and Triplett, 1986), the United Kingdom (Davies and Cannell, 1975), Europe (Bakermans and DeWit, 1970) and the tropics (Greenland, 1975). Increased interest in conservation tillage arises from the advantages these systems offer over conventional tillage practices. Advantages include: reduced soil erosion losses and increased use of land too steep for farming by conventional tillage; improved timing for planting and harvesting and increased potential for double cropping; conservation of soil water through decreased evaporation and increased infiltration; increased production per unit area of land; and a reduction in fuel, labor, and machinery requirements.

Adoption of reduced tillage techniques in the United States has increased steadily during the last three decades. In a preliminary technological assessment, the USDA (1975) predicted that by the year 2000 over 80% of U.S. cropland would be under some type of reduced tillage management of which 45% would be no tillage. Between 1973 and 1981, the U.S. crop area in minimum tillage increased by 20 million ha or 125% (Christensen and Magleby, 1983). Expansion of no-tillage production during the same period was 1.5 million ha or 78%. Conventional-tillage acreage increased by only 1% during this period, but in 1981 it was still the most used practice on the majority (65%) of U.S. cropland. Estimates and projections for conservation tillage usage in the U.S. have been complicated by vague definition of terms. This difficulty has been partially overcome by the adoption in 1983 of a definition of conservation tillage as "*Any tillage and planting system in which at least 30% of the soil surface is covered by plant residue after planting or where at least 1 120 kg ha*$^{-1}$ *of flat small grain residue are on the soil surface during critical periods for wind erosion*" (CTIC, 1983). Using this definition, Schertz (1988) reported that conservation tillage acreage had increased from 2% of the total planted cropland in

1968 to 33% in 1986 and projected that conservation tillage would be practiced on 63 to 82% of total U.S. planted cropland by the year 2010.

Adoption of conservation tillage management practices is, however, hampered by certain disadvantages when compared with conventional tillage systems. These include: cooler soil temperatures, which in temperate and cold climates impede germination and early crop growth; uncontrolled compaction; increased potential for insect and disease damage to crops resulting from residue accumulation at the soil surface; difficulty for application of fertilizer, herbicides, and lime; and need for more precise management of soil fertility and weed control in achieving desired yields.

Tillage and the soil environment

Tillage and the associated management of crop residues are major determinants of soil temperature, water, aeration regimes, and availability of energy and nutrients to microorganisms. In general, conservation tilled soils are cooler, wetter, and less aerobic than their conventionally tilled counterparts (Doran and Smith, 1987; Mielke et al., 1986). Soil organic matter distribution and the cycling and availability of nutrients to crop plants can be altered greatly by reduced tillage management (Baeumer and Bakermans, 1973; Fox and Bandel, 1986; House et al., 1984). Microorganisms, soil insects, and organic matter are often more concentrated near the soil surface with reduced-tillage management which greatly influences nutrient cycling and potential tie-up or loss of fertilizer N (Doran, 1980; Doran, 1987). Increased N fertilizer requirements and/or yield reductions with no-tillage management indicate that fertility management may need to vary with tillage practice (Thomas and Frye, 1984). Observed responses to management, however, are not always consistent and often vary with differences in climate, soils, cropping, and time.

Degree of soil tillage can also profoundly influence oxygen dependent microbial transformations of C and N due to a greater relative predominance and activity of anaerobic versus aerobic organisms in the surface of no-tillage compared with plowed soils (Linn and Doran, 1984). These differences are associated with generally wetter more compact conditions with reduced tillage. Greater soil water content and reduced air-filled porosity, shortly after rainfall or irrigation, may enhance denitrification and gaseous losses of N in no-tillage as compared with plowed soils (Aulakh et al., 1991). The potential for less aerobic conditions with reduced tillage is site specific and depends on climate, soil porosity and drainage characteristics, and quantity of crop residues maintained on the soil surface (Figure T12). In the drier climates greater potential for denitrification with reduced tillage may rarely result in significant losses of N because soil aeration is only occasionally limited by excessive water contents. Significant denitrification losses of N from reduced tillage soils appears limited to poorly or imperfectly drained soils. In the case of ridge-tillage management, the periodic tillage of untilled between-row trafficked areas may be needed to reduce losses of soluble N due to denitrification and to enhance mineralization of crop residues (Doran and Smith, 1991).

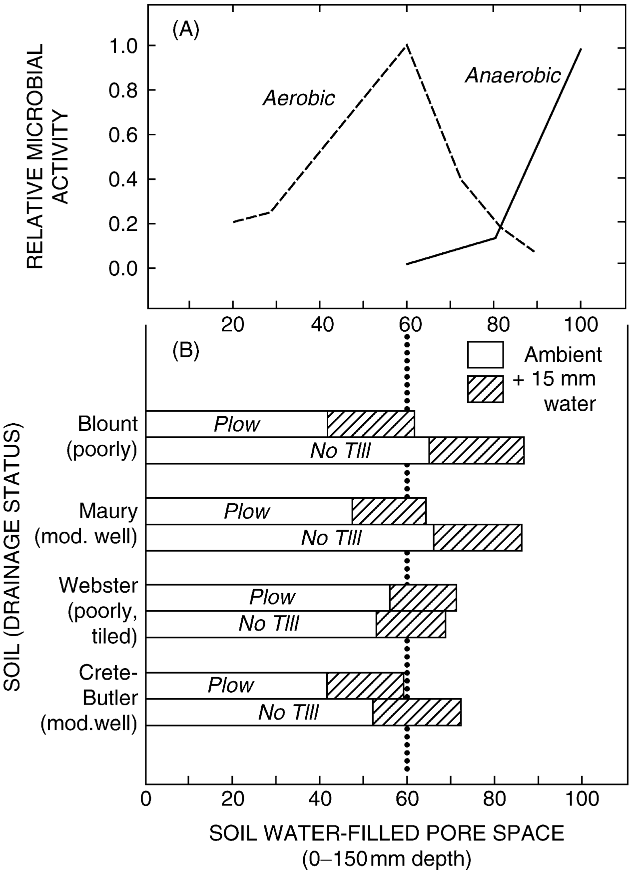


Figure T12 Relationships between water-filled pore space, microbial activity, tillage management, and soil drainage status (after Mielke et al., 1986).

Tillage management strategies

Agriculture is challenged to develop sustainable management systems, which provide adequate and economic crop yields, protect the environment, and conserve soil resources for present and future generations. Increasing the efficiency of conservation management systems requires understanding the complex effects of tillage, residue, and cropping management systems on the soil environment for microbial activity and plant growth. Most farmers adopting conservation tillage systems practice some periodic or zonal disturbance of soil. Tillage should be considered a powerful technique for managing soil nutrient pools. This is especially important where cover crops are used to provide biologically fixed N, reduce off-season N leaching losses, protect the soil from erosion, and to build soil organic reserves. Combining use of cover crops with conservation tillage may result in more sustainable agricultural crop production but the unique soil environments created by such practices must be considered in refining management systems for optimal crop growth and nutrient supply.

Although complicated by the climate and soil specific effects of tillage, it is possible to devise management systems which include "rotational" or "zonal" tillage to optimize the time or spatial relationships between conservation requirements and crop nutrient needs. Important in designing such systems, however, will be conservation of sufficient surface soil organic matter levels to maintain the physical and biological stability of soils.

John W. Doran and Lloyd N. Mielke

Bibliography

Allmaras, R.R., Langdale, G.W., Unger, P.W., Dowdy, R.H., and Van Doren, D.M., 1991. Adoption of conservation tillage and associated planting systems. In Lal, R., and Pierce, F.J., eds., *Soil Management for Sustainability.* Ankeny, IA: Soil and Water Conservation Society, pp. 53–83.

Aulakh, M.S., Doran, J.W., and Mosier, A.R., 1991. Soil denitrification – significance, measurement, and effects of management. *Adv. Soil Sci.*, **18**: 1–57.

Baeumer, K., and Bakermans, W.A.P., 1973. Zero tillage. *Adv. Agron.*, **25**: 77–123.

Bakermans, W.A.P., and DeWit, C.T., 1970. Crop husbandry on naturally compacted soils. *Neth. J. Agric. Sci.*, **18**: 225–246.

Campbell, C.A., Paul, E.A., and McGill, W.B., 1976. Effect of cultivation and cropping on the amounts and forms of soil N. In Rice, C.A., ed., *Proc. Western Canada Nitrogen Symp. (Calgary, Alberta, Canada).* Edmonton, Alberta, Canada: Alberta Agriculture, pp. 9–101.

Christensen, L.A., and Magleby, R.S., 1983. Conservation tillage use. *J. Soil Water Conserv.*, **38**: 156–157.

CTIC (Conservation Tillage Information Center), 1983. National survey of conservation tillage practices. Fort Wayne, Ind.

Davies, D.B., and Cannell, R.Q., 1975. Review of experiments on reduced cultivation and direct drilling in the United Kingdom, 1957–1974. *Outlook Agri.*, **8**: 216–220.

Doran, J.W., 1980. Soil microbial and biochemical changes associated with reduced tillage. *Soil Sci. Soc. of Am. J.*, **44**: 765–771.

Doran, J.W., 1987. Microbial biomass and mineralizable nitrogen distributions in no-tillage and plowed soils. *Biol. Fert. Soils*, **5**: 68–75.

Doran, J.W., and Smith, M.S., 1987. Organic matter management and utilization of soil and fertilizer nutrients. In Follett, R.F., Stewart, J.W. B., and Cole, C.V., eds., *Soil Fertility and Organic Matter as Critical Components of Production Systems.* Madison, WI: SSSA Special Publication # 19, ASA, pp. 53–72.

Doran, J.W., and Smith, M.S., 1991. Overview: role of cover crops in nitrogen cycling. In Hargrove, W.L., ed., *Proceedings of an International conference "Cover crops for clean water".* Ankeny, IA: Soil and Water Conservation Society, pp. 85–90.

Fenster, C.R., and Peterson, G.A., 1979. Effects of no-tillage fallow as compared to conventional tillage in a wheat-fallow system. Res. Bull. No. 289, Univ. of Nebraska-Lincoln.

Fox, R.H., and Bandel, V.A., l986. Nitrogen utilization with no-tillage. In Sprague, M.A., and Triplett, G.B., eds., *No-Tillage and Surface-Tillage Agriculture: The Tillage Revolution.* New York: Wiley, pp. ll7–l48.

Greenland, D.J., 1975. Bringing the green revolution to the shifting cultivator: better seed, fertilizers, zero or minimum tillage, and mixed cropping are necessary. *Science*, **190**: 841–844.

House, G.J., Stinner, B.J. Crossley, D.A., Jr., Odum, E.P., and Langdale, G.W., l984. Nitrogen cycling in conventional and no-tillage agroecosystems in the Southern Piedmont. *J. Soil Water Conser.*, **39**: l94–200.

Linn, D.M., and Doran, J.W., l984. Aerobic and anaerobic microbial populations in no-till and plowed soils. *Soil Sci. Soc. Am. J.*, **48**: 794–799.

Lowdermilk, W.C., 1953. Conquest of the land through 7000 years. *USDA Soil Conserv. Serv. Inform. Bull.*, **99**.

McCalla, T.M., and Army, T.J., 1961. Stubble mulch farming. *Adv. Agron.*, **13**: 125–196.

McDonald, A., 1941. Early American soil conservationists. Misc. Publ. No. 449. U.S. Dept. Agric., Soil Conserv. Service. Reprinted Oct. 1959. Washington, DC: U.S. Gov't Printing Office.

Mielke, L.N., Doran, J.W., and Richards, K.A., 1986. Physical environment near the surface of plowed and no-tilled surface soils. *Soil Till. Res.*, **5**: 355–366.

Pereira, H.C., 1975. Agricultural science and the traditions of tillage. *Outlook Agric.*, **8**: 211–212.

Phillips, R.E., and Phillips, S.H., 1984. *No-Tillage Agriculture: Principals and Practices.* New York: Van Nostrand Reinhold.

Power, J.F., and Papendick, R.I., l985. Organic sources of nutrients. In Engelstad, O.P., ed., *Fertilizer Technology and Use,* 3rd edn. Madison, WI: Soil Science Society of America, pp. 503–520.

Schertz, D.L., 1988. Conservation tillage: An analysis of acreage projections in the United States. *J. Soil Water Conserv.*, **43**: 256–258.

Soil Conservation Society of America, ed., 1982. *Resource Conservation Glossary*, 3rd edn. Ankeny, IA: Soil Conservation Society of America.

Soil Science Society of America, ed., 1987. *Glossary of Soil Science Terms*. Madison, WI: Soil Science Society of. America.

Sprague, M.A., and Triplett, G.B., 1986. *No-Tillage and Surface-Tillage Agriculture: The Tillage Revolution.* New York: Wiley.

Thomas, G.W., and Frye, W.W., l984. Fertilization and liming.. In Phillips, R.E., and Phillips, S.H., eds., *No-Tillage Agriculture.* New York: Van Nostrand Reinhold, pp. 87–l26.

Triplett, G.B., Jr., 1982. Tillage and crop productivity. In Rechcigl, M., Jr., ed., *CRC Handbook of Agricultural Productivity, Vol. 1. Plant Productivity.* Boca Raton, FL: CRC Press, pp. 251–262.

U.S. Department of Agriculture, 1975. Minimum tillage: A preliminary technology assessment. Back, W.B., assessment leader. Washington, DC: Office of Planning and Evaluation, USDA.

Cross-references

Agronomy
Compaction
Conservation
Microhabitats
Nitrogen Cycle
Soil Biology
Soil Chemistry
Soil Microbiology
Soil Physics
Tillage
Water Content and Retention
Water Erosion
Wind Erosion

TOPOGRAPHY

The shape of a land surface in terms of hills, valleys, plateaus and so on, the total ensemble of landforms and relief. Also sometimes used as the word for the discipline of geomorphology, which deals with the study of the land surface.

Cross-reference

Landscape and Soils

TOPOSEQUENCE

A sequence of soils in which the dominant factor accounting for any physical, chemical and biological differences has been the local variation in topography and landform under which the sequence has developed.

Cross-reference

Factors of Soil Formation

TOPSOIL

The upper part of the solum, essentially the part affected directly by plowing (the plow-layer). More or less synonymous with the A horizon.

TRACE ELEMENTS

Fourteen elements in the soil (aluminum, carbon, calcium, iron, hydrogen, potassium, magnesium, nitrogen, sodium, oxygen, phosphorus, sulfur, silicon, and titanium) constitute over 99% of the total elemental content (Mason, 1958; Lindsay, 1979). The remaining elements are the so-called trace elements. This term "trace elements" is generally used for those elements occurring in the soil in minute amounts without regard to their requirement by organisms. The occurrence of trace elements in soils as well as their reaction with soil constituents is of interest to the agronomist, soil scientist, and even the exploration geochemist. Accounts detailing the geographic distribution; forms (inorganic/organic, adsorbed, complexed, fixed, etc.); and elemental content of soils are given in the following noteworthy works: Swaine (1955), Vinogradov (1959), Mitchell (1965), Ermolenko (1972), Aubert and Pinta (1977), Kabata-Pendias and Pendias (1984), Adriano (1986), and Alloway (1990). Information regarding concentrations in the soil is generally available for the following trace elements: silver, arsenic, gold, boron, barium, beryllium, bismuth, bromine, cadmium, cerium, chlorine, cobalt, chromium, cesium, copper, fluorine, gallium, germanium, hafnium, mercury, iodine, indium, lanthanum, lithium, manganese, molybdenum, niobium, nickel, lead, radium, rubidium, antimony, scandium, selenium, tin, strontium, tantalum, tellurium, thorium, thallium, uranium, vanadium, wolfram, yttrium, ytterbium, zinc, and zirconium.

The term *micronutrients* (*q.v.*) is used for trace elements in the soil that are essential for healthy development of plants, animals, or microorganisms (boron, chlorine, cobalt, chromium, copper, fluorine, iodine, manganese, molybdenum, nickel, selenium, vanadium, and zinc and possibly barium, bromine, and strontium (Underwood, 1962, p. 2).

Trace element forms

The forms in which trace elements occur determine their movement and availability to plants. The following discussion of the different forms comes from Kabata-Pendias and Pendias (1984, p. 33–40).

Clay minerals. Clay minerals (kaolinite; montmorillonite; illite; chlorite; vermiculite) may contain negligible amounts of trace elements as structural components, but their ability to adsorb trace elements is important. The cation exchange capacity values vary with the type of clay in the following sequence: montmorillonite, vermiculite > illite, chlorite > kaolinite. Usually the greater the cation exchange capacity, the greater is the amount of cation adsorbed.

Oxides and hydroxides. The most important oxides in soils, as far as trace-element behavior is concerned, are iron and manganese oxides. Aluminum hydroxides can adsorb a variety of trace elements, and in some soils the role of these oxides can be more important than that of iron oxides in retaining trace elements. The mechanisms of sorption involve the substitution of divalent or trivalent cations for iron and manganese ions, the cation exchange reactions, and the oxidation effects at the surface of oxide precipitates.

Carbonates. Carbonates in soils are often in metastable and polymorphic forms. They are common constituents in soils where evapotranspiration exceeds rainfall. But, in soils with a high rate of percolating water, carbonates are readily dissolved and leached out. Nevertheless, calcium is usually the predominant cation in solutions of almost all soils. Calcite is the most widespread and relatively mobile form of calcium carbonates in soils. It has a major influence on pH of soils and, thus, on trace-element behavior.

Phosphates. Crystalline forms of phosphate minerals rarely occur in soils. However, many varieties of metastable and metamorphic phosphates are important in pedogenesis. Several of the rock phosphates contain large amounts of trace elements, especially fluorine and cadmium.

Sulfides, sulfates, and chlorides. Sulfides, sulfates and chlorides are negligible compounds in soils that developed in humid climates. But, in soils of arid climates, they can play a dominant role in controlling the behavior of trace elements. The metallic ions (mainly Fe^2, Mn^{2+}, Hg^{2+}, and Cu^{2+}) may form relatively stable sulfides of acidic or neutral reducing potential in flooded soils. Several other heavy metals (cadmium, cobalt, nickel, tin, titanium, and zinc) can also be easily coprecipitated with iron sulfides. Sulfides of heavy metals are not common in soils, especially in soils with good drainage. Sulfates of metals, mainly of iron, are likely to occur under oxidizing soil conditions. They are readily soluble and available to plants. Chlorides are the most soluble salts and occur mainly in soils of arid or semiarid climates.

Trace element content

Trace elemental composition of soils is determined in terms of total and extractable amounts present per unit weight of dry soil (Table T5). Total amount is commonly measured by dry ashing (500 to 550 °C for 3 to 4 h) or by wet ashing with a mixture of perchloric ($HClO_4 \cdot H_2O$) and nitric (HNO_3) or sulfuric (H_2SO_4) acids. Mixtures of acids that do not include hydrofluoric acid (HF) (for breaking down silicates) cannot be regarded as suitable for estimation of total amounts. Extractable amounts, obtained to evaluate availability to higher plants, are determined by using mineral acids (for example, 0.1 M hydrochloric acid (HCl)); organic acids (for example, acetic, citric); and chelating agents (for example, EDTA or ethylenediaminetetraacetic acid, and DTPA or diethylenetriaminepentaacetic acid). Hot water extraction is also done, especially for trace elements that occur as anions (boron, molybdenum, and selenium).

The lack of a universally acceptable, standard procedure for extraction of trace elements from soil, and the resulting diverse methods now in use, has been an intractable problem for soil science. Not all extractants extract similar amounts. In fact, they tend to be rather dissimilar. In addition, the duration of extraction, solid to extractant ratio, and chemical composition of the extractant (e.g., concentration, pH, presence or absence of buffer) all affect the amount extracted. The reader is referred to the following references for further discussion: Borggaard (1976), Norvell (1984), O'Connor (1988), Risser and Baker (1990), Soltanpour et al. (1976).

The references given at the bottom of Table T5 state the method used to determine extractable amounts cited in the table. Examples of extractants used are the following (Aubert and Pinta, 1977, p. 3–4): water at 100 °C (boron); oxalic acid-ammonium oxalate buffer, pH 3.3 (molybdenum); 0.1 N hydrochloric acid (zinc); 1 N ammonium acetate, pH 7 (copper, zinc, cobalt, molybdenum, manganese); 2.5% acetic acid, pH 2.5 (manganese, copper, zinc, nickel, cobalt, chromium); 0.05 M EDTA, pH 7 (copper and zinc); 1 N hydrochloric acid and 1 N nitric acid (copper, zinc, nickel, cobalt).

The concentrations listed in Table T5 are for non-polluted soils. This article will not consider *pollution* (*q.v.*), even though

Table T5 Trace element content of soils

Element	mg/kg[a]		Comment
	Total	Extractable[b]	
Ag	0.1(0.01–8)	0.02(0.01–0.05)	Tightly bonded by organic and inorganic soil constituents. Usually <0.01 mg kg^{-1} in plants.
As	6(<0.1–95)	2.7(0.03–11)	Accumulates in clay soils. AsO_2^-, AsO_4^{3-}, $HAsO_4^{2-}$, and $H_2AsO_3^-$ are common mobile forms. Soils containing enough As to be toxic to mammals occur in Argentina and New Zealand.
Au	0.002(0.0008–5)	...[c]	Stays in oxidized zone in soil formation. Accumulates in soils through solubilization and re-precipitation. Little information on Au content of soils.
B	10(<1–467)	1.9(0.01–130)	Highest in saline and alkaline soils. In parts of California, plants and animals may be poisoned by excessive B in soil. Deficiencies in B lead to poor crops in many other areas. Present in soil largely as H_3BO_3. Can be readily leached in acid soil. Lime promotes fixation.
Ba	500(10–3 500)	138(4–3 500)	More common in soils near mines, where toxicity to plants may occur. Can be fixed by clay minerals such as vermiculite.
Be	6(0.1–40)	...	Acts in soil similarly to Al. Not accumulated by plants.
Bi	0.2(0.13–13)	...	Difficult element to analyze. Little information on Bi content of soils. Is readily oxidized during weathering.
Br	33(<0.5–515)	...	Enriched in soil organic matter and coal. Considered nonessential and nontoxic to plants. Marine plants contain more Br than land plants. Coal and organic matter accumulate Br. Readily leached.
Cd	0.5(0.01–2.53)	0.06(0.01–0.5)	Acts in soil similarly to Zn and Ca. High levels of Zn in can reduce Cd uptake by plants.
Ce	50(30–50)	...	Concentrates in soil clays. Humus reduces Ce uptake. Chelates increase solubility and leaching. Some mobility in soils. Much remains within a few centimeters of surface.
Cl	100	10(7–50)	Much higher in alkaline soils, near the sea, and in salt deserts. A major exchangeable anion in many soils.
Co	8(0.05–300)	1.1(0.001–26)	Higher in soils derived from basalt or serpentine. Extensive areas of soil deficiency are known, which can cause diseases of ruminant mammals.
Cr	100(1.4–4 000)	0.3(0.01–3.9)	Cr(VI) more mobile in soils than Cr(III). Accumulates in roots and is not translocated. Usually <1 mg kg^{-1} in plants. Highest in soils derived from basalt or serpentine. Such soils may have an adapted flora.
Cs	6(0.3–500)	...	Can be fixed on montmorillonite and vermiculite. Is strongly adsorbed on soil.
Cu	20(1–323)	2.9(0.002–180)	Strongly adsorbed by humus. Extensive areas of soil deficiency, as in northern Germany, cause plant and animal diseases. Toxicity rare. Soils able to fix large amounts of Cu.
F	200(<10–1 360)	...	Fixed in many clay minerals and in apatite. Vegetation from F-rich soils in Madras, India, and South Africa toxic to grazing mammals. F deficiency associated with dental decay.
Ga	30(0.4–300)	...	Accumulates in humus layer and in illuvial horizons. Congener of Al. Seldom occurs in concentrations over 1 mg/kg in plants.
Ge	1(0.1–50)	...	Adsorbed by humus, especially in alkaline soils. More reactive than Si. Most Ge salts have low toxicity to man and plants. Reacts similarly to Si in soils and waters. Difficult element to analyze. Data are rare.
Hf	6	...	Chemically similar to its congener Zr. Low toxicity to plants and mammals.
Hg	0.03(0.008–5.8)	...	Lowest in upper layer of soil because it volatilizes.
I	3(<0.1–41)	0.01	Strongly adsorbed by humus. Extensive areas of soil deficiency, resulting in mammalian goiter. Soils of maritime regions have higher I contents than soils of continental regions.
In	0.2(<0.2–2.6)	...	Congener of Al. Commonly found in coals and crude oil. Associated with organic matter.
La	30(0.1–5 000)	...	Concentrates in clay fraction. Addition of chelating agent increases soil mobility.
Li	30(1.4–200)	...	Li^+ freely mobile in soils. May be involved in dental caries.
Mn	850(100–10 000)	110(15–1 250)	May be a major exchangeable cation in very acid soils. Oxidation state (usually Mn II or Mn IV) depends on microbial action. Available form: Mn^{2+}. Toxicities occur on poorly drained and acid soils. Remedied by liming, drainage. Mn toxicity sometimes found in autoclaved (sterilized) soils. Deficiencies chiefly on neutral or alkaline soils, particularly those high in organic matter. Mn-deficient soils lead to infertility in mammals.
Mo	2(0.013–24)	0.9(0.001–27)	Adsorbed by humus, especially in alkaline soils. A few soils are rich enough in Mo to yield herbage toxic to animals, whereas others give poor crops owing to Mo deficiency. Deficiency corrected by liming.
Nb	12(5–100)	...	Essentially unavailable in soils. Little leaching. Uptake of Nb by plants limited.
Ni	40(0.2–5 000)	18(0.01–403)	Higher in soils derived from serpentine, where it may limit or prevent the growth of woody plants, although an adapted flora survives. Ni contents increase with depth in soils.
Pb	10(1.5–1 200)	4.4(0.05–46)	Low soluble amounts in most soils. Higher in some limestone soils. Strongly adsorbed by humus.
Ra	0.8×10^{-6} $(0.3 \times 10^{-6}–2 \times 10^{-6})$	...	Chemistry of Ra similar to that of Ca. Leaches readily in many soils. Not highly mobile in plants. All isotopes radioactive. ^{226}Ra of surface soils higher than that of deeper soil horizons because of radionuclides added to soils from anthropogenic sources.

(Continued)

Table T5 (Continued)

Element	mg/kg[a]		Comment
	Total	Extractable[b]	
Rb	100(10–600)	...	Organic matter and micaceous clay minerals increase sorption capacity.
Sb	0.9(0.05–2.32)	...	Decreasing pH increases sorption of Sb on soil. Moves in neutral and alkaline soils, not acid soils. Sb taken up by plants, fixed in root, but some accumulates in leaves. Moderately toxic to plants. Few data.
Sc	7(0.5–46.4)	...	Congener of Al. Sc content related to clay content of soil. Is tranlocated downward. Plants contain <0.01 mg kg^{-1}. Environmental enrichment of Sc caused by coal and oil combustion.
Se	0.2(0.005–38)	0.1(0.005–9.1)	Reactions like those of sulfate. Ionic species of Se in soils: Se^{2-}; SO_4^{2-}; SO_3^{2-}; $(CH_3)_2Se$; Se^o. Adsorbed by humus, especially in alkaline soils. Vegetation from Se-rich soils may be toxic to mammals, as in Queensland, Australia; Ireland; South America; western United States; and other areas of low rainfall. Exceptional values of 360 to 1 200 mg kg^{-1} found in peat. Livestock poisoned above a value of 50 mg kg^{-1} in soil. Diseases livestock also due to Se deficiency.
Sn	10(<0.1–200)	1.4(0.04–6.8)	Strongly adsorbed by humus. Usually less than 2 m kg^{-1} in plants. Sn in plant not related to Sn in soil. Distribution of Sn between different soil horizons generally follows that of organic matter and clay. Data are rare.
Sr	300(5–3500)	...	Chemical properties similar to those of Ba and Ca. Concentrations as high as 17 500 mg kg^{-1} in plants. Sr^{2+} may partially replace Ca^{2+}.
Ta	0.65(0.17–3.87)	...	Essentially unavailable in soils. Little Ta leaches with water in soil. Little Ta uptake by plants, and Ta concentrates in roots. Resembles Nb, but is less mobile than Nb.
Te	0.5–37	...	Biological cycling of Te resembles that of Se. Microbes metabolize Te like Se. Bacteria capable of methylating As and Se also can methylate Te. Concentrates in onion and garlic.
Th	5(0.1–12)	...	Accumulates in silt or clay fraction. Not available for plant uptake. Introduced into biosphere from fossilfuel power plants. Hydrated cation, Th^{4+}, is soluble over a broad range of soil pH.
Tl	0.27(0.02–5)	...	Congener of Al. Strongly fixed by soils. In neutral soil, not phytotoxic except at high levels (100 mg kg^{-1}). Coal combustion an anthropogenic source of Tl.
U	1(0.10–11.02)	...	Accumulates in top soil by tight bonding to organic matter. Accumulates also in silt or clay fractions. Can be oxidized from IV to soluble VI oxidation state, where it can be readily leached by dilute acids or complexing agents. Concentrated in coal or peat and introduced into biosphere from fossilfuel power plants.
V	100(0.7–500)	0.17(0.01–8.8)	Adsorbed by humus, especially in alkaline soils. Vanadyl cation ($V0^{2+}$) may be an important form in many soils and mobilized when complexed with humic acids. Favors fixation of nitrogen by nodules.
W	0.68–2.7	...	Related to Mo. More strongly sorbed onto acid than alkaline soils and more tightly bound to kaolinite and illite than bentonite. Moves readily in alkaline soils when leached with water. Moderately toxic to plants. Easily available to plants. Data are rare.
Y	25(<10–500)	...	Concentrated in clay fraction. High concentrations in phosphate rock. Strongly adsorbed by soils. Unavailable for plant uptake. Data are rare.
Yb	3(<1.0–20)	...	Toxic to cell metabolism. Data for soils and plants are rare.
Zn	50(<5–900)	9.6(0.01–200)	Some soils yield poor crops owing to Zn deficiency. Zn toxicity rare and only found near zinc ores. Can be lost by leaching in acid soils. Organic-matter complexes relatively unavailable.
Zr	300(30–2 000)	...	Congener of Hf. Hf found distributed in nature in all Zr materials at less than 2% of their Zr content. Low solubility in soil. Generally not detectable in plants.

(Compiled from Swaine, 1955; Vinogradov, 1959; Bowen, 1966; Ermolenko, 1972; Aubert and Pinta, 1977; Kabata-Pendias and Pendias, 1984).

[a] The number preceding parentheses is the mean value found in the references cited.

[b] See text for type of extractants. Range results, in part, from different extractants being used.

[c] No data available.

it is a worldwide problem (Nriagu, 1992). Kabata-Pendias and Pendias (1984) give concentrations of trace elements in contaminated soils. Also, this article will not consider statistical or geostatistical techniques used to analyze contaminated soils (Davies, 1989; Boekhold and van der Zee, 1992) or models of trace element adsorption (Sposito, 1984; Harmsen, 1992).

Distribution in soil profiles

The pedological factors involved in soil profile distribution of the trace elements include the following (Mitchell, 1965; Korte et al., 1976; Aubert and Pinta, 1977; Alloway, 1990)

1. Surface enrichment because of trace elements taken up by plants. This is especially obvious in profiles with surface horizons rich in organic matter (see *Humic substances*). Certain elements, like manganese, tend to accumulate in surface layers of soil, while others, like chromium, are often higher in subsurface layers.
2. *Leaching* (*q.v.*) of mobilized constituents such as boron, lithium, manganese, or selenium either completely out of the profile or to zones of accumulation. This is particularly important in soils of tropical, humid regions.
3. Translocation, in the course of soil-forming processes such as podzolization, of trace elements together with iron and aluminum. Organic mineral complexes are probably involved.
4. Mobilization of trace elements through breakdown of soil minerals as a result of alternate wetting and drying.
5. Mechanical translocation of clay, whereby trace elements, more abundant in clay than in other soil fractions, increase in layers of clay accumulation.
6. Surface accumulation of soluble salts such as borates in arid regions (see *Salt leaching*; *Soil salinity and salinization*).
7. Mobilization or fixation arising from microbiological activity (see *Enzymes and proteins, interactions with soil-constituent surfaces*).

Trace element availability

The availability to plants of the micronutrient trace elements is influenced by many factors (Allaway, 1968; Hodgson, 1963; Mortvedt et al., 1972; Alloway, 1990). The important roles of some soil properties that may enhance or retard micronutrient availability are discussed briefly below. For a more comprehensive consideration of the role of trace elements in plant nutrition and of the factors that influence the mobility of trace elements in soil systems see also *Law of the minimum*; *Micronutrients*; *Nutrient potentials*; *Plant nutrients*; and *Soil fertility.*

pH. The availability of boron, cobalt, copper, manganese, and zinc decreases with increasing pH; the availability of molybdenum and selenium, however, increases with increasing pH. The application of lime is the most widespread method used to control trace element movement from the soil to the plant. In general, liming tends to reduce the availability of the metallic cations and to increase the availability of trace elements taken into the plant as anions (see *Lime*). Changes in soil reaction (see *Acidity*) resulting from liming can affect the solubility of trace elements by changing the oxidation state of the element.

Acidic deposition from the atmosphere, which is of environmental concern, is changing soil pH and the availability of trace elements (Løbersli et al., 1991; Wyttenbach et al., 1991).

Organic matter. Applications of organic matter to the soil are used to increase or decrease trace element concentrations in plants. The presence of organic matter can promote the availability of trace elements, presumably by supplying soluble complexing agents that interfere with their fixation. However, soils that are commonly deficient in certain metallic trace elements, especially copper, are organic in nature. Organic matter chelates the metals and makes them less available to plants (see *Humic substances*). Chelation appears to be more important than cation exchange in binding the elements to the organic matter (Bowen, 1966). At low pH, organic matter in soil reduces metal availability. At high pH, organic matter appears to increase availability, at least for zinc.

Cation exchange capacity. The cation exchange sites of the soil are important in binding the cationic trace elements. Therefore, soil horizons rich in clays or organic matter generally have higher contents of trace elements than silty or sandy horizons (Ermolenko, 1972).

Oxidation-reduction. Many trace elements (cobalt, copper, manganese, molybdenum, nickel, lead, vanadium, and zinc) are mobilized in poorly drained soils. The increased movement of trace elements under conditions of even slightly impeded drainage is often so marked that changes in extractable trace element contents due to other causes are obscured. Drainage of wet soils can affect the availability of trace elements because more highly oxidized forms of these elements are formed. For example, toxicities of manganese that occur on poorly drained soils are remedied by drainage.

Microorganisms. Deficiency of trace elements is aggravated by microorganisms, because they either compete directly for nutrients or decompose organic moieties that bind them. They can oxidize an element, usually to a less available form, or reduce an oxidized form of an element under conditions where oxygen is limited. They can also make trace elements more available for plant uptake by releasing inorganic ions or soluble organic complexes during decomposition of organic materials. Mycorrhizae, or the fungi associated with roots, have been shown to increase uptake of some micronutrients like copper. Bacterial activity is implicated in weathering, leaching, and deposition of mineral ores. Bacteria also can accumulate metals from solution by biosorption at the cell surface. For example, *Pedomicrobium*-like budding bacteria in Alaska accumulate gold (Mann, 1992).

Phosphorus. Phosphate is well known for decreasing injury caused by excessive levels of trace elements, and heavy application of phosphate fertilizer (see *Fertilizers, inorganic*) is one way to reduce trace element toxicity in plants (Chaney, 1973). However, cadmium occurs naturally in phosphate rock used for phosphate fertilizers (Gilliam et al., 1985). Cadmium has accumulated in plants and animals as a result of the use of phosphate fertilizers in the United Kingdom, New Zealand, and Tasmania (Bramley, 1990; Sparrow et al., 1992), but not in the United States (Mortvedt, 1987).

Ion competition. Competing elements are used to reduce the uptake and accumulation by plants of specific trace elements. For example, plants generally take up more cadmium if the zinc content of the soil is low. However, one of the most celebrated attempts to use ions that compete resulted in failure. In the western United States, sulfate was added to the soil to compete with undesired selenates in the plant-uptake process. The seleniferous soils, however, contained an abundance of native sulfates, and the experiment failed.

Plant type. Plant species and varieties differ widely in tolerance to trace elements. Leafy vegetables like lettuce accumulate high concentrations of trace elements. Tolerant ecotypes of grasses, which are found on ore outcrops or near mines, also contain high concentrations of trace elements. Plants vary in amounts of trace elements accumulated in roots, leaves, stems, flowers, and fruits. In general, roots contain the highest levels and fruits the lowest levels.

Rhizosphere effects. Plant roots (see *Rhizosphere*) exude a variety of compounds in quantities sufficient to change the availability of nutrients in their environment. Exudates can alter the chemical environment of the root either directly through an interaction with trace elements in the soil or indirectly through their influence on microorganisms.

M. B. Kirkham

Bibliography

Adriano, D.C., 1986. *Trace Elements in the Terrestrial Environment.* New York: Springer, p. 533.

Allaway, W.H., 1968. Agronomic controls over the environmental cycling of trace elements. *Adv. Agron.*, **20**: 235–274.

Alloway, B.J., ed., 1990. *Heavy Metals in Soils.* Glasgow, Scotland/ New York: Blackie/Wiley, p. 339.

Aubert, H., and Pinta, M., 1977. *Trace Elements in Soils.* Amsterdam: Elsevier, p. 395.

Boekhold, A.E., and van der Zee, S.E.A.T.M., 1992. Significance of soil chemical heterogeneity for spatial behavior of cadmium in field soils. *Soil Sci. Soc. Am. J.*, **56**: 747–754.

Borggaard, O.K., 1976. The use of EDTA in soil analysis. *Acta Agric. Scand.*, **26**: 144–150.

Bowen, H.J.M., 1966. *Trace Elements in Biochemistry.* London: Academic Press, p. 241.

Bramley, R.G.V., 1990. Review. Cadmium in New Zealand agriculture. *N. Z. J. Agric. Res.*, **33**: 505–519.

Chaney, R.L., 1973. Crop and food chain effects of toxic elements in sludges and effluents. In *Recycling Municipal Sludges and Effluents on Land.* Joint Conf. Proc. (Champaign, Illinois). Washington, DC: National Association of State Universities and Land-Grant Colleges, pp. 129–141.

Davies, B.E., 1989. Data handling and pattern recognition for metal contaminated soils. *Environ. Geochem. Health*, **11**: 137–143.

Ermolenko, N.F., 1972. *Trace Elements and Colloids in Soils.* Jerusalem: Israel Program for Scientific Translations Ltd, p. 259. (translated from the Russian).

Gilliam, J.W., Logan, T.J., and Broadbent, F.E., 1985. Fertilizer use in relation to the environment. In Engelstad, O.P., ed., *Fertilizer Technology and Use,* 3rd edn. Madison, WI: Soil Science Society of America, pp. 561–588.

Harmsen, K., 1992. Long-term behavior of heavy metals in agricultural soils: a simple analytical model. In Adriano, D.C., ed., *Biogeochemistry of Trace Metals.* Boca Raton, FL: Lewis Publishers, pp. 217–247.

Hodgson, J.R., 1963. Chemistry of the micronutrient elements in soils, *Adv. Agron.*, **15**: 119–159.

Kabata-Pendias, A., and Pendias, H., 1984. *Trace Elements in Soils and Plants.* Boca Raton, FL: CRC Press, p. 315.

Korte, N.E., Skopp, J., Fuller, W.H., Niebla, E.E., and Alesii, B.A., 1976. Trace element movement in soils: influence of soil physical and chemical properties. *Soil Sci.*, **122**: 350–359.

Lindsay, W.L., 1979. *Chemical Equilibria in Soils.* New York: Wiley, p. 449.

Løbersli, E., Gjengedal, E., and Steinnes, E., 1991. Impact of soil acidification on the mobility of metals in the soil-plant system. In Vernet, J.-P., ed., *Heavy Metals in the Environment.* Amsterdam: Elsevier, pp. 37–53.

Mann, S., 1992. Biomineralization. Bacteria and the Midas touch. *Nature*, **357**: 358–360.

Mason, B., 1958. *Principles of Geochemistry*, 2nd edn. New York: Wiley, p. 310.

Mitchell, R.L., 1965. Trace elements in soils. In Bear, F.E., ed., *Chemistry of the Soil.* New York: Reinhold, pp. 320–368.

Mortvedt, J.J., 1987. Cadmium levels in soils and plants from some long-term soil fertility experiments in the United States of America. *J. Environ. Qual.*, **16**: 137–142.

Mortvedt, J.J., Giordano, P.M., and Lindsay, W.L., eds., 1972. *Micronutrients in Agriculture.* Madison, WI: Soil Science Society of America, p. 666.

Norvell, W.A., 1984. Comparison of chelating agents as extractants for metals in diverse soil materials. *Soil Sci. Soc. Amer. J.*, **48**: 1285–1292.

Nriagu, J.O., 1992. Worldwide contamination of the atmosphere with toxic metals. In Verry, E.S., and Vermette, S.J., eds., *The Deposition and Fate of Trace Metals in our Environment.* Symp. Proc. Gen. Tech. Rep. NC-150. St. Paul, Minnesota: United States Department of Agriculture, Forest Service, North Central Forest Experiment Station, pp. 9–21.

O'Connor, G.A., 1988. Use and misuse of the DTPA soil test. *J. Environ. Qual.*, **18**: 715–718.

Risser, J.A., and Baker, D.E., 1990. Testing soils for toxic metals. In Westerman, R.L., ed., *Soil Testing and Plant Analysis,* 3rd edn. Madison, WI: Soil Science Society of America, pp. 275–298.

Soltanpour, P.N., Khan, A., and Lindsay, W.L., 1976. Factors affecting DTPA-extractable Zn, Fe, Mn, and Cu from soils. *Commun. Soil Sci. Plant Anal.*, **7**: 797–821.

Sparrow, L.A., Chapman, K.S.R., Parsley, D., Hardman, P.R., and Cullen, B., 1992. Response of potatoes (*Solanum tuberosum* cv. Russet Burbank) to band-placed and broadcast high cadmium phosphorus fertiliser on heavily cropped krasnozems in north-western Tasmania. *Aust. J. Exp. Agric.*, **32**: 113–119.

Sposito, G., 1984. *The Surface Chemistry of Soils.* New York: Oxford University Press, p. 234.

Swaine, D.J., 1955. Trace element content of soils. *Commonwealth Agr. Bur. Tech. Commun.*, **48**: pp. 157.

Underwood, E.J., 1962. *Trace Elements in Human and Animal Nutrition*, 2nd edn. New York: Academic Press, p. 429.

Vinogradov, A.P., 1959. *The Geochemistry of Rare and Dispersed Chemical Elements in Soils.* New York: Consultants Bur., p. 209. (translated from the Russian).

Wyttenbach, A., Tobler, L., and Bajo, S., 1991. Correlations between soil pH and metal contents in needles of Norway spruce. *Water Air Soil Pollut.*, **57–58**: 217–226.

Cross-references

Acidity
Enzymes and Proteins, Interactions with Soil-Constituent Surfaces
Fertilizers, Inorganic
Humic Substances
Law of the Minimum
Leaching
Lime
Micronutrients
Nutrient Potentials
Plant Nutrients
Pollution
Rhizosphere
Salt Leaching
Soil Fertility
Soil Salinity and Salinization

TRANSPORT

The movement of materials by water, wind or ice, as part of the erosional cycle. Where water is the agent of transport, the material transported may be in the form of particles ranging from rock fragments to colloids, or as material in true solution. *Eluviation* (*q.v.*) is a particular form of transport in soil.

Cross-references

Erosion
Ice Erosion
Water Erosion
Wind Erosion

TRANSPORT PROCESSES

Soil is a three-phase system, and transport processes occur in each of the phases. The main entities of concern are matter (water, salt, nutrients, pollutants, oxygen, carbon dioxide), heat, and electric charge. For some processes, e.g., the transport of salt, it is sufficient to consider only one of the phases of the system, i.e., the liquid phase. For other processes, e.g., the transport of heat, it is mandatory to consider the mixture as a whole. In the case of heat transport, one has to consider both the conductive and the convective transport. Heat is conducted through the solid and the liquid phase. Because of the intricate geometry of both phases and their intimate contact, the conduction of heat through both phases is almost always inseparable. Convective transport of heat occurs when heat is carried along, e.g., by the liquid. Other transport processes may also consist of a conductive and a convective part. In case of the dispersion of solutes in soils, the conduction (diffusion) and convection (drag by the liquid) are usually highly interwoven. The most important transport processes occur in the liquid phase. However, the transport of oxygen, carbon dioxide, and water through the vapor phase are of great importance to plant growth. On the other hand, the solid phase itself might be moving as happens in swelling and frozen soils. The formation of cracks and ice lenses has important consequences for the physical properties of the soil.

Many books and articles have been published on transport processes in soils. The following references constitute only a small selection: Baver et al. (1972); Childs (1969); Hillel (1971) Kirkham and Powers (1972); Rose (1966); De Wiest (1969); de Vries and Afgan (1975).

Transport occurs due to the presence of a driving force or to convection. The process is then formulated by relating the flux of the entity of concern to the appropriate driving force. The contribution due to convection is then added as a separate term. The resultant constitutive equation is called the *transport equation*. To find the distribution of the entity in the space of concern as a function of time, the appropriate continuity equation has to be formulated. This equation contains the divergence of the flux. By substituting this flux by the one as formulated in the transport equation, one obtains the *flow equation*, which is usually a second-order, partial-differential equation. This flow equation has then to be solved for the appropriate boundary conditions. There is extensive literature on this part of the subject (cf. Carslaw and Jaeger, 1959; Crank, 1957; Bird et al., 1960).

To limit the discussion on transport processes in soils, the following will be concerned with only the transport equations. Inspection of the variety of transport processes in soils and all the possible interactions reveals that an attempt to formulate a general transport equation including all causes and effects will lead to an intractable result. Therefore, we will first describe the simple processes and from there expand into somewhat more complicated processes.

Darcy's equation

The liquid present in the soil (i.e., the water plus the dissolved salts and other solvents) moves due to a gradient of the hydraulic pressure $P^{\dagger}$. This hydraulic pressure is the sum of the equilibrium liquid pressure (as measured, e.g., by a tensiometer) and the pressure equivalent of the gravimetric potential. The movement of the liquid is expressed as a volume flux, e.g., in cubic centimeters of liquid per square centimeters of soil per second.

Darcy's Equation then states that a linear relationship exists between the liquid flux j^{V} and the gradient $\nabla P^{\dagger}$

$$j^{\mathrm{V}} = -L_{\mathrm{V}} \nabla P^{\dagger}$$

where L_{V} is the hydraulic conductivity. The magnitude of L_{V} depends strongly on the type of soil and the degree of saturation. This relationship holds for almost all liquid transport processes occurring in soils.

Fick's equivalent equation

Salt moves through the liquid phase in the soil due to a concentration gradient or, in case of the presence of a single salt, due to the gradient of the osmotic pressure of the equilibrium liquid $\nabla\pi$. The movement of the salt may be expressed as a macroscopic diffusion flux, e.g., in grams of salt per square centimeter of soil per second. Dividing by the equilibrium salt concentration, the preceding flux turns into a linear diffusion flux j^{D} in centimeters per second. Fick's Equation then suggests that a linear relationship exists according to:

$$j^{\mathrm{D}} = -L_{\mathrm{D}} \nabla \pi$$

Fourier's equivalent equation

A temperature gradient in the soil causes a heat flux. Although the system of concern is a mixture of phases, one may assume that the heat flux j_{q}' can be related to the gradient of the temperature according to

$$j_{\mathrm{q}}' = -L_{\mathrm{T}} \frac{\nabla T}{T}$$

Ohm's equivalent equation

Soil is an electric conductor. The application of an electrostatic potential gradient ∇E causes an electric current I. The relationship between the two appears again to be linear, viz.

$$I = -L_{\mathrm{E}} \nabla E$$

The preceding four equations formulate the main transport processes in soils. The parameters are characteristic of the soil. They depend on the type of soil, the packing density, the salt concentration, the temperature, etc. However, the relationships are linear for almost all practical purposes, provided that the "other" driving forces are absent. The possibility that a certain driving force contributes to a nonconjugated flux might result into the unwarranted conclusion that the flux-force relationships are nonlinear. In unsaturated soils, the interaction between the transport of heat and water is an important phenomenon. In particular, in clay soils the interaction of the movement of water and salts is of great practical interest. This interaction is directly related to the *permiselectivity* of the soil, being a property by which the soil can select between different molecules or ions during the transport process.

In the field where day and night, rainfall and evaporation, fertilizing, and water uptake by plants cause the simultaneous presence of temperature gradients, hydraulic pressure gradients, and salt concentration gradients, it is mandatory to consider the possibility of interaction between these processes. An attempt will now be made to formulate the flux-force relationships such that this interaction is taken into account. In principle, one first has to find an expression for the total energy dissipation in the system. The flux-force pairs in that equation then provide the lead, which together with the postulate that every flux is a linear function of every force appearing in the equation of energy dissipation, results into an appropriate set of flux-force relationships. The following development is taken from Groenevelt and Bolt (1969).

Expressing the thermodynamic forces F per unit macroscopic length of the porous system, the equations relating the chosen fluxes and forces in the present single salt system may be written as

$$j_\mathrm{q}' = L_\mathrm{T}F_\mathrm{T} + L_\mathrm{TV}F_\mathrm{V} + L_\mathrm{TD}F_\mathrm{D} + L_\mathrm{TE}F_\mathrm{E}$$

$$j^V = L_\mathrm{VT}F_\mathrm{T} + L_\mathrm{V}F_\mathrm{V} + L_\mathrm{VD}F_\mathrm{D} + L_\mathrm{VE}F_\mathrm{E}$$

$$j^\mathrm{D} = L_\mathrm{DT}F_\mathrm{T} + L_\mathrm{DV}F_\mathrm{V} + L_\mathrm{D}F_\mathrm{D} + L_\mathrm{DE}F_\mathrm{E}$$

$$I = L_\mathrm{ET}F_\mathrm{T} + L_\mathrm{EV}F_\mathrm{V} + L_\mathrm{ED}F_\mathrm{D} + L_\mathrm{E}F_\mathrm{E}$$

in which

$$F_\mathrm{T} = \frac{(-\Delta T)}{T\Delta X}; \qquad F_\mathrm{V} = \frac{\left(-\Delta P^\dagger\right)}{\Delta X}$$

$$F_\mathrm{D} = \frac{(-\Delta \pi)}{\Delta X}; \qquad F_\mathrm{E} = \frac{(-\Delta E)}{\Delta X}$$

The four straight coefficients are all positive and describe the above-mentioned primary transport phenomena, i.e., those of Fourier, Darcy, Fick, and Ohm. Comparison with these equations gives: $L_\mathrm{T}/T = \lambda$(soil), the thermal conductivity of the soil, and $L_\mathrm{V} = K_\mathrm{h}$ (hydraulic conductivity). $L_\mathrm{D} = D$(soil)/R$T\rho$-$_{\mathrm{s}/M\mathrm{s}}$, with D(soil) equal to the effective salt diffusivity in the soil system. Of course D(soil) should be related to D_0 (diffusion in aqueous solutions), insofar as the frictional resistance of the salt against the water will be roughly the same as in solution (aside from the reduction of the cross-section available for diffusion θ and a tortuosity effect). In addition, however, D(soil) contains the effect of the volume flux induced by the very gradient of the osmotic pressure (cf. the coupling phenomenon discussed below). M_s indicates the molecular weight of the salt. $L_\mathrm{E} = \kappa$(soil), the effective electrical conductivity of the soil system. There exists a relationship between κ(soil) and κ_0 (the conductivity of the equilibrium solution) comparable to the relationship between D(soil) and D_0. Obviously, all straight coefficients are defined as the ratio of a flux to its conjugated force at zero value of all other forces.

The twelve coupling coefficients, which are defined as flux-force ratios at zero value of the other three forces, are equal in pairs carrying the same two subscripts (*Onsager relations*). In the following, these pairs of coefficients will be discussed qualitatively by describing the mechanisms causing a flux j_i to arise in the presence of a nonconjugated force F_k. In certain cases the existence of coupling is easier demonstrated by a complementary phenomenon, i.e., the fact that a finite value of the conjugated force F_i arises if a zero flux j_i is maintained in the presence of an applied nonconjugated force F_k. It should be pointed out that the linearity of the relations between a flux and the nonconjugated forces is an intrinsic consequence of the linearity of the main relations. As long as the straight relations are linear, the coupling processes are adequately formulated by linear relationships. In general, it may be stated that coupling arises as a result of "selective" properties of the transporting medium with respect to the transported matter. The coupling coefficients may be positive or negative, and their absolute value must lie between zero (no coupling) and the geometric mean value of the corresponding straight coefficients.

L_DV and L_VD, filtration (salt-sieving effect) and osmosis

The simplest example of the mentioned selection mechanism is found in systems with very fine pores (in the Å range), where the resistance against passage of water molecules is much smaller than that for dissolved larger molecules. A pressure gradient will then cause preferred transport of the water, giving rise to a net movement of the solute with respect to the solvent in a direction opposite to the solvent flow. Thus L_DV is negative and finite (salt-sieving effect). Alternatively, a gradient of the osmotic pressure (in the absence of a pressure gradient) across such a barrier will lead to a net force on the solution as a whole (a relatively larger share of the diffusive "force" on the solute molecules being used to overcome the friction of the membrane), and j^V becomes finite. Accordingly, L_VD is again negative and finite. The two extremes of this situation are found in the perfectly semipermeable barrier where $-L_\mathrm{DV} = -L_\mathrm{VD} = L_\mathrm{V} = L_\mathrm{D}$ and a non-selective solution column where $L_\mathrm{DV} = L_\mathrm{VD} = 0$. The permiselectivity of soil systems may be substantial even for much thicker water layers as a result of the electric double layer formed on the pore walls.

L_EV and L_VE, streaming current and electroosmosis

Another familiar example of coupling coefficients of finite magnitude is found in the electrokinetic phenomena. These arise if the solution phase carries a net volume charge as a result of an electric field emanating from charges present on the solid matrix. This field exerts a selectivity with regard to the passage of cations and anions. A pressure gradient will then cause preferred movement of one of the two species, giving rise to a streaming current, which shows that L_EV has a finite value. This streaming current requires a possibility for return flow of, e.g., electrons outside the system as may be provided by, e.g., inserting a set of shorted electrodes (condition of macroscopic electroneutrality of the system!).

If such an "external connection" is not present, a macroscopic gradient of the electric potential will arise instantaneously, making the net current zero. The existence of this potential gradient (termed *streaming potential*) proves again the existence of the coupling coefficient L_EV. Alternatively, an imposed gradient of the electric potential will lead to a net force on the solution phase (because of the presence of non-equivalent amounts of cations and anions). The ensuing volume flux is termed *electro-osmosis* (*q.v.*), its coefficient being L_VE. The coupling coefficients vanish in the absence of the selective action of the electric field emanating from the pore wall.

L_ED and L_DE, "diffusion" current and electrophoresis

The coupling between diffusion of salts and an electric potential gradient is of course almost always present in any aqueous solution. Here the selectivity mechanism lies in the (usually) unequal resistance exerted by water on diffusing ions. A concentration gradient of salts will thus induce a "diffusion" current provided an external return flux of electrons is possible. Usually such an external connection (via shorted electrodes) is absent; then a diffusion potential arises.

The complementary phenomenon, i.e., the transport of salt under influence of a gradient of the electric potential, is well known from, e.g., the determination of transport numbers with the *Hittorf method*. The effects vanish for equal mobilities, e.g., in KCl solution. The magnitude of these effects in porous systems may be substantially larger than in aqueous solutions if the transport number of either one of the ion species is influenced substantially. This is almost always the case in soil systems where the mentioned electric field in the liquid layers against the solid matrix induces high or sometimes very high values for the transport number of the cation. The potential gradient then arising as a result of concentration gradients (even of KCl) has been discussed extensively in soil science literature in relation to potentiometric measurements in soils involving salt bridges and was then referred to as "liquid junction potential."

L_{TV} and L_{VT}, "thermofiltration" and thermoosmosis

The coupling between heat and mass fluxes is less obvious on first sight. In line with the preceding reasoning, coupling will arise only if the system exerts a selectivity with respect to "hot" and "cold" molecules ("hot" molecules indicating the molecules with a high value of $(\bar{H} + \Psi)$ or total specific enthalpy, or specific heat content). In that case, an applied pressure gradient causes, e.g., preferred transport of the "hot" ones, thus increasing the heat content of the system at the low pressure end, which amounts to a heat flux in addition to the mass-flux ($L_{TV} > 0$). In a liquid saturated soil system, not much can be expected of this effect, unless the liquid layers are extremely thin (which is difficult to effectuate in the saturated system). As follows from the observed heat of wetting of dry soil, the heat content is indeed decreased for the first few layers of water due to the presence of strong adsorption fields. These layers are presumably also less mobile than further layers. For thick water films, the difference in the "average" heat content of the mobile layers as compared to that of the entire film becomes vanishingly small. Alternatively, a temperature gradient applied to a water film subject to an adsorption field will induce a mass flux as a temperature rise will "lift" a larger part of the molecules from the adsorbed (immobile) layer to the mobile one. Again this effect should be expected to be quite small for the saturated soil system because of the width of pores, which is usually of concern.

For unsaturated and frozen soils, the phenomena of thermofiltration and thermoosmosis are quite important (cf. Kay and Groenevelt, 1974; and Groenevelt and Kay, 1974).

L_{TD} and L_{DT} and L_{TE} and L_{ET}, thermodiffusive and thermoelectric phenomena

In these phenomena coupling will arise if the selection mechanism operates on the salt molecules and the countercharge, distinguishing between "hot" and "cold" specimen. For the salts present in charged pores, the effect must be extremely small. The salt being repelled from the immobile layer close to the liquid-solid interface, only a tiny fraction of the salt (this time the fraction with high heat content) is situated in this layer. The difference in average heat content of the mobile part compared with that of all salt molecules will be vanishingly small. A locally applied temperature increase will likewise not contribute measurably to a decrease of mobile salt molecules. The coefficients L_{TD} and L_{DT} will thus be negative in principle and presumably zero in practice. In contrast the countercharge is accumulated in the immobile layer, so L_{TE} and L_{ET} should be positive (for a positive countercharge). As to the practical significance of these coupling phenomena, it appears that L_{ET} might indeed be easily detectable. As was indicated earlier in the discussion of L_{EV}, this effect is usually met in the form of a gradient of the electric potential arising here when a temperature gradient is applied under the condition of zero current. In systems with low electrolyte concentration, the majority of the "relatively few" conducting ions is situated close to the solid surface, where the ionic mobility may be impaired considerably. A temperature increase could then increase substantially the number of actually conducting ions. A considerable gradient of the electric potential might thus be necessary to maintain a zero current when a temperature gradient is applied.

P. H. Groenevelt

Bibliography

Baver, L.D., Gardner, W.H., and Gardner, W.R., 1972. *Soil Physics.* New York: Wiley, 498 pp.

Bird, R.B., Stewart, W.E., and Lightfoot, E.N., 1960. *Transport Phenomena.* New York: Wiley, 780 pp.

Carslaw, H.S., and Jaeger, J.C., 1959. *Conduction of Heat in Solids.* Oxford: Clarendon Press, 510 pp.

Childs, E.C., 1969. *The Physical Basis of Soil Water Phenomena.* New York: Wiley, 493 pp.

Crank, J., 1957. *The Mathematics of Diffusion.* Oxford: Clarendon Press, 347 pp.

De Wiest, R.J.M., 1969. *Flow Through Porous Media.* New York: Academic Press, 530 pp.

Groenevelt, P.H., and Bolt, G.H., 1969. Nonequilibrium thermodynamics of the soil-water system, *J. Hydrol.*, **7**: 358–388.

Groenevelt, P.H., and Kay, B.D., 1974. On the interaction of water and heat transport in frozen and unfrozen soils: II. The liquid phase. *Soil Sci. Soc. America Proc.*, **38**: 400–404.

Hillel, D., 1971. *Soil and Water.* New York: Academic Press, 288 pp.

Kay, B.D., and Groenevelt, P.H., 1974. On the interaction of water and heat transport in frozen and unfrozen soils: I. Basic theory: The vapor phase. *Soil Sci. Soc. America Proc.*, **38**: 395–400.

Kirkham, D., and Powers, W.L., 1972. *Advanced Soil Physics.* New York: Wiley, 534 pp.

Rose, C.W., 1966. *Agricultural Physics.* Oxford: Pergamon Press, 226 pp.

de Vries, D.A., and Afgan, N.H., 1975. *Heat and Mass Transfer in the Biosphere.* New York: Wiley, 594 pp.

Cross-references

Conductivity, Electrical
Conductivity, Hydraulic
Conductivity, Thermal
Diffusion Processes
Electro-osmosis
Energy Balance
Flow Theory
Thermal Regime
Thermodynamics of Soil Water
Water Budget in Soil

TROPICAL SOILS

The term 'tropical soils' is not as geographically inclusive as might be inferred from the name. From a pedological point of view, the term traditionally does not include all soils occurring in tropical environments, soils of low-latitude deserts typically being excluded, as are some pedogenically young (poorly developed) soils. The inclusive and exclusive terminologies are somewhat inconsistent and their applications depend of specific reference points, most commonly referring to extreme degrees of biochemical weathering for prolonged periods of time. Tropical soils are thus defined principally by climate and stage of genetic development with particular examples dependent upon parent material and topography. Identification of tropical soils is partially dependent on the classification system and its interpretation of the convergence of the factors of soil formation that come together to produce mantles of intensely weathered materials.

As interpreted by the FAO-UNESCO-ISIC (1990) system of soil classification (Nachtergaele et al., 2000), tropical soils cover about 30 million km^2 of the Earth's surface and are loosely defined as those weathering profiles that are characteristic of the non-desertic low latitudes. Tropical soils form under tropical climates, of which there are several main types. The tropical climates are roughly those where the mean annual temperature exceeds 20 °C and no monthly mean falls below 18 °C. Geographic boundaries, so constrained, are roughly the Tropic of Cancer and Tropic of Capricorn (23° N and S), from which some authorities would exclude the tropical equatorial climate, specifically the equatorial rainforest belt. With the latter proviso, the tropics are then distinguished by seasonal rainfall (part wet – part dry) but exclude hot desert regions with less than 25–40 mm annual precipitation, thus excluding much of the Sahara Desert (south of 23° N to 15° N), although they would include a specific tropical savanna-type climate with seasonal precipitation less than 1 000–1 400 mm (see Oliver and Fairbridge, 1987).

Tropical soils, disregarding those relating to specific geological histories such as recent volcanism, coastal plain eustatic fluctuations and principal river valleys, reflect extreme longevity, leaching, and (geo)chemical evolution (McFarlane, 1976; FitzPatrick, 1980; Eswaran et al., 1983; Nahon, 1991; Finkl, 1995). Soils formed in hot climates (subtropical, tropical, equatorial regions) where the effective precipitation produces environmental conditions that range from semi-arid to perhumid have common characteristics that are notably different from soils in other environments. Weathering of primary minerals is more complete than in temperate climates and it takes place to greater depths (e.g., Duchafour, 1978; Büdel, 1982). Because organic matter is subject to rapid biodegradation and recycling and tends to remain near the ground surface, weathering favors geochemical processes (e.g., neutral or slightly acid hydrolysis) that result in higher concentrations of free oxides than is typical of temperate-region soils. Soil color in hot climates is generally much more intense (brighter) than in temperate climates because the freed iron and aluminum oxides remain in the profile. The ratio of free iron: total iron of a weathering horizon on granite, for example, never exceeds 50% in a temperate acid brown soil, but reaches 60–70% in a fersiallitic red soil and 100% in a ferrallitic soil (Duchaufour, 1977).

Differences in soils from major world regions were highlighted in the last several decades by global soil mapping programs conducted under the aegis of the FAO and UNESCO (Deckers et al., 2002). The new soil maps of the world and development of modern national and international soil classification systems disclosed or unmasked the limitations of concepts, methods, and techniques based on experience and information acquired in mid-latitudes when applied to tropical soils (Steila, 1976; Lepsch and Buol, 1988; Finkl, 1995). Far too complex to fit readily into the framework of concepts based on mid-latitude soils, tropical soils are now regarded within modern soil paradigms as a distinctive climato-geographic grouping (e.g., Duchaufour, 1978; Jenny, 1980) with unique properties and characteristics that require special care in land use and environmental protection. Another, more specific point of view, is offered by reference to soil temperature regimes. While recognizing the continual warmth of tropical (equatorial) conditions, soil temperature is regarded in some modern classification systems as an important parameter in soil development but it is not a definitive criterion for identifying tropical soils. According to the (U.S.) Soil Survey Staff (1992), for example, soil temperature classes are used as family differentiae in all orders. For soil families that have a difference of less than 5 °C between mean summer and mean winter soil temperatures at a depth of 50 cm from the soil surface, the temperature classes in warm climatic regions are defined as isothermic (10 to 22 °C) and isohyperthermic (22 °C or higher).

In the classical sense of tropical soil development, based largely on their experience in Indonesia, Mohr et al. (1972) helped to firmly establish that 'tropical soils' are products of long-term intense weathering under low-latitude conditions. However, readers should be aware that Mohr's model, Indonesia, is largely dominated by youthful volcanoes, and, with something like ten thousand islands, by littoral deposits, both of which are excluded from our global generalizations. Soil scientists traditionally recognize the importance of climate (*re* the climatic regime) among the five factors (topography or relief, biological activity, climate, parent material, and time) of soil formation, as described by Jenny (1941) in his functional-factorial approach to soil genesis. Historically known as soil-forming factors, Jenny (1980) regarded them as a group of variables that are ecosystem determinants or variables. Long-term cycles of precipitation and temperature, as well as seasonal variations in evapotranspiration, are regarded by pedologists as important factors in the development of soil properties that may, in turn, by used as indicators of past climates and changing environmental conditions. Although climatic regimes in the tropics range from deserts to perhumid conditions, weathering profiles of the humid tropics are commonly included in the concept of tropical soils (e.g., Ganssen and Hadrich, 1965; Duchaufour, 1978; Buol et al., 1980; Richards, 1996).

When viewed in detail, pathways of soil development in the humid tropics show great variation with climate being the primary and overriding controlling factor for many key soil properties in equatorial regions. These properties relate not only to pedogenic processes but also to soil as an essential natural resource (Jenny, 1980; Hassett and Banwart, 1992) and potential of the land to produce crops (Aubert and Tavernier, 1972; Foth and Schafer, 1980; Anderson and Ingram, 1993), particularly within the context of sustainable development as the human population of tropical regions continues to expand exponentially (Bouma et al., 1996).

Soils of the tropics are well known for their inherent low fertility, with the exception of some that are developed in alluvial or volcanic parent materials (Sanchez, 1994). The ability of tropical soils to support crops is limited by properties that are different from middle-latitude soils and that is why tropical soils require special management techniques to realize their yield potential (Steila, 1976; Foth and Schafer, 1980; Hassett and Banwart, 1992; Juo and Franzluebbers, 2003; van Wambeke and Nachtergaele, 2003).

Environments of formation for tropical soils

Tropical soils occur in regions that are humid enough to allow development of woody plants such as hygrophilic forest (ferrallitic soils of humid climates), xerophytic forest (fersiallitic soils of semi-arid evergreen forests), or mixed savanna or bush (ferruginous tropical soils) (Duchaufour, 1977). When the climate becomes even dryer, xerophyllic steppe takes the place of forest and the soils become transitional to other kinds of weathering products. While climate remains the fundamental factor of pedogenesis in hot climates, its duration, seasonality, and long-term alteration or replacement by other climatic regimes during plate-tectonic migrations and ice ages (e.g., low-latitude cycles of aridity or pluviosity) becomes an important consideration in the development of profiles of deep chemical weathering on stable land surfaces. During the Quaternary ice ages there were severe climate fluctuations in the tropics (perhumid to arid and back) (Fairbridge, 1976; Fairbridge and Finkl, 1980; Retallack, 1990).

Characteristic of a different climatic zone, three basic phases of weathering (where organic matter is not significantly involved) are often recognized in hot climates. Pedologists have noted (e.g., Duchaufour, 1977; Goudie and Pye, 1983), however, that these phases of weathering can occur simultaneously in the same climatic zone and, when conditioned by site factors that may affect the relative duration or intensity of pedogenesis, they can also be considered as phases in the same overall weathering process. These three phases, following the nomenclature of Duchaufour (1977), are characterized by an increasing degree of weathering of primary minerals, an increasing loss of combined silica, and increasingly marked dominance of neoformed clays. In Phase 1 (fersiallitization), there is a dominance of 2 : 1 (expanding lattice) clays rich in silica, considerable amounts of free iron oxides that are more or less rubified (red or ochrous color), and the exchange complex is almost saturated by the upward movement of bases during the dry season. An argillic horizon often occurs as a result of illuviation and cheluviation. This phase is typical of subtropical climates with a dry season. Phase 2 (ferrugination) features stronger weathering (some primary minerals such as orthoclase or muscovite may persist), marked desilication, and more 1 : 1-type clays (kaolinite) than 2 : 1 transformed clays. Iron oxides may not be rubified, and base saturation is variable, depending upon the humidity of the climate and the importance of the dry season. Illuvial horizons are less well developed than in fersiallitic soils. Phase 2 weathering represents the final stage of pedogenesis in climates that are less hot (humid sub tropics) or marked by a dry season (dry tropics); these weathering products more or less correspond to ultisols (USA) and Acrisols (WRB). Phase 3 (ferralitization) is characterized by complete weathering of primary minerals (except quartz) and the clays are all neoformed, consisting solely of kaolinite. Gibbsite occurs frequently but its presence is not essential. Although illuviation still occurs, there is no true argillic horizon. This phase in the tropical climofunction, which is generally reached in hot climates on those materials that are the oldest or where very rapid development can occur, produces ferrallitic soils, which more or less correspond to the oxisol order (USA) or the Ferralsols (WRB).

Humid tropical regions are characterized by a continually moist environment with a pattern of two precipitation maxima, a total rainfall of at least 2 000 mm or more, and a mean temperature greater than 25 °C with only slight daily variation. Within the tropics three basic climatic types, based on rainfall contrasts, are identified in the Köppen-Geiger climate classification system (Köppen and Geiger, 1930; see also Trewartha, 1954): the constantly wet or tropical rainforest climate (*Af*), an Am monsoon rainforest climate in which unusually heavy rain compensates for a short dry season, and the *Aw*, tropical wet-and-dry (savanna) climate, with its summer or zenithal rains and low-sun dry season. In the savanna climates that occur towards the subtropics, there is only one rainy season corresponding with the high sun period; that season may be split in half, however, by the forward advance and retreat of the monsoon front (Smith, 1967). Rainfall varies considerably with location and altitude from 600 mm to 1500 mm per annum, and although the average temperatures are similar to those of the humid tropics, the range (20 °C) is much greater, frequently exceeding 40 °C near the end of the dry season and falling to 0 °C in nighttime lows near the winter solstice.

Climatic changes associated with Pleistocene glaciations in upper and middle latitudes also affected the margins of tropical areas (Büdel, 1982; Arnold et al., 1990). Much of tropical Africa, Australia, Brazil, and India underwent stages of ice-age hyperaridity (Fairbridge, 1972). Sand dunes from the Sahara reached as far south as the Congo (Zaire) Basin, as did Kalahari sands from the south. In South America, dune sands reached from Patagonia to the Amazon Basin; even in the littoral rainforest belt of Brazil, the geomorphology and sediments show cyclic evidence of extended seasonal aridity (Bigarella and de Andrade, 1965; Fairbridge and Finkl, 1980). Thus, in the case of the tropical arid Sahara (*BWh* climate) and the subtropical Sahelian region savanna (*BSh* climate), i.e., the belt that runs from Senegal and Sierra Leone to Nigeria and the southern Sudan, when subjected to arid conditions during these dry phases, the restricted vegetative growth led to more rapid natural soil erosion. In the moist or pluvial phases, corresponding to interglacial climates, semi-arid boundaries (with monsoonal summer rains) shifted poleward and the vegetative balance was permitting more growth of savanna-type trees, which resulted in greater soil stability. During the approximately 2 million years of the Quaternary Period, there were at least 20 cycles of alternating humidity and aridity (interglacial-glacial global regimes). These changes in climatic regime affected the distribution and density of vegetation cover which in turn resulted in stabilized-destabilized phases on land surfaces that profoundly affected the areal extent and degree of weathering (saprolitization), formation of duricrusts, and soil development as well as the loss of soil materials from hills lopes (e.g., Finkl and Churchward, 1976; Williams, 1985; Finkl, 1988). Strong climatic fluctuations were not limited to the Quaternary ice age, but can be traced back in geological time. Ancient soil surfaces, notably with formation of duricrusts (e.g., laterite) (Beckmann, 1983), can be identified and dated 50, 100 or even 200 million years (Retallack, 1990). Examples of laterite deep weathering profiles developed in crystalline rocks are found on the tropical/subtropical shield areas of Australia, Africa, and South America. Figure T13 shows typical profile development in the granitic terrain of the Darling Ranges in southwestern Western Australia. A similar deep weathering profile on the Brazilian craton is shown in Figure T14. Both profiles are developed in situ with a truncated surface (eroded surface horizons) and extensive mottled (oxidized) zone. The Brazilian example (Figure T14) shows more extensive development of pallid clays near the base of the road cut. Remains of some of these ancient paleosols still provide the framework of some modern tropical soils (Finkl, 1988; Nahon, 1991). Pedologic mantles of tropical humid (equatorial) regions, which often reach thicknesses of 100 m or more of chemically weathered or altered materials (alterites), often

Figure T13 Chemical alterite of the lateritic type near Toodyay (85 km east of Perth) in the Darling Ranges, escarpment of the Darling Fault line. The results of deep chemical weathering shown in this railway cut shows oxidation of granite parent rocks to produce thick zones of chemically altered materials. Quartz veins comprise less weathered residuum that features small core stones and provides proof of in situ development. The cut shown here is about 20 m deep, but these deeply weathered soil mantles typically extend to great depths that are often in excess of 50 to 100 m. The mottled zone shown here overlies pallid kaolinitic clays at depth.

contain several differentiated zones that are superposed vertically and which are strongly lithodependent in the lowermost portions. As a consequence of climatic change and continental drift due to shifting of tectonic plates, deep weathering profiles with or without protective duricusts now often occur as relict soil formations in many subtropical and temperate zones (Fairbridge, and Finkl, 1980; Retallack, 1990). In contrast to their great longevity in the landscape, duricrusts formed during the Holocene (the last 10 000 yr or so) were mostly established within a century or two (Goudie, 1973; Fairbridge, 1976).

Tropical geomorphic environments and soils

Many inter-tropical areas have been dry land for long periods of geological history (in places 200 million yr or more), and the deposits on them are often deeply weathered terrestrial materials dating back at least to mid-Cenozoic times (Bridges, 1978; Bremer, 1981). Within any particular region, geomorphologists commonly recognize several surfaces associated with cycles of erosion of different ages (King, 1962; Twidale and Campbell, 2005). Although different kinds of subdued relief states (including soils and weathering mantles) associated with near end products of climatomorphogenic planation are recognized in tropical and peritropical regions (e.g., peneplains, pediplains), the widespread occurrence of etchplains is becoming quite generally appreciated. As Büdel (1982) stresses, the existence of etchplains as a dominant relief type is proof that rivers cannot cut down faster than planation and cannot carve valleys even over very long periods of time. Inextricably intertwined in the etchplain concept is the prolonged and intense chemical weathering (alteration) of parent rocks on stable cratons where the basal surface of weathering (weathering front) chemically decomposes at depth, while in the rainy season finely worked material is correspondingly removed from the groundsurface by highly effective sheet wash. Büdel (1957) proposed that this "mechanism of double planation surfaces" (Mechanismus der doppelten Einebnungsflächen) is responsible for creating etchplains over long periods of geologic time. Other workers have confirmed the deduction as a general rule and emphasized its importance to the development of tropical landscapes in South America, Africa, and Australia (e.g., Finkl and Churchward, 1973; Thomas, 1974; Finkl, 1979; Bremer, 1981; Spath, 1981; Twidale and Campbell, 1993, 2005). As explained by Büdel (1982), Bremer (1981) and Spath (1981), this pedogeomorphological concept is of fundamental importance to understanding tropical landscapes because in the entire ectropics, and in arid and humid tropical mountains, mass wasting increases as the slope becomes steeper. In the humid tropics and peritropical zones, the situation is completely reversed – only where soil is present does erosion occur, continuing the development of flat surfaces. Where bedrock is exposed, as in inselbergs, shield inselbergs, or tors, the rock surfaces are edaphically arid and physical weathering, consisting of small-scale exfoliation and grus weathering, works far more slowly than chemical weathering (Bremer, 1975; Twidale and Campbell, 2005). The rock surface itself is frequently "armor-plated" by superficial concentration of silica, iron and magnesium oxides (see Fairbridge, 1968, pp. 552, 556, 1 104).

Figure T14 Laterite developed on shield rocks in southeastern Santa Catarina State, Brazil. The oxidized mottled zone (*upper part of the profile*) and kaolinitic pallid zone (*lower part of profile*) are typical of chemical laterites that are differentiated into zones based on fluctuating water tables and oxidation. Much of the mottled zone has been eroded away at this location leaving a thin oxidized layer that transitions in pallid kaolinitic clays that may extend for many tens of meters below the surface.

These planation surfaces have soils of different ages upon them with different profiles and properties. On tropical cratons (stable platforms or continental crustal areas with a nucleus of Archean age), Fairbridge and Finkl (1980) recognize a "cratonic regime" that is characterized by long-term (on the order of 10^7–10^8 yr) alternations between distinct high and low relief states. Dependent upon these two conditions are the vegetation, weathering, and soils. The stable biostatic state is characterized by high sea levels, when land areas are reduced in size, and maritime climates associated with the thalassocratic condition. In the unstable rhexistatic state when land areas are expanded, relief is amplified, and continental climates spread out under the epeirocratic condition, vegetative cover is reduced and soils become eroded. The extensive redistribution of materials which thus takes place on geomorphic surfaces of great antiquity results in complicated patterns of soils, which can be understood only if their mode of origin is first deciphered.

Concepts of erosional and depositional phases in soils, as developed in Australia (e.g., Butler, 1959), have greatly assisted in the elucidation of soil patterns found on these old continental blocks. Also, in many parts of the tropics and sub tropics there are various types of duricrusts (e.g., ferricrete, silcrete, calcrete) (Fairbridge, 1968; Goudie, 1973; McFarlane, 1976; Goudie and Pye, 1983) that have a striking impact on the landscape, a fact appreciated by many of the great explorers and travelers of the nineteenth century. Perhaps their strongest visual impact is on landforms, but their effect on vegetation associations and protection of underlying soils is considerable, as is their impact on human activities and the cultural landscape. The importance of an indurated laterite crust in the landscape is emphasized by recognition of distinct environments commonly referred to as "lakere" and "bowe" in West Africa where they stretch over considerable portions of east and southeast Senegal; southern Mali, Chad, and Sudan; the Fouta Plateaux of Guinea; and the north parts of the Central African Republic. Bowe may develop extremely quickly, within one season of vegetation clearance for plantation crops or grazing land, as seen in India and Amazonia when cleared tracts became virtually pavements of rock in five years (McNeil, 1964). Modern examples of the bovalization process occur in many parts of Amazonia where tropical rainforests are cut down for grasslands that feed beef stock. This anthropogenic duricrust formation appears to be related to the dehydration of silica and ferruginous gels. These develop in poorly drained rainforest soils, evaporation initiates a rapid loss of soil moisture and cement-hard cryptocrystalline mineralization occurs (creating ferricrete and silcrete).

At low and intermediate elevations within the tropics, temperatures are high throughout the year without substantial seasonal variations. In these high isothermic regimes, soil-forming processes (see *Weathering systems in soil science*) occur faster than in temperate regions (Bridges, 1978; Nahon, 1991), particularly the processes leading to advanced weathering stages of the parent materials. High temperatures also accelerate the biological turnover of organic matter in tropical soils (by bacteria, earthworms, and termites), a process that builds up humic complexes (Martius et al., 2001). The advanced stages of weathering, which occur in the humid tropics, are partly due to rapid rates of decomposition for long periods.

Age is a significant variable that determines many attributes of soils in tropical environments and distinguishes them from younger soils in temperate regions. The largest land areas of the tropics belong to tectonically stable continental shields (cratons) and tablelands, which have not been subjected to geologically recent folding. Rather, they have been subjected to gentle upwarping into continental swells, described by King (1962) as cymatogens, and broad downwarping into large basins. This tectonic framework is particularly true for much of Africa, Australia, the Brazilian and Guinean shields in South America, and the Gondwana part of the Indian peninsula. Soil erosion has not been strong enough to remove the products of weathering on these relatively flat-lying cratons of low relief and consequently vast waste mantles have accumulated from deeply weathered materials (e.g., Finkl, 1988). The weathered materials comprising these waste mantles possess a very low mineral reserve for supplying nutrients to plants, are largely dominated by kaolinite in the clay fraction, and have retained a high concentration of free iron oxides in the parent material. Low cation absorption capacities have these soils particularly susceptible to leaching, although most tropical soils contain some free aluminum oxides. In general, they have a deep acid solum that is poor in both major nutrients and micronutrients. Generally, they are well drained and their structure provides good aeration. However, as a result of their evolution during millions of years under varying environmental conditions, they often show an altered upper layer in which gravels and even stones play an important role. These deep, well-drained soils of the humid tropics have been called by such names as latosols, sols ferrallitiques, ferrisols, kaolisols, oxisols, etc. in different countries (cf. Figures T13 and T14 for examples in Australia and Brazil).

Not all soils within inter-tropical environments are developed on old landscapes and some highly productive soils may occur on young constructive geomorphic surfaces in equatorial regions. Recent mountain building in alpine orogenic belts has exposed fresh rock to erosion and provided a source of mineral nutrients to crops in the foothills of the Andes, Himalayas, and Southeast Asia. Depressions and valleys in tropical Asia, for example, are filled with detrital materials that react to management differently from the soils on continental shields. A greater variability occurs within the profile characteristics of these soils and no longer is the low mineral supply a major limiting factor for plant growth. During a long dry season in areas with *Aw* and *BSh* climates (or humid subtropical climatic regimes), however, these soils may develop a structure unfavorable to rainwater penetration and root development, which increases the erosion hazard. Soil scientists have variously referred to these soils as: sols ferrugineux tropicaux, sols ferrallitiques lessives, red yellow podzolics, ferrisols (in part), ultisols, ferruginous soils, krasnozems (red earths), zheltozems (yellow earths), or gray podzolics (Aubert and Tavernier, 1972). The younger or rejuvenated soils developed from various parent materials have been called sols bruns, tropepts, ferrisols, or alluvial soils; those from basic volcanic rocks such as basalts, reddish brown lateritic or terra roxa estruturada; and those from volcanic ash have been referred to as Andosols or andisols. The most productive soils are those among Nitisols (cf. nitosols) (Spaargaren, 1994).

Distribution of major tropical soils

Due to the complexity of soil geography in equatorial environments and the desire to perceive an overall view of tropical soil distributions that can be reasonably grasped, simplification of data is necessary. Because there are a large number of soil classification systems in use with regional specializations on different continents and within separate counties (see, for example, discussions in Buol et al., 1980; FitzPatrick, 1980; Finkl, 1982a,b; Eswaran et al., 1983; FAO-UNESCO-ISRIC, 1990;

Van Wambeke et al., 1990; Soil Survey Staff, 1992; Spaargaren, 1994; Deckers et al., 2002), it is advantageous to consider a global regionalization of tropical soils in terms of a single comprehensive international system. It is also seen from geographical applications of modern soil classification systems, summarized on a worldwide basis by Buol et al. (1980) and Finkl (1982a,b), among others, that tropical soils comprise a major part of many systems of classification. The complexity of nomenclature has, to a large extent, been rationalized in the FAO legend for the Soil Map of the World (FAO-UNESCO, 1974, and subsequently updated with the release of additional map sheets). For the sake of clarity, the common language of the FAO-UNESO Soil Map of the World (FAO-UNESCO-ISRIC, 1990) is used as a central reference system in the following discussion of tropical soils. In their 30 million km^2 extents, they are typical of the ancient cratons, specifically the Precambrian shields of South America, Africa, India, and Australia. As described below, the main categories of tropical soils are Acrisols (1 000 million ha), Ferralsols (750 million ha), Fluvisols (350 million ha), Lixisols (435 million ha), Luvisols (650 ha), Nitisols (200 million ha), sesquisols (60 million ha), and Vertisols (335 million ha). Synonymous terms or previous widely used terminologies are indicated where appropriate in reference to the FAO terminology (Deckers et al., 2002).

Soils of humid tropical environments

From a pedo-geographic perspective, soils of the tropical soil-forming environment are restricted to lowlands in the equatorial domain. Tropical soils are known as those with the greatest depth and intensity of chemical weathering. Because there are almost no weatherable minerals left in the plant-rooting zone, many tropical soils have a low nutrient status and require special land care procedures to maintain natural productivity.

Sesquisols

Sesquisols (from E. *sesquioxide*; connotative of iron and aluminum; soils containing a petroplinthite or plinthite layer) are soils either containing at shallow depth a layer indurated by iron (petroplinthite), or at some depth mottled material that irreversibly hardens after repeated drying and wetting (plinthite). These soils mainly occur in the tropics but examples also are found in subtropical and temperate regions, such as the rafia surface of central Spain or the Great Plateau of Western Australia. Those with a shallow petroplinthic horizon were also known as high-level laterites, ironstone soils, or sols ferrugineux tropicaux a cuirasse (Soil Survey Staff, 1992). They have widespread occurrence in western Africa, especially in the Sudano-Sahelian region where they cap structural tablelands; central-southern India; the upper Mekong River catchment area, parts of northern and western Australia, and the eastern part of the Amazon region in Brazil and on shield areas of Surinam and the Guianas.

The sesquisols with plinthite are known as Plinthosols (FAO-UNESCO-ISIC, 1990), groundwater laterite soils, low-level laterite, lateritas hidromorficas, sols gris lateritiques, or plinthaquox (Soil Survey Staff, 1992). They are found in extensively flat terrains with poor exorheic (external) drainage, such as the late Pleistocene or early Holocene sedimentary plains of eastern and central Amazonia, the central Congo basin, lowlands of Indonesia, and older Mesozoic surfaces in Western Australia. In many regions, the subsurface petroplinthite layer becomes exposed at the surface by erosion to form a ferricrete caprock or duricrust. Geomorphically, the soils may occur on gentle rectilinear slopes with an impermeable substratum and in foots lope positions along concave slopes in rolling or tableland landscapes.

Well-drained soils with loose ironstone concretions (pisolitic materials) are frequent nearly everywhere in the tropics and subtropics, in many landscape positions. The gravelly material is the result of former plinthite formation, subsequent hardening, and transport or re-weathering. The soils concerned are geomorphically related to sesquisols, but pedomorphometrically belong to other soil classes. The global extent of soils with plinthite is estimated at about 60 million ha (FAO-UNESCO-ISIC, 1991). Those soils with a shallow petroplinthic horizon have poorer, stunted natural vegetation than consociated soils without such a hardpan. Where the horizon is less shallow, less dense, broken up, or transported downslope into sesquiskeletal accumulations (e.g., colluvial pisolitic gravel deposits commingled with freshly weathered rock fragments), the vegetation may be even more luxurious than its non-stony counterparts because of the presence of less weathered pockets within the plinthic material. Arable cropping and tree planting is problematic because of the stoniness of the soils, but the latter feature is often welcomed by construction engineers who use the materials in road construction and for building purposes.

Imperfectly drained soils with a plinthite horizon are more sparsely vegetated by phanerophytes than geographically associated well-drained soils, for instance tree savanna or grassy savanna instead of closed-canopy high forest. Also, the land use on such soils is often restricted to extensive grazing because arable crops would suffer from poor rooting conditions. Artificial drainage of the soils would entail a serious hazard of irreversible hardening of the plinthic material. The hardening liability is, however, an asset for non-agricultural uses, including mining (for iron ore, manganese, bauxite) and building material (brick making, road building, terracing). Weathered alluvial materials, which sometimes contain placer deposits (e.g., gold, diamonds, and tin), are mined in deeply weathered landscapes.

Ferralsols

Ferralsols (from L. *ferrum*, iron; connotative of a high content of sesquioxides; soils with a ferralic, oxic B horizon) are deeply weathered, iron-rich soils that are often associated with a hard horizon generally known as laterite. These soils include most of the soils previously called laterite, groundwater laterite, and latosols (Soil Survey Staff, 1992; Spaargaren, 1994). In the soil continuum, soils with ferralic properties represent the weathering extreme of the spectrum. These soils are formed by the progressive hydrolysis and complete transformation of the parent rock into clay minerals, oxides, oxyhydroxides, concentrations of the resistant residue, and loss in the drainage of much material, particularly basic cations and silica (Buol et al., 1980; Nahon, 1991). The central concept is represented by a soil formed on a stable landscape having been subjected to weathering and soil formation for a long time. Profile development follows a number of different pathways as determined by the nature of the parent material and drainage characteristics. The upper parts of these soils that have free drainage may become saturated with water during the rainy season but this condition does not persist because there is no evidence of reduction. In the lower part of the soil, the mottled clay that seems to derive its color pattern from prolonged periods of wetness in an anerobic environment contributes to ferruginous nodular differentiation (FitzPatrick, 1980; Nahon, 1991).

This tropical formation of soils, ferralsolization, characterized by a colloidal fraction dominated by low activity (kaolinitic) clays and sesquioxides produces Ferralsols (Eswaran et al., 1983). These soils have very low amounts of weatherable minerals that have the potential to release nutrient cations on weathering, a uniform profile characterized by its lack of horizonization, a reddish color, weak expression of pedal structure, and few marks of other soil forming processes such as clay accumulation through translocation (Paramanathan and Eswaran, 1981). Weathering has been sufficiently advanced that rock fragments with weatherable minerals are absent. Secondary accumulation of stable minerals (e.g., gibbsite or iron oxyhydrates) may be present in concretionary (pisolitic) forms or as part of the fine earth fraction of the soils (e.g., Fairbridge and Finkl, 1984). Typical soils are situated on geomorphologically old surfaces, which have been formed through erosion and deposition (Van Wambeke et al., 1980). Many such soils are formed in transported and reworked materials and may have little relationship to the underlying geological strata. Figure T15 shows a soil profile in Western Australia that contains transported laterite gravels (pisoliths) that have moved down slope under the influence of gravity. The pisoliths and finer-grained soil materials have no genetic (parent material) relationship with the underlying granite.

Figure T15 Transported lateritic detritus moving down slope on the West Australian craton near Narrogin (east of Perth). Derived from lateritic materials farther upslope, these colluvial deposits move down slope to a point where they become stabilized and form new parent material for another phase of soil formation. The materials here are unconformably overlying granitic boulders. Surface horizons commonly contain pisoliths (ironstone gravels). Indurated ferricrete boulders are often associated with these transported or secondary laterites.

Environment of laterite (ironstone)

The term *laterite* was reportedly first used in India (cf. Buchanan, 1807; Babbington, 1821) in reference to the vesicular mottled, red and cream, clay which was dug out of the ground, shaped into bricks, and allowed to dry in the sun. Because the early workers did not describe the morphological properties of the material in great detail nor provide chemical analyses, the term has been used rather loosely for ferruginous clayey material that was hard or would harden on exposure. In addition, the term was often stretched and widely applied to many weathered materials so that red, strongly weathered, tropical soils became known as lateritic soils and, consequently, the term was often applied whether or not soils contained true laterite. In spite of these difficulties, modern researchers now apply the term laterite (plinthite, petroplinthite) to a soil horizon that is hard or will harden on exposure and is composed mainly of the oxides, oxyhydroxides of iron and/or aluminum with varying amounts of kaolinite and quartz and sometimes oxides of manganese.

This broad definition of laterite includes quite a range of material, because horizons that are hard or harden, can be vesicular, concretionary, massive, or mixtures of these types (FitzPatrick, 1980). Although vesicular laterite is very common, the greatest variability seems to be in the number and type of concretions (glaebules) in anyone formation. Some workers divide the concretions into two main types – pisolitic and nodular. Here there is also confusion, because some rounded fragments of detrital vesicular laterite are termed pisolites. There are a large number of profile and landscape positions in which laterite will form. In the majority of cases, laterite seems to be a specific soil horizon formed above or within the mottled clay. Such a type of laterite occurs dominantly on flat or gently undulating landscapes and is attributed to a fluctuating water table. Because laterite hardens on exposure, in many (now semiarid) landscapes it forms a surface capping following uplift and aeration of the topsoil, so that the landscape has a number of mesas (or buttes) and escarpments (called breakaways in Australia) below which are long pediment (or parapedimented) slopes with a cover of pedisediments. With time, the laterite weathers, breaks off into fragments of various sizes and forms relatively thin <1 m) colluviual covers on the slope but with much thicker accumulations on foots lopes and in valleys (McFarlane, 1976). In some circumstances, this colluvium becomes cemented to give a secondary type of laterite.

Although the morphology, mineralogy, and genesis of laterites is extremely variable, several general types are recognized, as summarized by FitzPatrick (1980): (1) mottled red and cream material with weak vesicular structure composed of kaolinite, iron oxides, gibbsite with partially preserved rock structure; will harden on exposure. This type is derived from the characteristic mottled clay of the tropics, (2) vesicular, composed of a hard continuous phase of dark brown or black, iron impregnated material surrounding cream kaolinitic or gibbsitic clay, (3) very dense massive material dominated by subspherical black iron oxide concretions embedded in a reddish-brown matrix, (4) reddish-brown massive with abundant black concretions and thin veins of well crystalline kaolinite between the concretions, (5) yellowish-brown to reddish-brown, hard, scoriaceous and composed dominantly of gibbsite, (6) yellowish-brown, massive, dominated by gibbsite concretionary material, (7) black or very dark brown massive containing much quartz sand, gravel and small rock fragments on lower slope positions, (8) black or very dark brown, fused nodular concretions, very high bulk density, composed mainly of iron oxide and manganese dioxide in wet lower slope and depression situations, (9) yellowish-brown to red cemented black concretions, very high bulk density in a high porosity mass of fused concretions that have been concentrated by differential erosion and then cemented, (10) massive, dark-brown to black, containing abundant black spherical units and rounded rock fragments forming a cemented colluvial deposit. Sometimes two different layers of laterite occur one above the other in the same profile. Since most laterites are very old, they are often influenced by later pedogenic processes so that some have accumulations of calcite, gypsum and may even be silicified.

Ferralsols cover an estimated worldwide area of about 750 million ha with roughly 60% found in South and Central America, and the rest in Africa (FAO, 1991) and Australia. These soils are geographically associated with Cambisols in areas with rock outcrops or where rock comes near to the surface. On the stable surface they occur together with Acrisols, which seem often to be related to the presence of more acidic parent materials (e.g., gneiss). On more basic rocks they occur associated with Nitisols, with no apparent relation to underlying rocks or topographic positions. Near valleys, Ferralsols merge into Gleysols, Planosols or even Arenosols (the southern African dambo system) and sequisols (in the eastern Amazon basin).

The low nutrient (base) status and low organic matter content give these soils very low natural fertility but they often support high forest. The relationship between Ferralsols and their natural forest vegetation is a good example of the delicate balance of nature in which nutrients are constantly recycled to maintain the forest community. When the forest cover is removed by land clearing and agriculture is practiced, fertility is quickly exhausted and crop failure normally results. This closed forest-soil nutrient recycling system accounts for the practice of shifting cultivation so highly developed in parts of equatorial Africa, Brazil, Malaysia, Borneo (Kalimantan) and Sumatra, and Papua New Guinea (Steila, 1976; Anderson and Ingram, 1993). Modern practices, including liming and application of fertilizers, provide a more stable agricultural system but no completely satisfactory system of land use has been developed for many of these soils. In some cases, the greatest success is achieved with tree crops such as cocoa, oil palm, tea, coffee, and rubber (Spaargaren, 1994). Very hardy plantation crops such as sugar cane are successful. Because the profit per hectare for carbohydrate crops is small, these soils seldom sustain a high standard of living except when their utilization is on an extensive scale.

Nitisols

Nitisols (from L. *nitidus*, shiny; connotative of shiny ped surfaces) are very common in tropical and subtropical areas and were first given a separate designation in the Australian soil classification system. These soils cover more than 200 million ha globally, of which almost half is found in eastern Africa (FAO, 1991). Other regions with Nitisols are found in southern Brazil, Central America, Java, and the Philippines. These well-drained soils contain dusky red to dark brown clays with a strongly developed fine blocky (polyhedric) structure and shiny ped faces. Initially named nitosols (FAO-UNESCO, 1974), Nitisols soils have a high aggregate stability, friable consistence, high porosity, fair to good soil moisture storage capacity (5–15%) per unit volume, and an easy rooting. They may contain variable amounts of organic matter and be acid or neutral in reaction. As strongly weathered kaolinitic soils, their characteristic feature is a steady increase in clay content with depth to a maximum in the middle part of the profile, thereafter remaining uniform for some depth. Then there is a steady decrease in clay-sized particles with depth as the saprolite (alterite) becomes progressively less weathered (FitzPatrick, 1980). In many cases, intrinsic properties of the individual layers are similar to Ferralsols.

Nitisols are frequently derived from weathering products of basic rocks. Intense rapid weathering of these parent rocks results in deep profiles with a high clay content, a high amount of total and active iron, a low silt content, and a clay fraction dominated by kandites by minor amounts of gibbsite and other accessory minerals. Lateral (facies) relations observed in the landscape are controlled by topographic-hydrologic position, age of the landscape elements, and the degree of admixture with airborne materials, especially volcanic ash (Spaargaren, 1994). In undulating landscapes on basic and ultrabasic (mafic) rocks, Nitisols tend to occupy upper and middle slopes, merging into soils with Vertisols or vertic units of other major soil groups on the lower slopes and in valleys. This is the classic Lateritic-Margalitic sequence of Edelman, as described by Mohr et al. (1972). On volcanic landscape, Andosols occupy the upper slopes while Nitisols occur on the lower slopes. The Kikuyu Red Loam Nitisols of the Kenyan highlands are an example (Wakatsuki and Kyuma, 1988). On uplifted and remodeled plateau landscapes on old land surfaces, Nitisols occupy the slope positions whereas Ferralsols occur on flatter plateau parts. A classic example is the pattern of terra roxa estruturada (a Nitisol) and the terra roxa ligitima or latossolo roxo (a Rhodic Ferralsol) of the basaltic plateaus of southern Brazil (Lepsch and Buol, 1988). On landscapes formed on limestone, Nitisols may occur as pockets and frequently in juxtaposition to shallower reddish soils (e.g., Luvisols, Chromic Cambisols). Examples are found in the Mediterranean region, for instance in Italy.

Acrisols

Acrisols (from L. *acris*, very acid; connotative of low base status) are characterized by a subsurface accumulation of low activity clays, a distinct clay increase with depth, and a base saturation (by 1 M NH_4Oac) of less than 50%. These soils have been named red-yellow podzolic soils, podzólicos vermelho-amarelo distróficos a argila de atividade baixa, sols ferrallitiques fortement ou moyennement désaturés (CPCS, 1967), red and yellow Earths, latosols, and oxic subgroups of alfisols and ultisols. The latter have recently been redefined as kand- and kanhapl- great groups in the USDA's Soil Taxonomy (Soil Survey Staff, 1992).

Acrisols are common in tropical, subtropical and warm temperate regions, on Pleistocene and older surfaces where arid and humid periods have alternated. Acrisols are estimated to cover almost one billion ha worldwide (FAO, 1991), where about one-third is found in South and Central America and about 25% in southern and southeastern Asia.

On ancient shield landscapes in tropical regions, Ferralsols and Acrisols are a dominant consociation. The former soils, present on the flatter parts of the landscape or where sediments derived from weathered soils on uplands have been deposited, are little affected by erosion. Acrisols, however, are often found in these landscapes on surfaces subject to erosion. For example, they are found on low hills covered by quartz and ironstone gravel, surrounded by pediments with Ferralsols, or on lower surfaces cutting into stable uplands with Ferralsols. Old alluvial fans in tropical regions often have Acrisols, with sesquisols in associated depressions.

Acrisols border a number of other kinds of soils with which they have linkages. These are mainly Ferralsols, Cambisols, and Arenosols. Acrisols are distinguished from Ferralsols by having a larger range in cation exchange capacity of the clay (24 versus 16 cmol(+) kg^{-1}). Clay increase in Cambisols is not uncommon (Spaargaren, 1994). However, to qualify for a cambic horizon, the clay increase should not exceed the amounts set for the agric horizon. Thus, a continuum exists between Cambisols dominated by intermediate activity clays and Acrisols. Where the agric horizon is overlain by deep coarse textured horizons, linkages exist with Arenosols. By definition, the diagnostic agric horizon should occur within 2 m of the soil surface; below this depth these soils become Arenosols.

Most Acrisols in tropical regions are still under forest vegetation, which ranges from high canopy dense rain forest to open woodland or savanna. With the bulk of the nutrients concentrated in the vegetation, various forms of "slash-and-burn" have developed to cultivate these soils under traditional agriculture. Shifting cultivation (also known by such names as milpa, swidden, ladang, caingin, roza) therefore is the most common use of Acrisols. When the fallow period is sufficiently long to allow regeneration of the vegetation, this practice is probably the most sustainable form of agriculture on Acrisols. Continuous cultivation requires recurrent high input in terms of fertilizers and lime as well as other costly land management practices such as occasional ripping and deep plowing. Removal of the surface organic layer inevitably leads to significant yield decrease as the acid and aluminum toxic subsoil layers are exposed at the surface (Spaargaren, 1994).

Perennial crops like coffee, oil palm, rubber, cashew, mango and plantation of *Pinus caribaea* are well adapted to these soils. In South America, Acrisols are also common under savanna vegetation with a strong dry season. Some of these soils are placed under rainfed and irrigated agriculture after liming and fertilization. Rotation with annual crops in improved pastures should be recommended to maintain or improve the organic matter content.

Soils of wet dry (sub)tropical and warm temperate environments

Soils of savanna, steppe, and subtropical forest regions with dry periods are mainly characterized by profile varieties with cambic or argillic B horizons. Soils of the warm-temperate east coast margin climate (*Caf* in the Köppen-Geiger system) suggest the effects of strong leaching (podzolization) and ferralitization.

Lixisols

Lixisols (from L. *lix*, lye; connotative of high base saturation) are characterized by subsurface accumulations of low activity clays (cation exchange capacity of the clay is less than 24 cmol(+) kg^{-1}) and moderate to high base saturation. They show a distinct clay increase with depth in the B horizon (agric horizon). The agric horizon in Lixisols often lacks clear illuviation features and most Lixisols are therefore characterized by a sharp clay increase occurring over a short distance. Root penetration is usually good as there are no chemical barriers as in Acrisols. The absolute amount of exchangeable bases is generally not more than 2 cmol(+) kg^{-1} fine earth due to the low cation exchange capacity. Many surface horizons of Lixisols are thin with a low amount of organic matter, especially in regions with pronounced dry seasons. Only under fairly humid conditions and/or low temperatures, as occur in tropical highlands, is there considerable accumulation of organic matter.

These soils have been named red-yellow podzolics, podzólicos vermelho-amarelo eutróficos a argila de atividade baixa, sols ferrugineux tropicaux lessives, and sols ferrallitiques faiblement desatures appauvris (CPCS, 1967), red and yellow earths, latosols, and oxic subgroups of alfisols. These soils are found mainly in seasonally dry tropical, subtropical, and warm temperate regions and in areas with frequent additions of airborne dust, on Pleistocene and older surfaces. Lixisols cover an estimated area of about 435 million ha, of which more than half is found in Africa and one-quarter in South and Central America (FAO, 1991).

Lixisols are differentiated from the Nitisols by lacking a nitic horizon with its moderate to strong straight edged blocky structures and shiny ped faces that cannot be associated with illuviation cutans in thin sections. Lixisols may merge into Nitisols where the clay content of the soils is fairly high (more than 30%) and where the nitic horizon is located deeper in the soil. Lixisols are distinguished from Ferralsols by having a larger range in cation exchange capacity of the clay (24 cmol(+) kg^{-1} versus 16 in the ferralic horizon). Where the agric horizon occurs under deep coarse-textured over-lying horizons, linkages exist with Arenosols. By definition, the diagnostic agric horizon should occur in these cases within 2 m of the soil surface. Below this depth, these soils become Arenosols.

On ancient shield landscapes in the tropics, Lixisols are found in association with Ferralsols. Lixisols tend to occur on slopes and surfaces subject to erosion. Old alluvial fans in tropical regions often have Lixisols, with sesquisols in associated depressions.

The natural vegetation of most Lixisols in the tropical and subtropical regions is savanna (see *Savanna*) and open woodland. Such areas with Lixisols are often used for extensive grazing. Because Lixisols are relatively well supplied with nutrients, they are frequently brought into cultivation. The low absolute levels of nutrients require maintenance of soil fertility on a regular basis and the low cation exchange capacity often dictates split-level applications to prevent fertilizer loss.

Continuous cultivation is possible but requires recurrent fertilization and/or liming, and occasional ripping and deep plowing. Destruction of the surface organic layer degrades soil structure that in turn leads to subsequent sealing and crusting which inhibits infiltration of surface water (Juo and Franzluebbers, 2003; van Wambeke and Nachtergaele, 2003). Significant yield decrease due to adverse surface soil characteristics is regularly recorded on these kinds of soils. Rotation of annual crops with improved pastures should be recommended to maintain or improve the organic matter content. Perennial crops like cashew, mango, citrus and other fruit trees are well adapted to these soils, although some supplementary irrigation may be required in the drier parts of the tropics and subtropics.

Luvisols

Luvisols (from L. *luo*, to wash; connotative of illuvial accumulation of clay) cover some 650 million ha worldwide (FAO, 1991) for the greater part in the tropical wet-dry (*Aw* climates merging to *BSh* and *BWh*), humid subtropical (*Ca*, *Cs* climates), to subhumid temperate regions of central and Western Europe, the USA, Mediterranean regions, and Southern Australia. The dominant characteristic of Luvisols is the textural differentiation in the profile showing a surface horizon depleted in clay and an accumulation of clay in a subsurface argillic B horizon. These soils are further characterized by moderate to high activity clays and a low aluminum saturation. Luvisols form under aerobic conditions where there is free movement of water through the upper and middle parts of the soil. A distinct dry season is required for the soil to develop (FitzPatrick, 1980). The differentiation of most argillic B horizons seems to have taken place during the Holocene but some of these soils may be Pleistocene in age, especially those having formed under cooler climates.

The potential of the soils varies from moderate to good. Those soils with thick A horizons are included among the world's most productive soils. Because they occur under moist conditions, they are frequently used for mixed farming, dairying, or horticulture but wheat, oats, and maize can also be grown. Fertility is maintained by liming and fertilizer application. Erosion is a common feature and rigorous control methods must be maintained.

Vertisols

Vertisols (from L. *verto*, to turn; connotative of turnover of surface soil) occur in large areas in tropical and subtropical regions with pronounced uni- or bimodal rainfall regimes. These clayey soils, dominated by the expanding smectite (montmorillonitic) clay minerals, develop wide, deep cracks during the dry season. During the rainy season, the cracks disappear when the land becomes fairly inaccessible due to a slippery surface. The soils are very difficult to work, being hard when dry and sticky when wet. They tend to be dark colored but have a low organic matter content. The apparent shrinking and swelling of the soil mass often results in small mounds and depressions at the surface and hence the name grumosol (from L. *grumulus*, small earth mound). These soils are known by a variety of names from different regions viz. regurs (India), gilgai (Australia), adobe (USA, Philippines), badobes (Spain), tirs (Morocco, northern Africa), and margalite (Indonesia).

Vertisols generally have a high cation exchange capacity (CEC) on the order of 30 to 80 cmol(+) kg^{-1} soil. The pH (H_2O) is neutral or slightly alkaline in most cases. Base saturation (by NH_4Oac) is usually high, also because many Vertisols show accumulation of lime in some form or another. Dominant cations are Ca and Mg, while in place Na also plays an important role. In coastal regions, Vertisols occur with high amounts of soluble salts and/or sulfides or sulfates present. Vertisols are set apart from other soils by the combination of having a vertic horizon, a high clay content throughout, and deep, wide cracks upon drying. Vertisols normally occupy the lower parts of the landscape, comprising nearly level to gently undulating piedmont, flood and coastal plains (Spaargaren, 1994). Associated vertic intergrades occur in relatively higher positions, comprising strongly sloping to moderately steep plateau, mesa and piedmont surfaces.

Land use in Vertisol areas ranges from very extensive (rough grazing, firewood production, charcoal burning) through smallholder post-rainy season crop production (millet, sorghum, cotton) to small-scale (rice) and large-scale irrigated crop production (cotton, wheat, sorghum). Several management practices are deployed to improve the water dynamics. Beds, ridges and furrows protect crops from waterlogging in the rooting zone whereas contour cultivation and bunding improve infiltration. Vertisols are usually N-deficient due to the general low amount of organic matter. Other nutrients which may need correction are phosphorus and occasionally sulfur and zinc.

Charles W. Finkl

Bibliography

Anderson, J.M., and Ingram, J.S.I., 1993. *Tropical Soil Biology and Fertility.* Oxford: Oxford University Press, 240 pp.

Arnold, R.W., Szabolcs, and Targulian, V.O., 1990. *Global Soil Change.* Laxenburg, Austria: International Institute for Applied Systems Analysis, 110 pp.

Aubert, G., and Tavernier, R., 1972. Soil survey. In *Committee on Tropical Soils, Soils of the Humid Tropics.* Washington, DC: National Academy of Sciences, pp. 17–44.

Babbington, B., 1821. Remarks on the geology of the country between Tellichery and Madra. *Trans. Geol. Soc. Lond.*, **5**: 328–329.

Beckmann, G.G., 1983. Development of old landscapes and soils. In *Soils: An Australian Viewpoint.* Melbourne, Victoria: CSIRO/Academic Press, pp. 51–72.

Bigarella, J.J., and de Andrade, G.O., 1965. Contribution to the study of the Brazilian Quaternary. *Geol. Soc. Am. Spec. Pap.*, **84**: 433–451.

Bouma, J., Kuyvenhoven, A., Bouman, B.A.M., Luyten, J.C., and Zandstra, H.C., 1996. *Eco-Regional Approaches for Sustainable Land Use and Food Production.* Dordrecht, Netherlands: Kluwer, 505 pp.

Bremer, H., 1975. Intermontane Ebenen, Prozesse der Flachenbildung. *Z. Geomolphol.*, *Supplement-Band* **23**: pp. 26–48.

Bremer, H., 1981. Reliefformen und reliefbildende Prozesse in Sri Lanka. In Bremer, H., Schnutgen, A., and Spath, H., eds., *Zur Molphogenese in den feuchten Tropen.* Berlin: Gebruder Borntraeger, pp. 7–183.

Bridges, E.M., 1978. *World Soils.* London: Cambridge University Press, 128 pp.

Buchanan, F., 1807. *A Journey from Madras Through the Countries of Mysore, Canara and Malabar.* London: East India Company, 3 Vols. See Vol. 2, pp. 426–437, pp. 440–441, p. 460, p. 559; Vol. 3, p. 66, p. 89, p. 251, p. 258.

Büdel, J., 1957. Die "Doppelten Einebnungsflächen" in den feuchten Tropen. *Z. Geomorphol., NF*, **1**: 201–228.

Büdel, J., 1982. *Climatic Geomorphology.* Princeton, NJ: Princeton University Press, 443 pp. (translated by Fischer, L., and Busche, D.).

Buol, S.W., Hole, F.D., and McCracken, R.J., 1980. *Soil Genesis and Classification.* Ames, IA: Iowa State University Press, 404 pp.

Butler, B.E., 1959. *Periodic Phenomena in Landscape as a Basis for Soil Studies.* Canberra, ACT: CSIRO (Australia) Soil Publication No. 14, 20 pp.

CPCS, 1967. *Classification des sols.* Grignon, France: ENSA, 87 pp.

Deckers, J., Driessen, P., Nachtergaele, F., and Spaargaren, O., 2002. World reference base for soil resources. In Lal, R., ed., *Encyclopedia of Soil Science.* New York: Marcel Dekker, pp. 1446–1451.

Dent, D., 1986. *Acid Sulphate Soils: A Baseline for Research and Development.* Wageningen, Netherlands: International Institute for Land Reclamation and Improvement, 204 pp.

Duchaufour, P., 1977. *Pedology: Pedogenesis and Classification.* London: Allen and Unwin, 448 pp.

Duchaufour, P., 1978. *Ecological Atlas of Soils of the World.* Paris: Masson, 178 pp.

Eswaran, H., Ikawa, H., and Kimble, J., 1983. Oxisols of the world. *Poceedings of the Symposium on Red Soils. Beijing, China.*

Fairbridge, R.W., ed., 1968. *The Encyclopedia of Geomorphology.* New York: Van Nostrand Reinhold, 1295 pp.

Fairbridge, R.W., 1972. Climatology of a glacial cycle. *Quatern. Res.*, **2**: 283–302.

Fairbridge, R.W., 1976. Effects of Holocene climate change on some tropical geomorphic processes. *Quatern. Res.*, **6**: 529–556.

Fairbridge, R.W., and Finkl, C.W., 1980. Cratonic erosional unconformities and peneplains. *J. Geol.*, **8**: 69–86.

FAO, 1991. *World Soil Resources. An Explanatory Note on the FAO World Soil Resources Map at 1:25000000 Scale.* Rome, Italy: Food and Agriculture Organization of the United Nations, World Soil Resources Report No. 66, 58 pp.

FAO-UNESCO, 1974. *Soil Map of the World*. Volume I. Legend. Paris, France: Unesco, 59 pp (updated with subsequent releases of different map sheets).

FAO-UNESCO-ISRIC, 1990. *Soil Map of the World. Revised Legend*. Reprinted with corrections. World Soil Resources Report No. 60. Rome, Italy: FAO, 119 pp.

Finkl, C.W., 1979. Stripped (etched) land surfaces in southern Western Australia. *Aust. Geogr. Stud.*, **17**(1), 33–52.

Finkl, C.W., ed., 1982a. *Soil Classification.* Stroudsburg, PA: Hutchinson Ross, 391 pp.

Finkl, C.W., 1982b. The geography of soil classification. *Quaestiones Geographicae*, **8**: 55–59.

Finkl, C.W., 1988. Saprolite, regolith and soil. In Finkl, C.W., ed., *The Encyclopedia of Field and General Geology.* New York: Van Nostrand Reinhold, pp. 726–737.

Finkl, C.W., 1995. New interpretations of chemical alterites on paleosurfaces. In Menon, J., ed., *Trends in Chemical Geology,* Vol. 1, Trivandrum, India: CSIR Research Trends, pp. 187–198.

Finkl, C.W., and Churchward, H.M., 1973. The etched land surfaces of southwestern Australia. *J. Geol. Soc. Aust.*, **20**(3): 295–307.

Finkl, C.W., and Churchward, H.M., 1976. Soil stratigraphy in a deeply weathered shield landscape in south-western Australia. *Aust. J. Soil Res.*, **14**: 109–120.

FitzPatrick, E.A., 1980. *Soils: Their Formation, Classification and Distribution.* London: Longman, 353 pp.

Foth, H.D., and Schafer, J.W., 1980. *Soil Geography and Land Use.* New York: Wiley, 484 pp.

Ganssen, R., and Hiidrich, F., 1965. *Atlas zur Bodenkunde.* Mannheim, Germany: Bibliographisches Institut AG, 85 pp.

Goudie, A., 1973. *Duricrusts in Tropical and Subtropical Landscapes.* Oxford: Clarendon, 174 pp.

Goudie, A.S., and Pye, K., 1983. *Chemical Sediments and Geomolphology.* London: Academic, 439 pp.

Hassett, J.J., and Banwart, W.L., 1992. *Soils and Their Environment.* Englewood Cliffs, NJ: Prentice-Hall, 424 pp.

Jenny, H., 1941. *Factors of Soil Formation.* New York: McGraw-Hill, 281 pp.

Jenny, H., 1980. *The Soil Resource.* New York: Springer, 377 pp.

Juo, A.S.R., and Franzluebbers, K., 2003. *Tropical Soils – Properties and Management for Sustainable Agriculture.* Oxford University Press, Oxford: 281 pp.

King, L.C., 1962. *The Morphology of the Earth.* Edinburgh: Oliver & Boyd, 699 pp.

Köppen, W., and Geiger, R., 1930. *Handbuch der Klimatologie.* Berlin, Germany: Gebrüder Borntraeger, 5 Vols.

Lepsch, I.F., and Buol, S.W., 1988. Oxisol-landscape relationships in Brazil. In Beinroth, F.H., Camargo, M.N., and Eswaran, H., eds., *Proceedings of the Eighth International Soil Classification Workshop. Classification, Characterization and Utilization of Oxisols* (Rio de Janeiro, Brazil). Part I: Papers, pp. 174–189.

McFarlane, M.J., 1976. *Laterite and Landscape.* London: Academic Press, 151 pp.

McNeil, M., 1964. Lateritic soils. *Sci. Am.*, **211**(5), 96–102.

Martius, C., Tiessen, H., and Vlek, P.L.G., 2001. The management of organic matter in tropical soils: what are the priorities? *Nutr. Cycl. Agroecosyst.*, **61**: 1–6.

Mohr, E.C.J., van Baren, F.A., and van Schuylenborgh, J., 1972. *Tropical Soils, A Comprehensive Study of Their Genesis*. The Hague: Mouton-Ichtiar Baru-van Hoeve. [1959 edition, The Hague: Uitgeverij W. Van Hoeve, p. 498].

Nachtergaele, F.O., Spaargaren, O., Deckers, J.A., and Ahrens, B., 2000. New developments in soil classification: world Reference Base for soil resources. *Geoderma*, **96**: 345–357.

Nahon, D.B., 1991. *Introduction to the Petrology of Soils and Chemical Weathering.* New York: Wiley, 313 pp.

Oliver, J.E., and Fairbridge, R.W. eds., 1987. *The Encyclopedia of Climatology.* New York: Van Nostrand Reinhold, 986 pp.

Oosterbaan, R.J., 1982. Natural and social constraints to polder development in Guinea-Bissau. In *Polders of the World.* Vol. 1, Wageningen, Netherlands: ILRI, pp. 141–160.

Paramanathan, S., and Eswaran, H., 1981. Morphology of Oxisols. In Theng, B.K.G., ed., *Proceedings of the Symposium on Soils with Vaiable Charge, New Zealand.*

Pons, L.J., and van Breeman, N., 1982. Factors influencing the formation of potential acidity in tidal swamps. In Dost, H., and van Breeman, N., eds., *Proceedings of the Bangkok Symposium on Acid Sulphate Soils.* Wageningen, Netherlands: ILRI Publication No. 31, pp. 37–51.

Retallack, G.J., 1990. *Soils of the Past.* London: HarperCollins Academic, 520 pp.

Richards, P.W., 1996. *The Tropical Rain Forest.* New York: Cambridge University Press, 600 pp.

Sanchez, P.A., 1994. Tropical soil fertility research: towards the second paradigm. *Trans. 15th World Congr. Soil Sci. (Acapulco, Mexico)*, **1**: 65–88.

Sanchez, P.A., and Logan, T.J., 1992. Myths and science about the chemistry and fertility of soils in the tropics. In Lal, R., and Sanchez, P.A., eds., *Myths and Science of Soils of the Tropics.* Madison, WI: Soil Science Society of America, SSSA Special Publication 29, pp. 35–46.

Smith, D.E., 1967. Equatorial and tropical climates. In Fairbridge, R.W., ed., *The Encyclopedia of Atmospheric Sciences and Astrogeology.* New York: Reinhold, pp. 364–367.

Spaargaren, O.C., ed., 1994. *World Reference Base for Soil Resources*. Rome, Italy: FAO, 161 pp.

Spath, H., 1981. Bodenbildung und Reliefentwicklung in Sri Lanka. In Bremer, H., Schnutgen, A., and Spath, H., eds., *Zur Morphogenese in den feuchten Tropen.* Berlin: Gebrüder Borntraeger, pp. 185–238.

Soil Survey Staff, 1992. *Soil Taxonomy.* Washington, DC: U.S. Government Printer.

Steila, D., 1976. *The Geography of Soils.* Englewood Cliffs, NJ: Prentice-Hall, 222 pp.

Thomas, M.F., 1974. *Tropical Geomorphology.* New York: Wiley, 332 pp.

Trewartha, G.T., 1954. *An Introduction to Climate.* New York: McGraw-Hill, 402 pp.

Twidale, C.R., and Campbell, E.M., 1993. *Australian Landforms.* Adelaide: Gleneagles, 560 pp.

Twidale, C.R., and Campbell, E.M., 2005. *Australian Landforms: Understanding a Low, Flat, Arid and Old Landscape.* New South Wales, Australia: Rosenberg, Dural Delivery Centre. 336 pp.

Wakatsuki, T., and Kyuma, K., 1988. Chemical characteristics of Kenyan Nitisols. In Hirose, S., ed., *Agriculture and Soil in Kenya, A Case Study of Farming Systems in the Embu District and Characterization of Volcanogenic Soils.* Tokyo: Department of Land Development, Nihon University, pp. 130–133.

van Wambeke, A., and Nachtergaele, F., 2003. *Properties and Management of Soils of the Tropics.* Rome, Italy: FAO Land and Water Digital Media Series, CD ROM.

Van Wambeke, A., Eswaran, H., Herbillon, A., and Comerma, J., 1990. Oxisols. In Wilding, L.P., Smeck, N.E., and Hall, G.F., eds., *Pedogenesis and Soil Taxonomy. Part II. The Soil Orders.* Amsterdam: Elsevier, pp. 325–350.

Williams, M.A.J., 1985. Pleistocene aridity in tropical Africa, Australia and Asia. In Douglas, I., and Spencer, T., eds., *Environmental Change and Tropical Geomorphology.* London: Allen and Unwin, pp. 219–233.

Cross-references

Alisols
Biomes and their Soils
Ferralsols
Geography of Soils
Nitisols
Thionic or Sulfidic Soils
Weathering Systems in Soil Science

TRUNCATED SOIL

A soil that has had part or all of its solum removed by erosion, or by human activity. In the Northern Hemisphere soils (technically paleosols) truncated by Wisconsinian ice are found sparsely in scattered localities (for example, in the Hastings Highlands of central Ontario, Canada). See also *Scalping*.

Bibliography

Chesworth, W., and Evans, L.J., 1982. *Weathering, Soil Formation and Land Use in South and Central Ontario*. International Association of Sedimentologists, 11th International Congress, Guidebook 10, 76 p.

TUNDRA

The treeless terrain north of the boreal forest or taiga, that is more or less concentric with the North Pole. In Canada, a synonym is barren ground or land, or more simply, the barrens. Much of the area is under permafrost, and Cryosols are common.

Bibliography

Moore, Peter D., 2006. Tundra. New York: Chelsea House. 220 pp.

Cross-reference

Biomes and their Soils

TURF

A block cut from the surface of a soil with the grass growing on it, and with roots and soil cohering. Also used for a block of peat, cut as fuel. See also *sod*.

TYPE

Used in Earth science to label a particular specimen of soil or rock, as the general representative of a specific kind of soil or rock. Also used as type-locality: the locality from which the type was first described.

U

UMBRISOLS

Umbrisols are soils with a surface accumulation of organic matter of low base saturation. They are well drained, permeable, moderately deep to deep soils, of medium-texture. The profile may contain gravel, stones and boulders throughout. The following account is from FAO (2001).

Connotation. Soils with a dark topsoil; from L., *umbra*, shade.

Synonyms. Only recently recognized at this high taxonomic level. In other classification systems they appear as umbrepts and humitropepts (USA Soil Taxonomy), humic cambisols and umbric regosols (FAO), sombric brunisols and humic regosols (France) or brown podzolic soil (in several systems, for example Indonesia).

Definition. In FAO (2001) Umbrisols are defined as soils having an umbric horizon. The only other possible horizons are an anthropedogenic horizon less than 50 cm thick, an albic horizon or a cambic horizon.

Parent material. Mostly formed on the weathering material of siliceous rock; predominantly in deposits of late Pleistocene and Holocene age.

Environment. Umbrisols form especially in mountain belts where there is little or no moisture deficit, under a natural or near-natural vegetation. Above the tree line in South American and Asian mountain belts a cover of short grasses of low nutritional value is common. The same is true in areas of cleared forest at lower altitudes in northern and Western Europe. In Brazil and the USA coniferous vegetation is characteristic. In the tropical mountain belts of south Asia and Australasia, Umbrisols occur under evergreen forest.

Distribution. They are about 100 million ha Umbrisols in cool humid regions such as mountain belts with little or no moisture deficit, e.g. in the western Cordillera of North and South America. In Europe they are to be found along the northwestern Atlantic seaboard, in Iceland, the British Isles and the Iberian Peninsula. In Asia, they occur in the mountains to the east and west of Lake Baikal, and in India, Nepal, and China in the foothills of the Himalayas, as well as similar regions in Manipur (eastern India), in the Chin Hills (western Burma) and in Sumatra (Barisan range). Umbrisols also occur in mountainous terrain in New Guinea and Southeast Australia and in the eastern parts of South Island, New Zealand. Figure U1 shows the global extent. They are the natural counterparts of soils with a mollic horizon (e.g., chernozems, kastanozems and phaeozems).

Characteristics. Umbrisols are soils with relatively simple profiles of AC and A(B)C type. They are deeply drained soils with a medium-textured and a dark, acid surface horizon rich in organic matter. Other horizons may be present in incipient form, but are not diagnostic, they simply indicate an early stage of pedogenesis. Texture and depth of these soils are very variable so that no distinct hydrological characterization can be made, though Umbrisols are generally permeable and well drained. Base saturation in the umbric horizon, as well as deeper in the profile, is less than 50 percent. The high organic matter content of the umbric horizon determines that fertility level is moderately high.

Origin. Formation of an umbric horizon is crucial to Umbrisols. Vegetation and climate are the joint influences and development of the profile is strongly dependent on the deposition of significant amounts of organic material with low base saturation at the soil surface. The occurrence of umbric horizons in young soils indicates that they can form relatively quickly. The development of an incipient, non-diagnostic, spodic or argic horizon by contrast, is slow. A weak cambic horizon is another possibility.

The characteristic humus of Umbrisols can comprise a variety of humus has been described as 'acid or oligitrophic mull', 'moder', 'raw humus' and 'mor'. A slow biological turnover of organic matter under acid conditions, a relatively low temperature, wetness at the surface, or some combination of the foregoing may be implicated. A diagnostic histic horizon does not develop however, probably because conditions do not become sufficiently cold and/or wet enough, for a long enough duration.

Use. Exploitation is restricted by slope and associated erosional problems, and by cool and wet conditions. Forestry and extensive grazing are the usual land use possibilities.

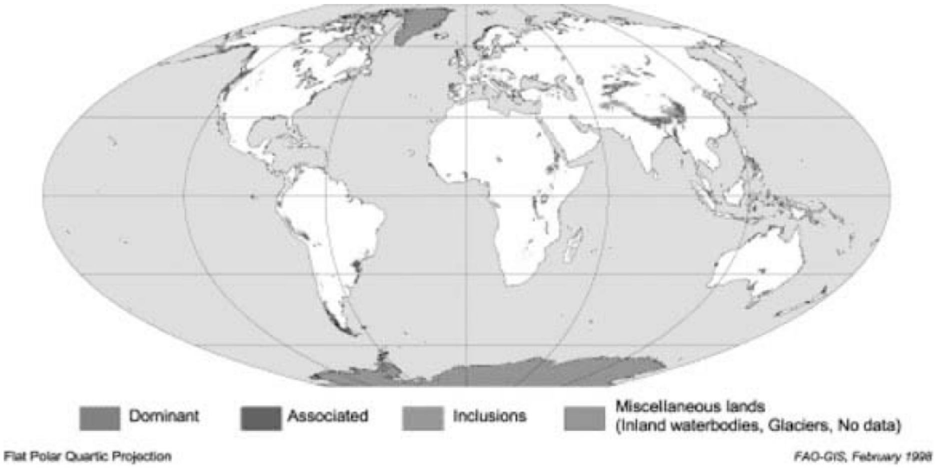


Figure U1 Global distribution of Umbrisols.

Under adequate management, Umbrisols may be planted to cash crops such as cereals, root crops, tea and coffee. Introduction of improved grasses and correction of the soil pH by liming are the principal management processes.

Where conditions are suitable and appropriate management practices are followed to control erosion, acidity and fertility, cash crops may be grown. These include cereals and root crops in the USA, Europe and South America, and tea and cinchona in southwestern Asia. In addition to cash crops, Umbrisols in New Zealand support intensive sheep and dairy farming.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science,* 2nd ed. Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

Cross-references

Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils

UNDIFFERENTIATED MAP UNIT

A map unit containing more than one soil type that cannot be readily separated from each other at the particular scale used for the map.

UNIVERSAL SOIL LOSS EQUATION

See *Revised Universal Soil loss Equation*.

UNSATURATED FLOW

The movement of water in a soil in which the pore space is not completely filled with water. Water movement in the vadose zone.

Cross-references

Flow Theory
Water Budget
Water Movement

V

VADOSE

See *Groundwater*.

VENTIFACTS

A wind-abraded pebble or boulder, a ventifact is distinctly faceted on one or more sides and is used by geologists as a diagnostic marker of an ancient climatic condition when powerful winds drove silt or sand as abrasive agents. They are often associated with soil surfaces in periglacial landscapes.

The term “ventifact” was first introduced by Evans (1911) to replace a confusing array of German terms such as “windkanter” and “dreikanter” (3-sided), and even “glyptolith” (for sculpted rock). The entry for “Ventifact” receives no less than eight citations in the *Encyclopedia of Geomorphology* (Fairbridge, 1968). A review and bibliography was provided by Bryan (1931) and experimental forms were demonstrated by Schoewe (1932). Contemporary examples were observed in the deserts of southern Iraq (Sugden, 1964).

Ventifacts are generally limited to 10–25 mm dimensions. Much larger faceted boulders are a product of glacial abrasion.

Rhodes W. Fairbridge

Bibliography

Bryan, K., 1931. Wind worn stones *or* ventifacts: a discussion and bibliography. Rept. Comm. Sedimentation, 1929–1930. *Natl Res. Council Cir.*, **98**: 29–50.

Evans, J.W., 1911. Dreikanter, *Geol. Mag.*, **8**: 334–335.

Fairbridge, R.W., 1968. *The Encyclopedia of Geomorphology.* New York: Van Nostrand Reinhold, 1295 pp.

Schoewe, W.H., 1932. Experiments on the formation of wind-faceted pebbles. *Am. J. Sci.*, **24**: 111–134.

Sugden, W., 1964. Origin of faceted pebbles in some Recent desert sediments of southern Iraq. *Sedimentology*, **3**: 65–74.

Cross-references

Erosion
Periglacial Soils
Wind Erosion

VERTISOLS

Vertisols are heavy clay soils with a high proportion of swelling clays with a 2:1 structure. As they dry out (which happens in most years) they form deep wide cracks from the surface downward. Surface soil falls into the cracks, and subsurface soil is pushed upwards, in a kind of pedoturbation called churning, which causes a mixing of the surface and subsurface materials. The following account is taken from FAO (2001).

Connotation. Churning heavy clay soils; from L. *vertere*, to turn.

Synonyms. Vertisol is a name common to several classifications. More parochial terms are some ‘black cotton soils’ (USA), ‘regur’ (India), ‘vlei soils’ (South Africa), ‘margalites’ (Indonesia), and ‘gilgai’ (Australia).

Definition. FAO (2001) defines Vertisol as soils with

1. a *vertic* horizon within 100 cm from the soil surface, and
2. after the upper 20 cm have been mixed, 30 percent or more clay in all horizons to a depth of 100 cm or more, or to a contrasting layer between 50 and 100 cm (e.g., a *lithic* or *paralithic* contact, *petrocalcic*, *petroduric* or *petrogypsic* horizons, or a sedimentary discontinuity), and
3. cracks, which open and close periodically.

Parent material. Sediments that contain a high proportion of smectitic clay, or products of rock weathering that have the characteristics of smectitic clay. The largest Vertisol areas are on sediments that have a high content of smectitic clays or produce such clays upon post-depositional weathering (e.g., in the Sudan) and on extensive basalt plateaux (e.g., in India and Ethiopia).

Environment. Depressions and level to undulating areas, mainly in tropical, semi-arid to (sub)humid and Mediterranean climates with an alternation of distinct wet and dry seasons. The climax vegetation is savanna, natural grassland and/or woodland. Vertisols are typically found in lower landscape positions such as dry lake bottoms, river basins, lower river terraces and other lowlands that are periodically wet in their natural state. Depending on parent rock and environmental conditions, Vertisols occur only in bottomlands or also on contiguous lower foot slopes or, as residual soils, even on (gently) sloping hillsides. A characteristic association of soils is shown in Figure V1, with Vertisols in the bottom lands.

Distribution. There are about 335 million ha of Vertisols globally (Figure V2), with some 150 million ha as potential cropland. There are approximately 200 million ha in the tropics, mostly, but not exclusively in semi-arid regions. A quarter of the tropical area is considered to have agricultural potential. Outside of the tropics, Vertisols occur prominently in Australia, southwestern USA (Texas), Uruguay, Paraguay and Argentina.

Characteristics. A(B)C-profiles are characteristic, with the boundary between A and B difficult to discern on account of the uniformity of properties such as color, particle size, texture and composition. A sharp textural change may be present at the top of the parent material. The A horizon includes a mulch or crust at the surface with the structured portion below. The B is vertic, and the underlying structured horizon that changes only gradually with depth. Calcite may precipitate below the vertic horizon as a distinct horizon or as a soft powdery accumulation. Gypsum is another possibility distributed uniformly throughout the matrix or as nests of crystals.

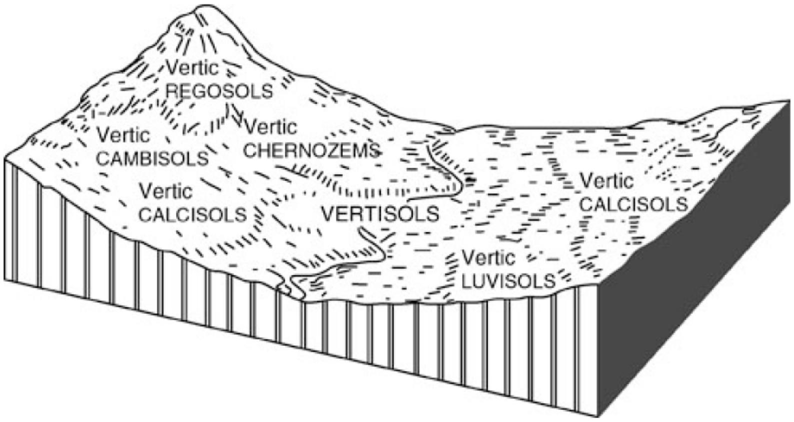


Figure V1 A typical association of soils in a landscape with Vertisols in the lowest physiographic position. Diagram from FAO (2001).

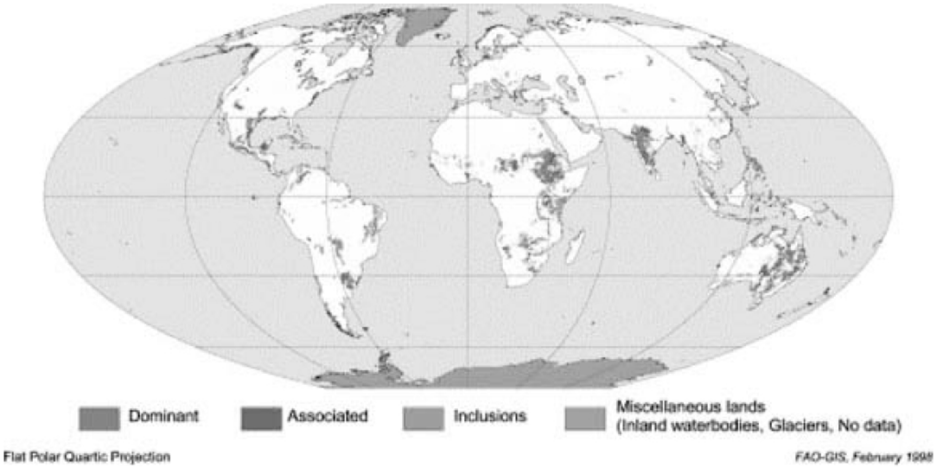


Figure V2 Global distribution of Vertisols.

Dry Vertisols have a very hard consistence; wet Vertisols are (very) plastic and sticky. It is generally true that Vertisols are friable only over a narrow moisture range but their physical properties are greatly influenced by soluble salts and/or adsorbed sodium.

Infiltration of water in dry, cracked Vertisols, with a surface mulch or fine tilth, is initially rapid. However, once the surface soil is thoroughly wetted and cracks have closed, the rate of water infiltration becomes almost zero. Vertisols usually have good water holding properties, a large proportion of the water is held between the 2 : 1 sheets of the smectites and is not available to plants.

By virtue of the smectite content, Vertisols mostly have a high cation exchange capacity (between 30 and 80 cmol (+) kg^{-1} of dry soil, measured in 1 M NH_4Oac at pH 7.0). In the general case Ca^{2+} and Mg^{2+} occupy more than 90 percent of the exchange sites with the Ca/Mg-ratio normally between 3 and 1. pH ranges from 6.0 to 8.0. Salic and Natric Vertisols become important in the more arid regions and pH values up to 9.5 are measured.

Origin. Vertisols form on smectite rich parent materials. The latter are characteristic of weathering in hot climates, generally with contrasted wet and dry seasons, where alteration of primary minerals is at a stage of bisiallitization. This is to say, that the soil solution retains a relatively high concentration of so-called basic cations, which in turn requires little or no leaching. The same conditions persist for the continued alteration of the parent material during pedogenesis. Clearly, water movement is a key factor, and environments which generally discourage leaching losses (clay-rich bottom lands for example) are typical.

The diagnostic vertic horizon is a consequence of the shrinking and swelling of smectites on drying and wetting respectively. In brief, shrinkage causes cracks to form from the surface down through the solum. Surface material falls into the cracks so that on wetting, sideways expansion of the swelling clay is relatively restricted and shear planes develop at about 20 to 30° to the horizontal. This pushes soil material upwards between cracks and begins a churning motion, which tends to mix the lower soil with the upper. The effects of shearing show up as slickensides – polished surfaces on peds grooved in the direction of shear. At the surface, the soil may develop a granular or crumb structure, in which case the material is referred to as a surface mulch, and the soil is said to be self-mulching. The preferential uplifting of soil between the cracks may result in a type of microrelief called gilgai, provided that the soil has sufficient cohesion to transfer pressures all the way to the surface.

Use. Vertisols are relatively nutrient-rich soils, generally on flat land. Consequently when properly managed they become productive farmland, and are used to produce millet, sorghum, cotton, chick peas, and rice at small scale. At a larger scale and with irrigation cotton, wheat, barley, sorghum, chickpeas, flax, noug (*Guzotia abessynica*) and sugar cane are produced. However, large areas are still unused for arable agriculture and are restricted to intensive grazing or wood collection for domestic burning of charcoal production. The tendency of Vertisols to become hard in the dry season and sticky in the wet season create difficulties in tillage, except during the short period between wet and dry seasons. Appropriate water management, with fallow periods in the drier climates, are necessary to avoid the build up of salts.

Otto Spaargaren

Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FitzPatrick, E.A., 1986. *An Introduction to Soil Science.* 2nd edn., Essex, England/New York: Longman Scientific & Technical/Wiley, 255 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer -Verlag 130 pp.

Cross-references

Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils

VOID

In a soil, pore space not occupied by solid constituents. The common dictionary meaning of the word – containing no matter; empty, unfilled – does not apply in that voids in soil may contain fluids. In micromorphology, voids due to the random packing of the solid components of a soil are termed packing voids.

Cross-reference

Micromorphology

VUGH

Relatively large voids visible under the microscope as discrete entities, not usually interconnected with each other. Derived from the term vug for similar, though macroscopic, voids in rock.

Cross-reference

Micromorphology

W

WASTELAND

Land that is unfit for cultivation or any economic use, especially used where such land is surrounded by economically productive terrain. Land colonised by weeds and ruderals.

WATER BUDGET IN SOIL

A soil's water budget quantifies the partitioning of water inputs into various outputs and storage. The balance between the outputs will determine, to a large extent, the nature of the physical, chemical, and biological processes that occur within the pedosphere. For example, variability in soil properties within catenary sequences form mainly due to changes in the rate of infiltration and subsequent soil water status along sloping landscapes.

An accurate assessment of a soil's water budget is a critical first-step in characterizing the contaminant flux to groundwater and other phenomena such as water available for plant growth, slope stability, and irrigation scheduling. A soil water budget consists of input, output and storage components as shown in Figure W1. Separate discussions on measuring each component of the budget follow.

Precipitation

Precipitation includes rain and snow as the two natural inputs for a soil's water budget. Accurate records of precipitation are available for many regions of the world. For example, in Canada records are available from the Meteorological Service of Canada (http://www.msc-smc.ec.gc.ca), a division of the Federal Government. In the United States, precipitation data is collected and archived by the National Climatic Data Center (http://www.ncdc.noaa.gov/oa/ncdc.html).

Automated recording stations have replaced manual measurements of precipitation in many countries. The tipping-bucket rain gauge is a common method of measuring rainfall automatically and continuously. Raindrops fall into a circular-topped funnel that narrows at the bottom to direct the drops into one of two small buckets that are balanced on a cantilever. When one bucket fills with water it falls and tips, emptying its load. Then the other bucket fills with rainwater and tips, completing one cycle. The cycles continue as long as rain keeps falling, each half-cycle (i.e., tip of a bucket) completes an electric circuit, with each tip counted by a datalogger. Typically, gauges are factory calibrated to record 0.2 mm of rainfall per tip, representing a high level of precision. To ensure accuracy however, each tipping-bucket gauge should be periodically calibrated. For more information on these commonly used devices see Lutgens and Tarbuck (2004).

In cold climates snowfall can be a significant component of annual precipitation. Historically, and even today, snowfall depth is often measured manually with a ruler and then precipitation is calculated by multiplying snow depth by the ratio of snow density to water density. Often, a ratio of 0.1 is assumed (Lutgens and Tarbuck, 2004). Snow depth on the ground surface can be monitored automatically using a sonic depth recorder (Chow, 1992). A heated tipping-bucket rain gauge can be designed to automatically record precipitation falling as snow. However, snowfall may be significantly underestimated due to evaporative losses of melted snow from the heated buckets. For more information on measuring snowfall see Dingman (2002).

An all-season precipitation gauge measures both rainfall and snowfall. The precipitation lands in a bucket and is recorded gravimetrically using a strain gauge attached to a datalogger. Anti-freeze can be placed inside the bucket to melt snow falling in the winter season.

Irrigation

Irrigation water may be a significant input into the budget, particularly in arid regions under intensive agriculture. Other anthropogenic inputs such as liquid manure and sewage biosolids usually add a minor amount of water that can be included under irrigation in the budget.

The amount of water applied to the soil surface during sprinkler irrigation can be measured very simply using an open-topped container. To calculate the amount of water applied to the soil

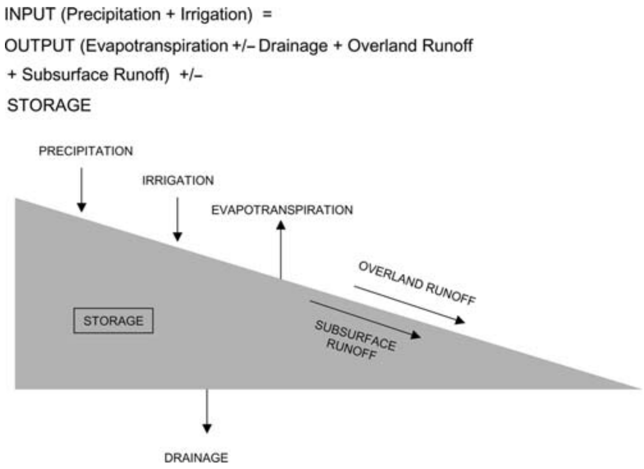


Figure W1 Relationships between the components of the soil water budget.

surface, divide the volume of water captured in the container by the cross-sectional area of the open top. To measure the amount of water that actually infiltrates into the soil under dripper or sprinkler irrigation systems or during a precipitation event, a method of measuring soil water status is required.

Time domain reflectometry (TDR), is a widely used method to measure soil volumetric water content directly in the field or laboratory. The TDR method of measuring soil volumetric water content was introduced to soil science by Topp et al. (1980). It has numerous advantages over other field methods including: (1) does not require a radioactive source; (2) high level of accuracy over a wide range of soil types using a single calibration curve such as Topp et al. (1980) equation; (3) consistent sample volume size regardless of soil water status; (4) nondestructive, so measurements can be repeated at a site; and (5) can be set-up for remote, automated data collection.

When using TDR probes installed vertically in the soil beginning from the soil surface, the increase in local soil water storage (mm) during irrigation is simply the measured volumetric water content multiplied by the TDR probe length. If the length of the vertical TDR probes is equivalent to the depth of the plant root zone, irrigation can be ceased, for example, when steady-state water content is measured by the TDR system. Automated irrigation control systems based on the TDR and other electromagnetic devices increase water use efficiency and are commercially available. For a more thorough review of these and other methods of measuring soil water content see Topp and Ferre (2002).

Evapotranspiration

Evapotranspiration is often the dominant output component of a soil water budget. It includes water that evaporates from bare soil and moist plant leaves to return to the atmosphere, transpiration of water by the plant, and use of water to grow plant tissue (Tindall and Kunkel, 1999). Both climatological factors (air temperature, wind speed, incoming solar radiation) and soil water status determine the rate of evapotranspiration. Many numerical methods exist to estimate potential evapotranspiration using climatological data (Jensen et al., 1990). However, these methods must consider different crop coefficients and available soil water to accurately estimate actual evapotranspiration. With recent reductions in the cost of meteorological instrumentation, the eddy-correlation method has become a viable means of directly measuring evapotranspiration (Verma, 1990). For more information on this accurate, direct method of measuring evapotranspiration above many different plant canopies see Brutsaert (1982).

An accurate assessment of agricultural and horticultural plant evapotranspiration demands is a critical component of a regional water management strategy plan (Rudra et al., 2000). With increasing competition for freshwater, water management policy must be based on sound scientific data making accurate evapotranspiration measurements invaluable.

Drainage

Positive drainage represents a net loss of water from the soil profile, whereas negative drainage represents a net gain of water. Positive drainage can be water that infiltrates into soil during precipitation and irrigation events and flows downward through macropores and/or smaller pores within the soil matrix past a depth representing the local soil profile thickness. Local soil profile thickness may be defined as the maximum depth of pedogenesis, an arbitrary distance such as 1 m below the ground surface, as the depth of the local plant root zone, or the depth to the water table in humid climate regions. After precipitation or irrigation ceases, positive drainage may also occur over a few days through downward redistribution of soil water. Eventually gravity becomes the only force pulling soil water downward as pressure gradients decline and soil water becomes roughly evenly distributed with depth, especially in uniform soil profiles.

Negative drainage is water that enters a soil profile from below its lower boundary due to plant root or evaporative water demands exceeding soil profile available water. Capillary forces pull water upward against the force of gravity, driven by higher to lower soil water pressure heads from the bottom to top of the soil profile.

Perhaps the most challenging component of the soil water budget to quantify, drainage can be directly or indirectly measured. Methods to directly measure local drainage include lysimeters and a recently developed soil water flux meter. One method of measuring drainage indirectly is to calculate downward soil water flux using Darcy's Law. Darcy's Law is a computation involving two factors: hydraulic head gradients in the soil profile measured with tensiometers placed at a minimum of two depths, and the local unsaturated hydraulic conductivity. This approach may suffer from enormous errors, as quantifying the unsaturated hydraulic conductivity of a soil is difficult, even with order of magnitude accuracy due to spatial and temporal variability in pore characteristics.

Lysimeters vary greatly in size and design, but can be subdivided into two types: weighing and non-weighing (Brye et al., 1999). Weighing lysimeters are more expensive and usually require disturbing and re-packing the soil profile. Non-weighing lysimeters, much easier and less disruptive to install, can be designed to collect drainage water under zero or non-zero tension lower boundary conditions. A saturated zone must develop above a zero-tension lysimeter before water can enter the drainage collection device installed at its base. This perched water table may create very unnatural soil water flow conditions in arid regions with deep unsaturated zones (Reeder, 1986). Therefore, zero-tension lysimeters are better suited for collecting drainage under wet soil, shallow groundwater conditions. Brye et al. (1999) were successful in developing an equilibrium tension lysimeter. They reported lower variability in measured drainage between their sampling locations than that reported for comparably sized zero-tension lysimeters installed in other soil systems. However, their system does require a vacuum pump to apply the tension.

A soil water flux meter designed by Gee et al. (2002) appears to be a very promising method of measuring drainage efficiently and accurately. Their flux meter design uses a passive capillary wick system to apply tension to the soil and does not require a vacuum pump, as does the system of Brye et al. (1999).

Drainage is the key component in a soil water budget with regards to quantifying transport of pollutants to groundwater. Therefore, it is imperative that an accurate assessment of the amount and timing of drainage be done to guide such things as agricultural nutrient management strategies.

Overland runoff

Overland runoff is excess rain, snowmelt, or irrigation water that does not infiltrate into the local soil profile, but flows down slope along the land surface into surface waters or becomes runon-contributing water for a different soil profile at a lower elevation. The amount of water that runs off a land surface during a particular rainfall, irrigation or snowmelt event depends on many factors, including percent slope and surface roughness of the landscape, type of vegetative cover, soil sorptivity, and intensity and duration of the precipitation event. Measuring overland runoff requires physically diverting runoff water into a well or sump located at the lowest point in a field. The volume of water collected in the well or sump divided by the area of the field is equal to the amount (mm) of overland runoff. Overland runoff is a critical component in estimating soil erosion losses from a landscape (Proffitt and Rose, 1991).

Subsurface Runoff

Subsurface runoff (or runon) is water that flows down a sloping landscape within a soil profile's depth below the soil surface. Baver et al. (1972) referred to this component of the soil water budget as ground water runoff and by Whipkey (1965) as subsurface storm flow. In their landmark study, Dunne and Black (1970) measured subsurface storm flow from a forested watershed by digging a shallow interceptor trench across the base of a slope. Overland runoff was directed away from the interceptor trench so as to only allow shallow subsurface flow to accumulate in the drainpipe installed in the bottom of the trench.

Although subsurface runoff has received much less attention than overland runoff in the literature, in cases where low hydraulic conductivity layers exist on sloping terrain subsurface runoff can be quite significant. For example, Hubbard and Sheridan (1983) determined that about 99% of nitrate in runoff from an agricultural field in southeastern USA occurred as subsurface flow.

Storage

Significant temporal changes in soil water storage may occur depending on the soil's geographic location and landscape position. However, this component is often ignored in annual soil water budget estimates as usually the amount of water stored in a soil profile is about the same at the beginning and end of the year of interest. In the case of shorter-term soil water budgets, a method such as TDR can be used accurately in the field to measure the initial and final soil water storage components.

Gary W. Parkin

Bibliography

Baver, L.D., Gardner, W.H., and Gardner, W.R., 1972. *Soil Physics*. New York: Wiley.

Brutsaert, W., 1982. *Evaporation into the Atmosphere: Theory, History, and Applications*. Dordrecht: D. Reidel Publishing Co., 299 pp.

Brye, K.R., Norman, J.M., and Bundy, L.G., 1999. An equilibrium tension lysimeter for measuring drainage through soil. *Soil Sci. Soc. Am. J.*, **63**: 536–543.

Chow, T.L., 1992. Performance of an ultrasonic level sensing system for automated monitoring of snowcover depth. *Agric. for. Meteor.*, **62**: 75–85.

Dingman, S.L., 2002. Physical Hydrology. New York: Prentice-Hall, 646 pp.

Dunne, T., and Black, R.D., 1970. An experimental investigation of runoff production in permeable soils. *Water Resour. Res.*, **6**(2): 478–490.

Gee, G.W., Ward, A.L., Caldwell, T.G., and Ritter, J.C., 2002. A vadose zone water flux meter with divergence control. *Water Resour. Res.*, **38**(8): 35–41.

Hubbard, R.K., and Sheridan, J.M., 1983. Water and nitrate losses from a small upland coastal plain watershed. *J. Environ. Qual.*, **12**: 291–295.

Jensen, M.E., Burman, R.D., and Allen, R.G., 1990. Evapotranspiration and irrigation water requirements. ASCE Manuals and Reports on Engineering Practice. No. 70. New York: American Society of Civil Engineers.

Lutgens, F.K., and Tarbuck, E.J., 2004. *The Atmosphere. An Introduction to Meteorology.* 9th edn. New York: Prentice Hall, 528 pp.

Proffitt, A.P.B., and Rose, C.W., 1991. Soil erosion processes. I. The relative importance of rainfall detachment and runoff entrainment. *Aust. J. Soil Res.*, **29**: 671–683.

Reeder, J.D., 1986. A non-weighing lysimeter design for field studies using nitrogen-15. *Soil Sci. Soc. Am. J.*, **50**: 1224–1227.

Rudra, R.P., Dickinson, W.T., Whiteley, H.R., Gayner, J.D., and Wall, G.J., 2000. Selection of appropriate evaporation estimation technique for continuous modeling. *J. Am. Water Resour. Assoc.*, **36**(3): 585–594.

Tindall, J.A., and Kunkel, J.R., 1999. *Unsaturated Zone Hydrology for Scientists and Engineers.* New York: Prentice-Hall, 624 pp.

Topp, G.C., and Ferré, P.A., 2002. Water Content. In Dane, J.H., and Topp, G.C., eds., *Methods of Soil Analysis, Part 4 – Physical Methods.* Madison, WI: Soil Science Society of America.

Topp, G.C., Davis, L., and Annan, A.P., 1980. Electromagnetic determination of soil water content: measurements in coaxial transmission lines, *Water Resour. Res.*, **16**(3): 574–582.

Verma, S.B., 1990. Micrometeorological methods for measuring surface fluxes of mass and energy. In Goel, N.S., and Norman, J.M., eds., Instrumentation for studying vegetation canopies for remote sensing in optical and thermal infrared regions. *Remote Sensing Rev.*, **5**(1): 99–115.

Whipkey, R.Z., 1965. Subsurface stormflow from forested slopes. *Int. Assoc. Sci. Hydrol. Bull.*, **10**(2): 74–85.

Cross-references

Flow Theory
Water Content and Retention
Water Erosion
Water Movement

WATER CONTENT

Used in two senses, the most fundamental being the total amount of H_2O in a soil or rock sample determined by a complete chemical analysis. As such it includes the OH groups incorporated into the structures of the so-called hydrous minerals e.g., mica, chlorite, amphibole, smectite. In soil science the water content refers to the second meaning: the loosely retained water in pores, in organic matter and adsorbed to mineral surfaces, together with at least some of the water held in interlayer positions in clay minerals, all of which is estimated by weighing before and after drying a sample at 105 °C.

WATER CONTENT AND RETENTION

The volumetric water content of a soil when saturated is the same as the volume of the pores. As the water content is reduced, the largest pores empty first, water being retained most forcefully in small pores, in the interstices between particles, and on particle surfaces. Additional structural water is present internally in the clay lattices and as water of crystallization. This water ordinarily is not regarded as a part of the *soil water* (*q.v.*). However, water content quantification requires a definition of a dry soil, and it is not always possible to distinguish clearly between structural water and absorbed water. Hence a dry state cannot be unequivocally defined, and where high accuracy in measurement is required, the method of removing water must be carefully specified. In soil science as well as in many other areas where water content determinations are made, the *dry state* is specified as that which exists when a sample is dried in an oven to constant weight at a temperature between 100 and 110 °C. The implications of such a temperature choice with respect to soil minerals are shown in Figure W2 where weight loss at increasing temperature for a variety of constituent minerals is plotted. It is evident from this figure that depending on the soil mineral, small errors in temperature measurement or control can easily lead to large errors in water content measurements. Data in Figure W2 suggest that a choice of, say, 165–175 °C would reduce the dependence on precise temperature control and measurement. However, at such high temperatures organic constituents would be lost rapidly through oxidation. Even at temperatures of 100–110 °C, organic materials oxidize, and a soil sample high in organic matter will continue to lose weight over a period of time in oven drying. Because of the decomposition problem, organic materials are often dried at 50–70 °C in the presence of drying agents or in a vacuum oven. Hence the choice of 100–110 °C for drying soil containing both minerals and organic matter may be seen to be a compromise. Where high precision and accuracy in water content measurements are required, careful control of both temperature and temperature distribution in an oven and specification of drying time become essential.

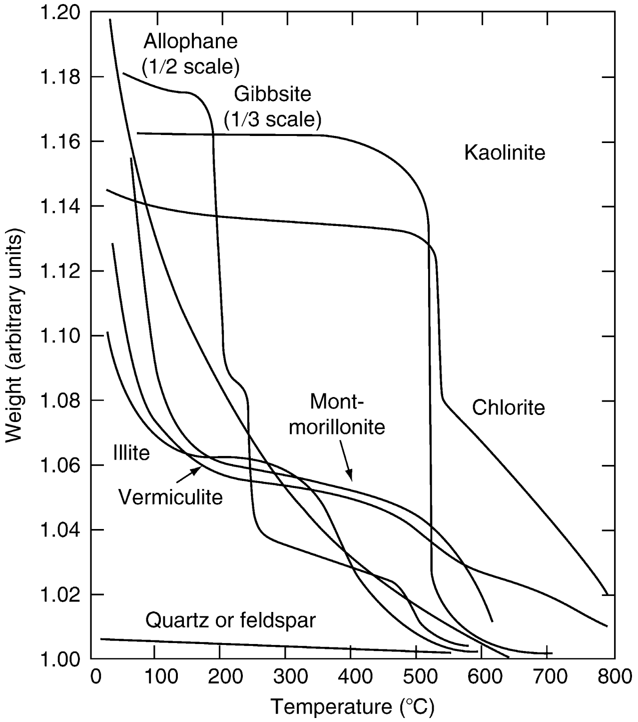


Figure W2 Weight loss of clay minerals as a function of temperature. The weight of the sample at a temperature of 800 °C or greater is taken to be unity. Water content percentages on a mass basis may be obtained by subtracting 1 from the ordinate figure and multiplying by 100 (the numbers to the right of the decimal thus may be regarded as percentages) (Nutting, 1943; from Gardner 1965, reprinted by permission of the publisher).

Expression and measurement of water content

Water content may be expressed in several ways. The most common, because of the fact that samples are weighed, dried, and reweighted to determine water loss, is the expression of mass of water per unit mass of oven-dried soil, referred to as “mass basis” or “dry mass basis” water content. Where a soil sample is taken in such a way that its in situ volume is known, the expression of mass or volume of water per unit of bulk volume becomes possible. In a great many situations the volume of water associated with unit volume of bulk soil is the most useful value. This value may be readily converted to the depth of water associated with a sample if it were accumulated in a layer. Thus, this value is obtained by multiplying the volumetric water content by the depth of soil to which it pertains to get the volume of water per unit area for the specified depth increment, or merely centimeters or inches of water, in the same way as rainfall is specified in length units. Water content on a mass basis may be converted to volumetric water content through multiplication by the ratio of the dry bulk density of the soil to the density of water. Both direct and indirect methods are employed in the analytical determination of water content (Topp and Ferré 2002).

Direct methods

The common and generally accepted standard for water content measurement in soil involves measuring the mass of the wet soil, oven drying to constant mass, and then computing the water content as the mass of water removed per unit mass of oven-dry soil. Problems of defining an unequivocal dry mass and problems of assuring that the temperature and drying time are appropriately controlled necessitate careful attention to technique and explicit description of the method used wherever high precision and accuracy are required. Because of such problems, it is more realistic to consider reproducibility rather than accuracy of measurement. Under less demanding conditions, it is possible to follow somewhat standard procedures using ordinary laboratory ovens and balances and to achieve a precision and reproducibility of roughly half of a water content percentage with most soils. Temperature must be controlled within a few degrees of 105 °C, and samples must be dried for a uniform period of at least 10 h where a forced-draft oven is used and for at least 24 h in a convection-type oven. Overloading an oven or adding wet samples prior to removal of almost dry samples will increase the size of errors. Considering weighing errors only, the size of oven-dry sample required to achieve a particular precision in water content determination is given in terms of standard deviations by the approximate equation

$$\text{oven-dry sample size} = \frac{2\sigma_b}{\sigma_\theta}\sqrt{\theta + 1}$$

where σ_b is the standard deviation for the balance used, and σ_θ is the standard deviation in mass basis water content θ associated with weighing.

Other methods for drying samples may be used. Use of a microwave oven is particularly attractive for rapid determination of water contents, it being possible to complete the drying process is as little as 15 min. Temperatures achieved in samples are as much as 200 °C, considerably higher than those usually specified for oven drying. Whether or not measurements made at such temperatures are useful depends on the purpose for which used and the precision required. A drying temperature of 200 °C would be as good or better than 105 °C for most soil minerals. However, such high temperatures would result in badly oxidized organic components and would introduce difficulties with some soil minerals.

Indirect methods

Several indirect methods for measuring water content of soils are available. Some examples are TDR (see Water Budget), the gypsum block method and the neutron-scattering method.

Gypsum block method. Porous blocks containing electrodes that permit measurement of electrical conductivity can be calibrated against water content. When these blocks are buried in soil, their water content comes to potential equilibrium with that of the soil. Measurement of electrical conductivity is usually made with an alternating current at about 1 000 cps to avoid polarization at the electrodes. Also instead of conductivity, some blocks and measuring units are made to read in electrical capacitance. Since *electrical conductivity* (*q.v.*) depends on ion content of the *soil solution* (*q.v.*), inert porous blocks are sensitive to solutes present in the soil solution. Use of slightly soluble substances like gypsum for the blocks reduces sensitivity to solutes through a buffering action. Many of these electrical conductivity blocks are insensitive in the very wet range, but by increase in pore size, the sensitivity can be extended somewhat into the wet range. These moisture blocks may also be calibrated to read matric potential rather than water content. Although useful in many applications, such blocks do not have the precision ordinarily obtained using oven-drying techniques. On the other hand, they have certain advantages in following water content changes with time inasmuch as they are not confounded with spatial variability as are destructive-sampling techniques.

Neutron-scattering method. Neutron-scattering techniques for water content measurements are based on the fact that fast neutrons emitted from a neutron source are slowed down to thermal energies to a considerably greater extent by light elements like hydrogen than by the heavier elements most common in soil. A neutron source (beryllium bombarded by gamma rays from Americium-241) is fit to a thermal neutron-detector probe and lowered into soil through a thin-walled metal access tube. The detector tube is essentially transparent to the fast neutrons emitted so these fast neutrons move outward into the soil in a solid angle. In the soil they are slowed down to thermal velocities, largely by interaction with water due to collisions with hydrogen and oxygen nuclei. The more water present in the soil, the less the distance of travel outward into the soil. A proportion of the thermalized neutrons interact with or are captured by heavier atoms, and a balance between neutrons emitted and thermalized and neutrons captured is almost instantly achieved with the density of the thermal neutrons in the vicinity of the thermal neutron detector being linearly related to the water content. Certain compensating factors exist between the processes of thermalization and capture in soil materials such that the relationship between thermal density and water content is to some degree independent of variation in soil materials, including the presence of hydrogen-containing organic matter. This factor is highly advantageous in practical application of the technique. However, in some soils calibration is desirable.

Apart from electronic problems that have been greatly minimized in recent years, the most important limitations of the method are lack of spatial resolution and precision errors associated with random emission of neutrons at the neutron source. Emission of neutrons follows a Poisson distribution for which the standard deviation is the square root of the number of neutrons emitted. Thus it is necessary to take into account the random nature of neutron emission. The greater the number of counts, the more reliable the count rate average from which the water content is inferred. Since the size of the neutron source is generally fixed in the design of the instrument, increased precision requires larger counts that are obtainable only by increasing counting time intervals. Because the standard deviation in neutron emission is a square root function, water content precision also depends on the square root of counting time. Hence reduction of standard deviation in water content by a factor of 2 requires counting 4 times as long. Commonly used counting times for equipment generally available varies from 20 s to 1 min, although much longer time intervals are used in special situations. The standard deviation associated with 10^5 counts in the reference standard is about 0.5% water content with good electronic equipment.

Spatial resolution of nuclear water content measurements is inherently limited by the fact that once in the soil, the path of a neutron is determined only by its collisions, which means that the region of influence cannot be limited to a fixed layer. Use of fast neutron absorbers to confine initial emission to a layer of soil rather than the solid angle achieved otherwise can increase the spatial resolution somewhat but not extensively. Water content-depth curves produced using nuclear scattering are generally smooth average curves, even under circumstances in which sharp breaks exist such as might be produced by soil stratification.

Water potential

Although indispensable in many situations, water content of a soil often is less useful than knowledge of how tightly water is held (Iwata et al., 1995). Supply of water for plant growth depends on two soil properties: (1) the forces with which water is held and (2) the water conductivity of the soil adjacent to absorbing roots. Many engineering properties of soil are more clearly related to forces of retention than to water content. For example, yield of water from a watershed and structural properties of soil at the foundation of buildings or bridges depend more directly on water-retention forces than on water content itself. Force of retention of water held in pores is generally a capillary force, i.e., the force associated with surface tension in the air-water interface. Forces holding water close to particle surfaces and in narrow interstices between particles are strong absorptive forces, generally called *van der Waal-London forces*. These vary with the 6th or 7th inverse power of the distance to the surface. Other forces retain water such as the force exerted by solutes on nearby water molecules, *osmotic forces*. Such forces are in evidence during evaporation and in the presence of membranes that limit the passing of dissolved ions. The complicated geometry of soil surfaces and the nature of the many forces associated with water in soil makes quantification of the retentive forces nearly impossible. Hence a unifying principle is used to deal with these forces. Rather than to specify the several forces explicitly, the energy required to move water from the soil to a reservoir of water at a defined reference state is used. By specifying only the work required, the nature and direction of forces need not be indicated. This work is generally specified on a unit mass or unit volume basis and is known as the *water potential. Kinetic energy*, or energy of motion, usually need not be specified in slow moving steady-state or quasi-steady-state water flow situations ordinarily encountered in soil. Use of potential terminology makes it possible to add the effects of the several types of forces acting on water in soil. The fundamental physics is treated by Hillel (2004).

Terminology

Water potential is made up of several components, the first two of which are closely related to water content: (1) *matric potential*, the work required to remove water against surface tension and particle surface forces, a negative value; (2) *osmotic potential*, the work necessary to remove water from ions in the solution, also a negative value; (3) *gravity potential*, the work involved in moving water from soil at a particular elevation to a reference elevation – this may be either positive or negative, depending on the choice of reference elevation; (4) *pneumatic potential* (or *gas pressure potential*), involved where a gas pressure gradient exists; and (5) *overburden potential*, involving the weight of those soil particles that are somewhat free to move and to exert a pressure on water below (somewhat comparable to the contribution of suspended materials to total pressure of a liquid column). For soil beneath the water table, the *matric potential* is replaced by a positive pressure or *submergence potential* that exists because of the weight of the water. Where a free water surface coincides with the soil surface, the *submergence potential* is exactly balanced by the *gravity potential.*

Water content and matric potential are usefully related by curves known as "sorption" or "desorption" curves or sometimes referred to as "characteristic curves." Figure W3 shows such curves covering a wide variety of soil materials. These curves are desorption curves, having been made by drying the soil step-wise down from saturation. Curves relating water content and matric potential are not unique, but depend on wetting history. Soils undergoing wetting are somewhat dryer at the same matric potential than soils undergoing drying. Reversal of the wetting or drying process at intermediate values between completely dries and saturation produces intermediate curves within what is known as the *hysteresis loop*. These are referred to as "scanning curves." This hysteretic phenomenon results from the fact that matric potential depends on the energy state of water at the entry or entries to larger soil pores and not on the water content of isolated large pores. The larger cross-sectional space may be either wet or dry depending on wetting history.

Matric potential and osmotic potential together determine the vapor pressure or relative humidity in the soil as given by

$$(\text{matric} + \text{osmotic potential}) = \frac{\mathrm{R}T}{V_\mathrm{m}} \ln \mathrm{R}H$$

where R is the universal gas constant, T is the absolute temperature, and V_m is the molecular volume of liquid water. In the water content range where air-liquid interfaces may be observed, the matric potential is a function of the radius of the air-water interface; thus

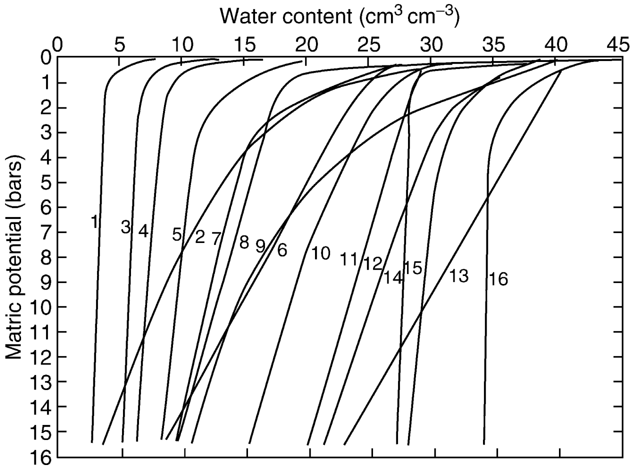


Figure W3 Desorption curves for various soils sketched from data at 0.1, 0.3, 0.6, 3, and 15 bars tension given by Holtan et al. (1968). (*1*) Continental gravelly sand loam, Arizona; (*2*) Sassafras sandy loam, Mayland; (*3*) Progresso fine sandy loam, New Mexico; (*4*) Vaucluse sandy loam, Georgia; (*5*) Albion loam, Oklahoma; (*6*) Abilene clay loam, Texas; (*7*) Hartsells loam, Ohio; (*8*) Palouse silt loam, Washington; (*9*) Fayette silt loam, Wisconsin; (*10*) Nellis gravelly loam, New York; (*11*) Larb-like silt clay loam, South Dakota; (*12*) Memphis silt loam, Mississippi; (*13*) Drummer silty clay loam, Illinois; (*14*) Auston silty clay, Texas; (*15*) Marshall silty clay loam, Iowa; (*16*) Bascom-like clay, South Dakota (from Baver et al., 1972, Gardner, and Gardner, 1972).

$$\text{matric potential} = h\rho g = \frac{2\sigma}{r}$$

where h is the height of a hanging water column in equilibrium with the soil, ρ is the density of liquid water, and σ is the surface tension of water.

In the absence of significant temperature gradients, soil temperature is usually neglected in dealing with water except that it does influence the size of the matric potential and the viscosity, which in turn affect water flow. However, if an appreciable temperature gradient exists, as is possible, say, due to solar heating at the soil surface, water flow is affected, particularly in the vapor phase. Under such conditions appreciable water vapor can move from regions of high to regions of low temperature. Such flow can give rise to return liquid flow, and in many irrigated areas, salt is transported in the liquid water toward warm regions and then evaporated, leaving salt behind. Apart from involvement with salt deposition, vapor flow has its greatest relative importance in the dry range where liquid flow becomes inappreciable.

Measurement

Several methods are available for measurement of water potential in soil. The most common and probably the most useful are methods for measuring matric potential and involve balancing the matric forces in the soil against the force exerted by a hanging water column across a porous cup, or alternatively balancing these forces against forces applied by means of air pressure across a porous plate. When equilibrium is reached, the potential may be obtained from the height of the hanging

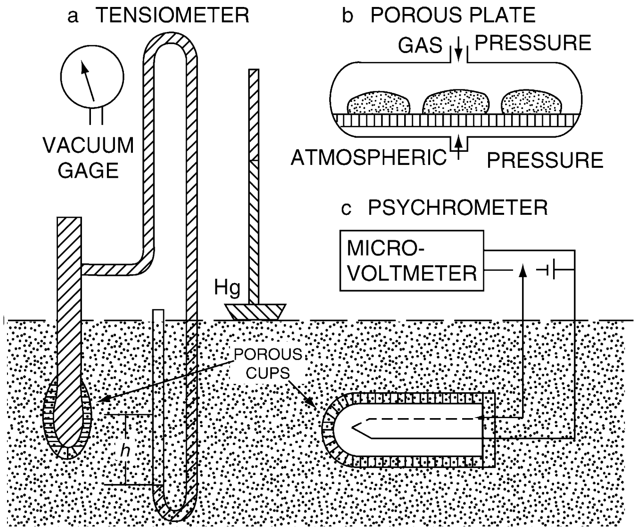


Figure W4 Tensiometer and pressure plate for measurement of matric potential in field soil and in the laboratory and thermocouple psychrometer for measurement of matric and osmotic potential. In practice, either the mercury manometer or the vacuum gage replaces the hanging water column shown attached to the tensiometer.

column or the pressure applied. These methods are shown diagramatically in Figure W4. Figure W4a shows a tensiometer where water in a porous cup comes to equilibrium with forces exerted by the hanging water column through the cup as indicated by the height of the column h. The potential is $-h\rho g/1020$ bars, where h is measured in centimeters, ρ is the density of water, and g is the acceleration of gravity. (Potential is the potential energy/unit volume, which is dyn-cm cm^{-3} or dyn cm^{-2}, which is a pressure, hence the use of a pressure unit; 1020 cm water is equivalent to 1 bar of pressure. Potential may also be given as potential energy per unit mass, but where the density of water may be taken as unity, the numerical value remains the same. The hanging water column is shown only to illustrate the principle of the measurement. In practice, this column is replaced by a mercury manometer, which may then be located above the soil surface, or by a vacuum gage. Figure W4b shows a pressure plate apparatus in which soil samples are brought to equilibrium with an applied gas pressure, which may be measured directly in bars. This equipment may also be used to determine the relationship between water content and matric potential. The tensiometer is limited practically to the wet range from 0 to about –0.85 bars by problems of cavitation in the water column.

A *soil psychrometer* may be used to obtain water potential measurements in soil below about –1/2 bar. The psychrometer measures the sum of the matric and osmotic potential so that an independent measurement of osmotic potential is necessary if matric potential is desired. However, in many instances where plant growth is involved, it is the sum of the two potentials that is often desired. The psychrometer consists of a tiny thermocouple encased in a porous cup together with a microvoltmeter and an electrical circuit for application of a 3–8 mA current to cool the thermocouple by Peltier cooling to below the dew point. In operation, the thermocouple is cooled for 5–15 s, condensing a thin layer of water on the thermocouple surface, after which the temperature of the thermocouple quickly comes to a value determined by rate of evaporation of the water back into the cup atmosphere. From the temperature difference between the thermocouple before cooling and that during evaporation afterward, the relative humidity may be determined. It is related to the sum of the matric and osmotic potential by the equation given earlier. Imperfect boundary conditions for the psychrometer prevent direct association of temperature measurements with relative humidity. Hence the instrument is calibrated against relative humidities established by osmotic solutions. Calibration is usually carried out to give the potential directly as a function of the microvoltage reading. The relative humidities in soil in the range of interest where plant growth is concerned are in the difficult range of about 99% and above. Hence temperature is an important factor. However, design and techniques have reduced the influence of temperature to the point at which practical measurements can easily be made. The psychrometer may also be applied to measurements on plants and to osmotic potentials of plant saps.

Walter H. Gardner

Bibliography

Baver, L.D., Gardner, W.H., and Gardner, W.R., 1972. Soil Physics. New York: Wiley, 498 pp.

Gardner, W.H., 1965. Water content, In Black, C.A., ed., *Methods of Soil Analysis*. Madison, WI: American Society of Agronomy, pp. 82–127.

Hillel, D.I., 2004. *Introduction to Environment Soil Physics*. Amsterdam; Boston: Elsevier/Academic Press, 494 pp.

Holtan, H.N., England, C.B., Lawless, G.P., and Shumaker, 1968. Moisture-tension data for selected soils on experimental watershed. U.S. Department of Agriculture, Agric. Res. Serv. ARS 41-144, 609 pp.

Iwata, S., Tabuchi, T., and Warkentin, B.P., 1995. *Soil-water interactions: mechanisms and applications*. 2nd ed. New York: M. Dekker. 440 pp.

Topp, G.C., and Ferré, P.A., 2002. Water Content. In Dane, J.H., and Topp, G.C., eds., *Methods of Soil Analysis, Part 4 – Physical Methods*. Madison, WI: Soil Science Society of America. 1692 pp.

Cross-references

Capillary Pressure
Conductivity, Electrical
Conductivity, Hydraulic
Flow Theory
Soil Solution
Soil Water
Surface-Soil Water Content

WATER EROSION

Soil erosion by water is the detachment and transport of soil particles by rainfall or runoff. Several mechanisms contribute to both processes.

Detachment

Detachment can occur through the rapid wetting or by the forces exhibited by raindrops and runoff. The rapid, mainly one-sided wetting causes air entrapment within and differential swelling of the aggregates. The pressure of the entrapped air or the shear forces resulting from anisotropic swelling produce (micro-) fissures weakening the aggregates. Especially a fast procession of the wetting front increases the extent of these processes. Hydrophobicity caused by organic substances may, therefore, stabilize the aggregates. The disintegration of the aggregate along these fissures leads to micro-aggregates that range in size, mainly from 0.2 to 1 mm. This process is called slaking. The micro-aggregates can be divided further into smaller particles down to primary particles by dispersion. The low electrolyte content of the rain water compared to the electrolyte content of the soil solution increases hydration of ions in the diffuse double layer after wetting and disperses primary particles. This is especially pronounced in soils containing monovalent cations that do not form bridging bonds and that have a large hydration energy. In arid and semi-arid regions dispersion increases mainly because of sodium, whereas in areas of intensive agriculture the heavy use of fertilizer potassium can have a similar effect.

The aggregates weakened by slaking and dispersion are further disintegrated by the forces of the raindrops. For short moments of about 50 μs, high pressures up to 10^6 Pa occur when the raindrop hits a rigid soil surface (Ghadiri and Payne, 1981). On a deformable soil surface the pressure is still in the order of 10^5 Pa with its maximum about 2 mm from the center of impact for a 5.6 mm drop (Nearing et al., 1987). The water of the raindrop cannot infiltrate the soil at the same velocity with which it is supplied to the soil surface. It must disperse radially along the soil surface. The velocity of the radially flowing water can be twice as high as the falling velocity of the drop. For a 4 mm drop, terminal falling velocity would be 9 ms^{-1}. The high flow velocity in a very short distance to the soil surfaces causes a high shear rate in the order of 10^5 s^{-1}. Except for cemented soil, the soil shear strength is often smaller than the resulting shear stress of the drops. Thus, the raindrops produce smaller, more easily transported particles and a puddled, sealed surface that reduces infiltration and increases runoff.

The runoff also produces shear stresses that can further loosen soil particles. Its stresses are lower than those of the drops (range of Pa) but as those stresses act on larger areas, they may loosen larger particles. In addition, they act over longer times. They therefore can loosen soil, which exhibits a Bingham fluid behavior that is common in soils. For short moments or in some places, eddies or turbulent burst stochastically can produce even higher stresses that override soil shear strength (Nearing, 1991).

Concentrated runoff loosens soil particles by additional mechanisms. Under supercritical flow conditions (Froude number >1), a hydraulic jump occurs that releases much of the energy of the runoff at the spot where it occurs. The concentrated release of energy detaches soil and produces a small headcut. The changing flow pattern at the headcut causes the hydraulic jump always to occur at this position. Thus the headcut increases in size and slowly advances upslope. Additional material is detached by scour hole formation, rill side sloughing and undercutting of the sidewalls in rills.

Transport

Detached material can be transported by the drop impact through splashing or by flowing water. Although splashing occurs randomly, a net transport downhill results because of the longer splashing distances downslope than upslope. The amount of transport and the direction of splash transport can be strongly influenced by wind (Erpul et al., 2002). Splashing decreases with increasing depth of the water layer on the soil surface. Detachment and transport also depends on the water layer thickness. The highest rates occur with very shallow water depths of about 1/10–3/10 of a drop diameter (Mutchler and Larson, 1971). Splash becomes small when the water layer thickness is more than 2–3 drop diameters.

Where the water concentrates to linear flows, the main transport is achieved by the runoff. The forces of the flowing water can be strong enough to carry even stones, whereas splash only transports particles up to 1–2 mm in size. The effectiveness of the runoff increases with flow velocity and therefore, with increasing flow thickness and slope steepness and with decreasing roughness.

At the transition between splash and flow transport, where water depth is already too thick for high splash rates but still too shallow for high flow velocities, a type of transport occurs that is called raindrop induced flow transport, RIFT (Kinnell, 1990). Soil particles that are too heavy to be transported by the runoff are entrained and kept in motion by raindrop forces. The random raindrop forces are superimposed on the weak flow forces downslope. A high net transport downslope results. This type of transport dominates on short slopes and on the interrill areas that deliver soil into the rills.

Types of erosion

Slaking, dispersion and raindrops act evenly on an unprotected soil surface. Soil is detached and transported, more or less evenly, where these mechanisms prevail. The resulting type of erosion is called *sheet erosion*. The forces of the runoff tend to occur locally and lead to an incision into the soil surface and to linear types of erosion. Where many linear elements develop, they are shallow (about 10 cm) because the runoff is dispersed. This type of erosion is called *rill erosion*. The distance from the interrill area to the rill is small. In models, often a distance between rills of 1 m is assumed. Sheet erosion on the interrill areas still contributes a significant amount to the total soil loss. Sheet and rill erosion are governed by similar principles and transitions between both forms are common. Therefore, both types are often addressed together.

The detachment by flowing water gains importance with increasing concentration of the overland flow. This increases the depth of the linear erosion elements. As long as the linear element is not deeper than the plowing depth, it can be filled in by cultivation. This type of erosion is called *ephemeral gully erosion*. It mainly occurs along slope concavities where tillage accumulated rich but loose topsoil material and where surface and subsurface runoff concentrate. Exfiltrating subsurface runoff or shallow ground water (seepage) initiates or fosters this process because the soil at the surface looses the stabilizing water menisci, which depend on air-filled pores (Römkens et al., 2002).

With permanent *gully erosion*, the linear element cannot be removed by cultivation. Raindrop impact is unimportant for soil detachment. The main effect of the raindrop impact is to seal the soil surface of the contributing watershed and thus increase surface runoff that concentrates in the gully.

The fourth type of erosion is *tunnel erosion* (pipeflow), where raindrops have lost all their importance. Tunnel erosion mainly occurs where a stable soil surface covers unstable subsoil. The stability of surface soil could come from an extensive root network or a cementation, by lime or Fe oxides for instance. The low stability of the subsoil, with a high potential for slaking and dispersion, could be caused by less organic matter, less structure formation or high exchangeable Na. However, also an impermeable layer underneath the subsoil like hard rock or permafrost is conducive to piping (Carey and Woo, 2002). Under those circumstances, infiltrating rainwater may flow laterally underneath the soil surface and remove the unstable subsoil. Pipes of several meters in diameter can develop (Zhu et al., 2002).

Erosion factors

The amount of soil loss is determined by rain characteristics, soil cover and their interactions, as well as by drainage area per unit width, slope steepness and soil properties. The ability of a rainstorm to create runoff increases with rain intensity. Also, its ability to detach increases because of growing raindrop size. Rain erosivity, therefore, increases with about the power of two of intensity.

The soil is protected from the action of the raindrop where it is covered. A mulch or low growing vegetation cover is especially effective by additionally retarding runoff and creating small water pools, which dissipate raindrop energy. Soil loss decreases exponentially with increasing coverage and a reasonable protection is achieved often with a 30 to 50% mulch cover (Figure W5). The protective action of the cover decreases with increasing height because the drops dripping off the leaves gain more kinetic energy. Tall crops like hops or maize are less protective than small grain or sugar beet. The coverage decreases for a given leaf area with increasing distance between the plants. Therefore, crops in wide rows and with low seeding density are less protective than crops with a narrow, random seeding distance.

Under most climates, rain erosivity varies seasonally. Crops and cultivation methods that provide an insufficient cover during high erosivity periods increase erosion, whereas only minor erosion occurs on uncovered surfaces (seedbed) in periods of low erosivity. Especially crops with slow initial growth that are planted in wide rows late in the growing season like cotton, maize or soy-bean, are prone to erosion. Minimum, reduced or mulch tillage are techniques to provide sufficient mulch cover also when the crop is young.

In climates with ground frost during the dormant season snow-melt erosion can occur. The precipitation accumulated within the snow cover over a long period of time may be released within a few days causing long-lasting and strong runoff on the soil surface. Snow-melt erosion may even occur where only little snow cover has been accumulated given that deep-reaching ground frost restricts infiltration or that the soil surface has been destabilized by freezing processes.

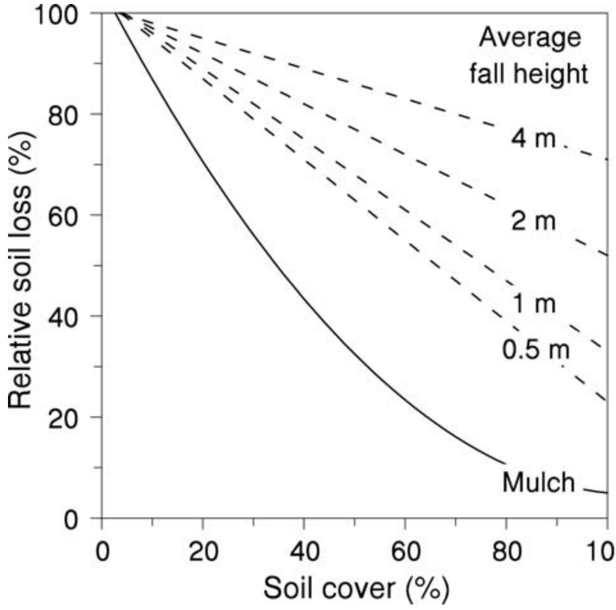


Figure W5 Influence of mulch cover and plant cover of various height on soil loss as it is considered in the models USLE/RUSLE, EPIC and WEPP.

The erosive power of the runoff increases with slope steepness and size of the contributing area per unit width at the lower end of the eroding area. While slope steepness cannot be changed usually, many conservation measures like contouring, terracing, drainage ditches or strip cropping can decrease the amount and velocity of the runoff.

Soils high in silt and very fine sand are especially prone to water erosion because of their low structural stability, the low density of the aggregates and the good transportability of silt-sized particles. With increasing content of clay and organic matter, the aggregate stability increases and detachment decreases. Except for soils with very high contents of clay (>40%) or organic matter (>6%), the erodibility of the soil decreases with increasing clay and organic matter content. A stone cover also lowers detachment. This makes stony soils often less erodible, but cases are also reported where stones had no effect or even accelerated erosion because of restricted infiltration (Poesen et al., 1994). Transportability decreases with increasing effective particle size. Especially for sheet erosion, the erodibility decreases with an increasing medium to coarse sand and gravel content.

Erosion rates

The natural erosion, sometimes called geologic erosion, depends mainly on the climate and slope steepness. Maximum rates occur in semi-arid to arid areas with sparse, natural vegetation cover and rare, but sometimes severe, rainstorms or in mountain areas with steep slopes. Except for these two conditions, erosion is mainly caused human activities, cultivation for example, which creates bare soil. This accelerated erosion is recognized as the greatest threat to the soil resource. Globally 1 094 million ha are affected by water erosion (Lal, 2003).

The reported erosions rates on arable land vary to a large extent, depending on the combination of influencing factors and on the time and spatial scale. For single events, soil losses up to several hundreds of t ha^{-1} have been measured. On a long-term average soil losses of up to 200 t ha^{-1} yr^{-1} for single fields have been quantified in temperate areas by using tracers (Schwertmann and Schmidt, 1980). The highest long-term average erosion rates are likely to occur in Southeast Asia. Annual losses of up to 1 000 t ha^{-1} are reported for Thailand and up to 1 500 t ha^{-1} for Java (Dregne, 1992). High erosion rates in tropical areas are especially reported for Parana and other regions of central Brazil, for alfisols in West Africa and Vertisols in central India and eastern Africa (Lal, 1990). In temperate countries, like the USA and Germany, long-term erosion rates of sheet and rill erosion were averaged to be about 10 t ha^{-1} yr^{-1} under the present soil management systems (Auerswald, 1991) but can be lowered to 1 t ha^{-1} yr^{-1} or less with conservation management systems.

The loss of soil material from a watershed is smaller than the total losses from the individual fields within the watershed. A significant proportion settles on the footslopes and in the riparian areas. With increasing watershed size, the sediment delivery ratio (= proportion of soil loss reaching the water course) decreases. For a 10 km^2 watershed, the expected sediment delivery is about 20%, whereas it decreases to almost 10% at the outlet of a 100 km^2 watershed.

Damages

Damages are manifold (Pimentel et al., 1995). Water erosion can decrease crop yields by the unproductive loss of rain through runoff, by nutrient loss and imbalances because of the nutrient dislocation, by pesticide concentrations that are too low at the eroding site and too high where runoff and sediment accumulates. It causes difficulties in crop management because of an uneven crop development and because of rills and gullies. Besides these short-term damages, soil erosion leads to long-term damages. These are more critical, because they increase slowly and are often undetectable for the farmer but accumulate with time and are almost irreversible due to the much slower soil formation rate. Those damages are caused by a decrease in soil depth and a loss of nutrient and water holding capacity. They are especially severe where a fertile but shallow soil material like loess covers a poor material like gravel, hard rock or an acid subsoil. Although any soil loss of more than 1 t ha^{-1} yr^{-1} can be considered to cause irreversible damages within the time span of 50–100 years, it is commonly accepted that agricultural soil can "tolerate" a certain amount of erosion, which typically ranges from 1 t ha^{-1} yr^{-1} on shallow sandy soils to 5 t ha^{-1} yr^{-1} on deeper soils (OECD, 2001).

Besides the on-site damages on the eroding areas, off-site damages occur where the runoff and sediment accumulates. Examples are the flooding of roads and houses, the undercutting of roads, the siltation of water reservoirs, and the input of nutrients, pesticides, heavy metals and other pollutants into streams. Those damages can be followed by many others like a decreased recreational value of water bodies or increased fish mortality. Off-site effects are especially harmful to society today whereas the loss of productivity mainly affects future generations. Today, transfer of nutrients especially phosphate to surface water bodies including marine systems is a main concern in many countries with intensive agriculture where (eroding) topsoils have been enriched by heavy fertilizer input in the past (OECD, 2001).

In some cases, soil erosion also may have beneficial effects. It can remove a depleted or very acid topsoil and uncover a more fertile subsoil. In alfisols, the loss of parts of the poorly structured eluvial horizon leads to an incorporation of the clay-enriched Bt horizon into the plow layer. This increases structural stability and nutrient holding capacity of the top layer. The input of eroded soil into streams acts as an adsorptive sink and may lower the concentration of dissolved nutrients or pollutants where heavy input from point sources exists.

Erosion control

Figure W6 provides a conceptual overview of the different types and targets of erosion control. The most important measure to lower soil loss is to provide more soil cover in time and space. This can efficiently be achieved by zero, reduced or mulch tillage. Ley-based arable systems especially increase soil stability, which can additionally be used to lower soil loss in periods of insufficient soil cover. Further methods decrease the size of the contribution watershed, e.g., diverting fields or creating terraces, or decrease flow velocity (rough surface; contour tillage). Grassed waterways, retention ponds with controlled outlets and filter strips reduce damages downslope and the input into downslope terrestrial or aquatic ecosystems.

Models

The extent of soil erosion is highly variable in space and time. Commonly, 50% of the total soil loss is caused by less than 1% of the erosive rains and less than 0.1% of all rains. This extreme variability complicates the quantification of damages and the planning of protection measures. Therefore, a large variety of prediction models has been developed. One of the oldest, best known and most widely used is the Universal Soil Loss Equation, USLE, (Wischmeier and Smith, 1978). Due to its universality and calibration to many regions it is recommended by the OECD (2001) to indicate erosion. The USLE computes the long-term annual soil loss A from eroding sites:

$$A = R\,K\,L\,S\,C\,P$$

Only six site-specific factors are necessary, the average annual rainfall and runoff erosivity R, the soil erodibility K,

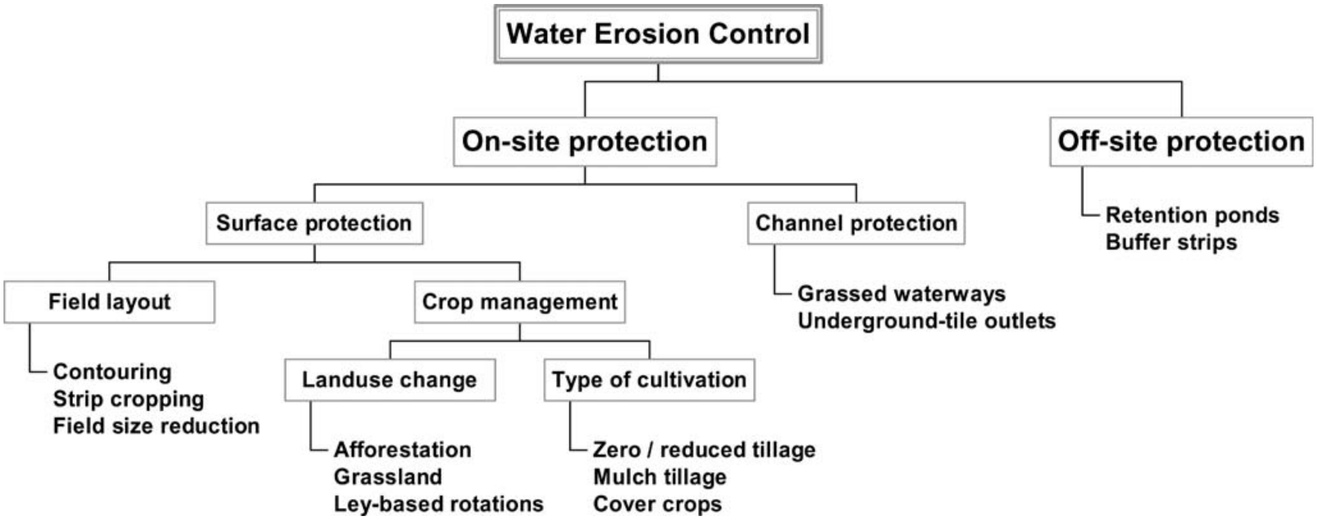


Figure W6 Conceptual framework of water erosion control.

Table W1 Main areas of application for five most common erosion models (special adaptations were not considered; *brackets* show a restricted applicability; frequency of use gives percentage in water erosion modeling in scientific articles between 2000 and 2003 among 15 common models)

Model	USLE/RUSLE	WEPP	EPIC	AGNPS	EUROSEM
Frequency of use	51%	16%	13%	5%	4%
Time scale					
Minute					x
Single event	(x)	x		x	x
Annual		x	(x)		
Long-term	x	x	x		
Spatial scale					
Field	x	x	x		x
Watershed	(x)	x		x	x
Soil use					
Agriculture	x	x	x	x	x
Rangeland	x	x		x	
Forests	x	x		x	
Construction sites	x	x		x	
Erosion control structures	x	x		x	
Types of erosion					
Gully erosion					
Ephemerial gullies		x	x	x	x
Sheet and rill	x	x	x	x	x
Snowmelt	(x)	x			x
Irrigation		x			
Wind erosion			x		
Sedimentation			x		x
Nutrient loss			x	x	
Pesticide loss					
Water movement (runoff, infiltration, percolation)		x	x	x	x
Weather generator		x	x		
Plant growth		(x)	x		
Economic evaluation			x		

Documentation:
USLE, Universal Soil Loss Equation: Wischmeier and Smith (1978).
RUSLE, Revised Universal Soil Loss Equation: Renard et al. (1997).
WEPP, Water Erosion Prediction Project: Flanagan et al. (1991).
EPIC, Erosion Productivity Impact Calculator: Sharpley and Williams (1990).
AGNPS, AGricultural Non-Point-Source pollution model: Young et al. (1995).
EUROSEM, EUROpean Soil Erosion Model: Morgan et al. (1998).

and factors that take into consideration slope length (*L*), slope steepness (*S*), crops and cover (*C*), and protective measures (*P*). The necessary factor values have been worked out for many situations and areas in the world. The USLE or parts of it are also included in many more recent models like AGNPS (Young et al., 1995) or WEPP (Flanagan et al., 1991). The estimation of all factors was improved and updated in the Revised Universal Soil Loss Equation RUSLE (Renard et al., 1997).

The variety of processes connected to erosion occur over a wide temporal scale from microseconds to centuries and on a wide spatial scale from aggregates to river basins and the global system. Hence a variety of erosion model exist, which differ in the processes that are included (sheet/gully erosion, rainfall/snowmelt erosion), in time scale (minutes to centuries), spatial scale (field/watershed) and modeling technology (lumped/mechanistic). Table W1 summarizes some common models. Especially the older models like the USLE have been modified or extended for the application in cases that were not intended originally. These extensions were not included in Table W1 because the modifications are often valid only under very special conditions. Every model has weaknesses and strengths. The selection of an appropriate model for a specific task is therefore essential to obtain reliable results. New technologies like digital elevation models, geographic information systems or remote sensing now allow to substantiate the models increasingly better.

K. Auerswald

Bibliography

Auerswald, K., 1991. Significance of erosion determining factors in the USA and in Bavaria. *Z. Geomorph. N.F. Suppl.*, **83**: 155–160.

Carey, S.K., and Woo, M.K., 2002. Hydrogeomorphic relations among soil pipes, flow pathways, and soil detachments within a permafrost hillslope. *Phys. Geogr.*, **23**: 95–114.

Dregne, H.E., 1992. Erosion and soil productivity in Asia. *J. Soil Water Conserv.*, **47**: 8–13.

Erpul, G., Norton, L.D., and Gabriels, D., 2002. Raindrop-induced and wind-driven soil particle transport. *Catena*, **47**: 227–243.

Flanagan, D.C., Ferris, J.E., and Lane, L.J., 1991. WEPP hillslope profile erosion model: Version 91.5. User summary. National Soil Erosion Research Laboratory Report, Vol. 2, 28 pp.

Ghadiri, H., and Payne, D., 1981. Raindrop impact stress. *J. Soil Sci.*, **32**: 41–49.

Kinnell, P.I.A., 1990. The mechanics of raindrop-induced flow transport. *Aust. J. Soil Res.*, **28**: 497–516.

Lal, R., 1990. *Soil Erosion in the Tropics – Principles and Management.* New York: McGraw-Hill, 580 pp.

Lal, R., 2003. Soil erosion and the global carbon budget. *Environ. Int.*, **29**: 437–450.

Morgan, R.P.C., Quinton, J.N., Smith, R.E., Govers, G., Poesen, J.W.A., Auerswald, K., Chisci, G., Torri, D., and Styczen, M.E., 1998. The European soil erosion model (EUROSEM): a dynamic approach for predicting sediment transport from fields and small catchments. *Earth Surface Processes Landforms*, **23**: 527–544.

Mutchler, C.K., and Larson, C.L., 1971. Splash amounts from water drop impact on a smooth surface. *Water Resour. Res.*, **7**: 195–200.

Nearing, M.A., 1991. A probabilistic model of soil detachment by shallow turbulent flow. *Trans. Am. Soc. Agric. Eng.*, **34**: 81–85.

Nearing, M.A., Bradford, J.M., and Holtz, R.D., 1987. Measurement of waterdrop impact pressures on soil surfaces. *Soil Sci. Soc. Am. J.*, **51**: 1302–1306.

OECD (ed.), 2001. *Environmental indicators for agriculture*, Vol. 3. OECD, 416 pp.

Pimentel, D., Harvey, C., Resosudarmo, P., Sinclair, K., Kurz, D., McNair, M., Crist, S., Shpritz, L., Fitton, L., Saffouri, R., and Blair, R., 1995. Environmental and economic costs of soil erosion and conservation benefits. *Science*, **267**: 1117–1123.

Poesen, J.W., Torri, D., and Bunte, K., 1994. Effects of rock fragments on soil erosion by water at different spatial scales: a review. *Catena*, **23**: 141–166.

Renard, K.G., Foster, G.R., Weesies, G.A., McCool, D.K., and Yoder, D.C., 1997. Predicting soil erosion by water: a guide to conservation planning with the revised universal soil loss equation (RUSLE). *USDA Agricultural Handbook.* Washington, DC: U.S. Department of Agriculture.

Römkens, M.J.M., Helming, K., and Prasad, S.N., 2002. Soil erosion under different rainfall intensities, surface roughness, and soil water regimes. *Catena*, **46**: 103–123.

Schwertmann, U., and Schmidt, F., 1980. Estimation of long-term soil loss using copper as a tracer. In DeBoodt, M., and Gabriels, D., eds., *Assessment of Erosion.* Chichester, NH: Wiley, 403–406.

Sharpley, A.N., and Williams, J.R., 1990. EPIC – Erosion Productivity Impact Calculator: I. Model documentation. *U.S. Dept. Agric. Tech. Bull.*, **1768**: 235 pp.

Wischmeier, W.H., and Smith, D.D., 1978. Predicting rainfall erosion losses – A guide to conservation planning. *USDA Agricultural Handbook*, Vol. 537. Washington, DC: U.S. Department of Agriculture, 58 pp.

Young, R.A., Onstad, C.A., and Bosch, D.D., 1995. AGNPS: an agricultural nonpoint source model. In Singh, V.P., eds., *Computer Models of Watershed Hydrology.* Morris: Water Resources Publications, 1001–1020.

Zhu, T.X., Luk, S.H., and Cai, Q.G., 2002. Tunnel erosion and sediment production in the hilly loess region, North China. *J. Hydrol.*, **257**: 78–90.

Cross-references

Aggregate Stability to Drying and Wetting
Conservation
Crusts, Crusting
Degradation
Imbibition
Infiltration
Puddling
Tillage
Water Movement

WATER FLUXES

See *Water Budget in Soil, Water Movement*.

WATER HOLDING CAPACITY

The ability of a soil to contain and to retain water. Dependent upon the factors, which determine hydraulic conductivity and permeability e.g., texture, organic matter, porosity, interconnectedness of pores and so on.

Cross-references

Soil Water and Its Management
Water Content and Retention

WATER MOVEMENT

Water movement into and through the soil is essential to the growth of natural vegetation and agricultural crops and essential in the replenishment of the groundwater aquifer, which is used increasingly as a water source for domestic and industrial purposes. Liquid entering the soil can have a natural origin such as rain but may also be added by man as *irrigation* water (*q.v.*) or as a liquid waste to be purified during soil percolation by processes of filtration and adsorption. Inadequate infiltration of liquid into the soil may result in surface runoff, which can have very serious environmental effects due to sediment and nutrient pollution of lakes and streams. Such processes may be caused by crusting or compaction of the infiltrative surface, which results in a sharp decline of the infiltrative capacity. Soils with a natural vegetation and a permanent vegetational cover have generally higher rates of *infiltration* (*q.v.*) and less erosion as compared with those that are used for agricultural practices that involve use of heavy machinery (see *Tillage*) and that imply the periodic exposure of the soil surface to the mechanical impact of raindrops. Water movement often implies the occurrence of flow through unsaturated soil, in which not all but only the finer pores are filled with liquid, down to the level of the groundwater, where all pores are filled with water. Major advances have been made in recent years in soil physics and hydrology in describing processes of water movement in soils (see Jury and Horton, 2004; Warrick, 2003).

Physical theory of water movement

Soil water potentials

Movement of water occurs from locations in the soil where the water in the soil has a high energy to locations where that energy is lower. The energy of soil water must be expressed in terms of the total potential, which is energy per unit quantity. The *total potential* of water ψ is defined as the mechanical work required to transfer unit quantity of water reversibly and isothermally from a standard reference state, where ψ is taken as zero, to the situation where the potential has the defined value. A pool of pure water at an elevation that can be arbitrarily specified and that experiences a gas pressure of 100 kPa is taken as the standard reference state. Many forces may affect the total potential of water in the soil. The *gravitational potential Z* is due to the attraction by the Earth and increases with height from the Earth's surface. The pressure in soil water at a particular point will be greater than one atmosphere if that point is submerged beneath a free-water surface, which can be the level of the groundwater. The potential due to this cause is the *submergence potential S.* If the soil is unsaturated, the pressure in the soil water is less than that of the local atmosphere. It is convenient to refer to a pressure less than atmospheric as a "suction" or "tension" (see *Wetting front*). The potential due to this cause is the *matric* or *capillary potential M.* From their character it follows that the *S* and *M* potential are mutually exclusive possibilities. Another possible cause of pressure change in soil water is a change in the pressure of the air adjacent to it. This may be expressed by the term *pneumatic potential* G. It is convenient to define the *pressure potential* P: $P = M$ (or S) $+ G$, which sums the effect of all pressure changes on the potential of soil water, whatever the cause of these pressure changes may be. In addition, osmotic effects of solutes in soil water must be considered because they affect the thermodynamic properties of the soil water. The effect of solutes on the total potential of soil water, expressed as the *osmotic potential* O, becomes of primary significance if the water is separated by a membrane whose permeability to water molecules differs from that to solute molecules. This aspect is relevant for water movement into and through plant roots. The total potential Ψ of soil water is the sum of all the component potentials:

$$\Psi = Z + P + O$$

It is often convenient to define potentials on a unit weight basis rather than on a unit mass basis. For example, for the gravitational potential Z, it follows that $Z_w = W/\rho g(dv) = z$ (cm) where W equals $\rho(dv)gz$; representing the work needed to transfer the quantity dv over a distance z (ρ equals density of water; g equals acceleration of gravity). For many flow problems, only the Z and P potentials are relevant. Therefore a *hydraulic potential* ϕ has been defined as follows: $\phi = Z + P$. When potentials are expressed per unit weight, it follows that $\phi = H$ (cm). The height H is called the *hydraulic head*.

Soil water movement and the law of Darcy

Whatever the state of saturation, the volume flux, or the volume of water crossing unit area per unit time, is proportional to the gradient of the hydraulic potential in the direction of the flux (see *Water budget in soil*). Thus denoting distance as s, we describe the law of Darcy

$$v = -K\frac{dH}{ds} \qquad (1a)$$

or

$$v = -K\left(\frac{dP}{dz} + 1\right) \qquad (1b)$$

Clearly, v has to be considered as a bulk flow velocity or rather as a hypothetical velocity that the water would have if flowing through the given cross-section quite unobstructed by solid particles. *Hydraulic conductivity* K is strongly dependent both on the detailed pore geometry of the soil and on its water content (see *Water content and retention*). Thus K is the volume flux resulting from unit gradient in hydraulic potential in the particular soil and water situation under consideration. Values of K are characteristic for different soils at a given moisture content. Flow rates, on the contrary, may vary greatly as a function of varying environmental conditions that determine the hydraulic gradients in the flow system. The analysis of vertical entry of water or drainage in the soil requires the addition of a term to satisfy the continuity requirement. Moreover, what is usually measured as v is not a real velocity but a change in volumetric moisture content θ in time at various depths. An expression for $\partial\theta/\partial t$ can be obtained by differentiating Equation (1) with respect to z and by substituting

$$D = -K\frac{\partial P}{\partial \theta}$$

where D is the soil water diffusivity.

$$\frac{\partial v}{\partial z} = -\frac{\partial}{\partial z}\left(D\frac{\partial \theta}{\partial z}\right) - \frac{\partial K}{\partial z} \qquad (2)$$

Considering the continuity requirement

$$\frac{\partial \theta}{\partial t} = -\frac{\partial v}{\partial z}$$

this changes to

$$\frac{\partial \theta}{\partial t} = -\frac{\partial}{\partial z}\left(D\frac{\partial \theta}{\partial z}\right) + \frac{\partial K}{\partial z} \qquad (3)$$

Sometimes it is advantageous to use the pressure-head form of the equation by using the *water capacity* C, which is defined as $\partial\theta/\partial P$, as follows:

$$C\frac{\partial p}{\partial t} = -\frac{\partial}{\partial z}\left(K\frac{\partial p}{\partial z}\right) + \frac{\partial K}{\partial z} \qquad (4)$$

Flow Equations (3) and (4) can be solved analytically or numerically. Many examples are presented in the literature (see review by Klute, 1973). For many field applications, approximate methods can be used that are much easier to work with but physically still quite acceptable in view of the variability found in the field (Bouma, 1973; Klute, 1972).

Methods to determine *K*

Hydraulic conductivity K values are needed to solve flow problems (see *Flow theory*). Many methods, both for laboratory and field use, are available (see Hillel, 2004). All analytical methods require the measurement of soil-moisture potentials with tensiometers at at least two locations and an estimate of a flow rate, occurring at that time of measurement. The flow rate, which may be upward or downward, is usually derived from successive measurements of moisture contents. Values of K are calculated with Equation (1). Generally, in situ measurements are preferable to those using "undisturbed" samples in the laboratory. The sampling procedure, transport, and laboratory conditions may induce changes in the sample that cause deviations from conditions existing in the field. Figure W7 shows a series of representative K curves for a sand, a sandy loam, a silt loam, and a clay soil. These curves, showing K as a function of the (negative) matric or capillary potential M, which can also be described as a positive soil-moisture tension in centimeters or millibar, express the effect of the pore-size distribution of the soil on the value of K. Sands, with only relatively coarse pores, have a relatively high value of K at saturation, but K drops strongly with increasing tension. Clays, with only relatively fine pores, have a low K at saturation, but K decreases more slowly on increasing tension. The curve for the silt loam demonstrates the physical effect of the occurrence of relatively large cracks between aggregates, and root and worm channels. The aggregates are fine-porous, and these fine pores hardly contribute to flow. The large structural pores result in high K values at saturation (140 cm d^{-1} for the silt loam), but K values drop very strongly between saturation and a tension of only 20 cm (1.5 cm d^{-1}) because then these larger voids are filled with air and do not contribute to flow, and flow can occur only through the peds. The functional relationships between pore sizes and

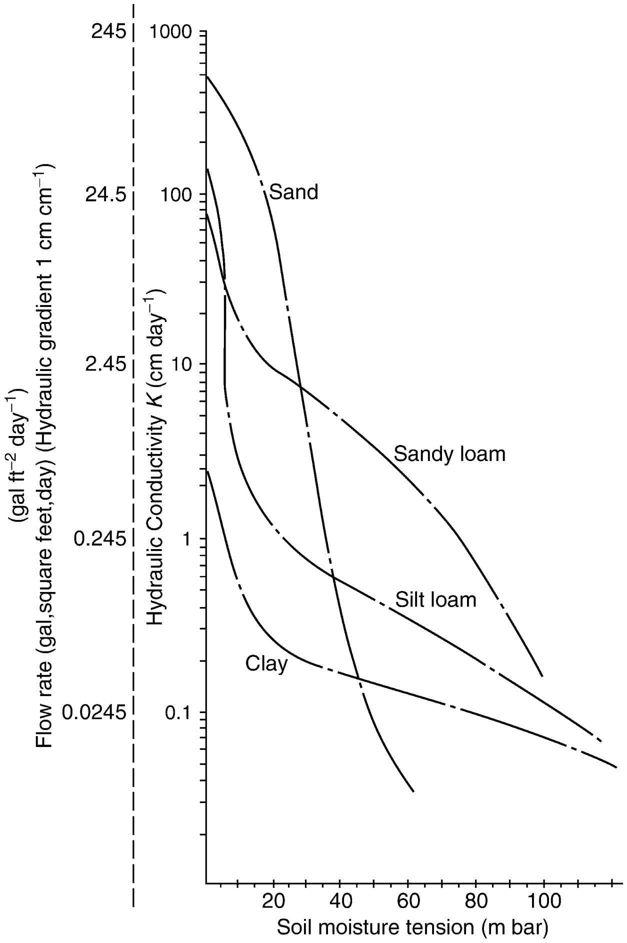


Figure W7 Hydraulic conductivity *K* as a function of soil moisture tension measured in situ with the crust-test procedure.

permeability (*q.v.*) has been used in attempts to calculate *K* curves (see review by Klute, 1972; Anderson and Bouma, 1973). The strong effect of pore size (see *Soil pores*) on measured permeabilities can be explained by considering that the flow rate through a tubular pore is proportional to r^4 (r equals radius pore), whereas flow through a plane slit is proportional to D^3 (D is the width plane slit) (Childs, 1969). Values of *K* are increasingly used in simulation models that attempt to predict soil hydrology as a function of climatic conditions and growth of certain crops (Amerman, 1973; De Laat et al., 1975). These models require *K* curves that have to apply to certain areas in a landscape rather than to just a point of measurement. Studies on variability of *K* in the field are limited, but a considerable variation is usually found (Nielsen et al., 1973). Use of soil maps, prepared in the context of the soil survey program, which is in progress in many countries, may be quite valuable to identify specific areas that may be expected to have particular types of *K* "bands." The soil survey program also defines certain soil-moisture regimes for the types of soil shown on the maps. Criteria used to define such regimes become increasingly specific although they still express a significant amount of practical experience and know-how of soil surveyors and farmers (Soil Survey Staff, 1993; USDA, 1999).

Complications associated with flow theory

Flow theory, as expressed by Equations (2), (3), and (4), really applies only to a very idealized porous medium that is rigid, does not swell or shrink, and is isotropic with respect to Darcy flow. Natural soils are anisotropic, and many soils with clay do swell on wetting (see *Imbibition*). This sometimes means that the flow theory does not adequately describe flow processes in soil (see review by Klute, 1973). A particular problem occurs during flow through natural heterogeneous soils. The flow rate in the Darcy Equation is a bulk rate. The real velocity of flow inside the pores is always higher since flow cannot occur through the solid particles in the soil. When saturated flow through aggregated clayey soils follows larger voids such as cracks between aggregates and worm and root channels (Anderson and Bouma, 1973), the flow theory cannot be used to predict patterns of water movement. Instead, the theory of hydrodynamic dispersion can be useful to predict the moment of breakthrough of a newly applied liquid, as well as the moment when all initially present liquid has been displaced. The calculation of an *apparent dispersion coefficient* D (not to be confused with the diffusivity) can be made from data derived from a breakthrough curve of a chloride solution displacing untraced water from a soil column (Brenner, 1962; Nielsen et al., 1972). This analysis is based on the solution of the following equation:

$$\frac{\partial C}{\partial T} + U\frac{\partial C}{\partial X} = D\frac{\partial^2 C}{\partial X^2} \qquad (5)$$

where T is the time from the commencement of the displacement, X is the distance from the point of introduction of the displacing fluid, $C = C(X,T)$ is the solute concentration, D is the axial dispersion coefficient, and U is the average interstitial velocity of the fluid. Equation (5) can be solved for specific boundary conditions (Brenner, 1962). Additional terms have to be added to express adsorption or precipitation of percolating compounds.

Johannes Bouma

Bibliography

Amerman, C.R., 1973. Hydrology and soil science. In Bruce, R.R., Flach, K.W., and Taylor, H.M., eds., *Field Soil Moisture Regime.* Soil Science Society of America Special Publication No. 5. Madison, WI: Soil Science Society of America, pp. 167–180.

Anderson, J.L., and Bouma, J., 1973. Relationships between saturated hydraulic conductivity and morphometric data of an argillic horizon. *Soil Sci. Soc. Am. Proc.*, **37**: 408–413.

Bouma, J., 1973. Use of physical methods to expand soil survey interpretations of soil drainage conditions. *Soil Sci. Soc. Am. Proc.*, **37**: 413–421.

Brenner, H., 1962. The diffusion model of longitudinal mixing in beds of finite length, *Chem. Eng. Sci.*, **17**: 229–243.

De Laat, P.J.M., van Den Akker, C., and van de Nes, Th.J., 1975. Consequences of groundwater extraction on evapotransporation and saturated-unsaturated flow. Proc. Symp. Application of Mathematical Models in Hydrology and Water Resources Systems *(Bratislava). IAHS-AISH Publ. No. 115*, pp. 67–76.

Hillel, D.I., 2004. *Introduction to Environmental Soil Physics.* Amsterdam/Boston: Elsevier/Academic Press, 494 pp.

Jury, W., and Horton, R., 2004. *Soil Physics*, 6th edn. Hoboken, NJ: Wiley, 370 pp.

Klute, A., 1972. The determination of the hydraulic conductivity and diffusivity of unsaturated soils, *Soil Sci.*, **113**(4): 264–277.

Klute, A., 1973. Soil water flow theory and its application in field situations. In Bruce, R.R., Floch, K.W., and Taylor, H.M., eds., *Field Soil Moisture Regime.* Soil Science Society of America Special Publication No. 5. Madison, WI: Soil Science Society of America pp. 9–35.

Nielsen, D.R., 1972. *Soil Water*. Madison, WI: American Society of Agronomy, 175 pp.
Nielsen, D.R., Biggar, J.W., and Erh, K.T., 1973. Spatial variability of field measured soil water properties. *Hilgardia*, **42**(7): 215–260.
Soil Survey Staff, 1993. *Soil Survey Manual*. Washington, DC: U.S. Dept. of Agriculture, 437 pp.
USDA, 1999. Soil taxonomy: a basic system of soil classification for making and interpreting soil surveys/by soil survey staff, 2nd edn. Washington, DC: U.S. Dept. of Agriculture, Natural Resources Conservation Service, 869 pp.
Warrick, A.W., 2003. *Soil water dynamics*. Oxford: Oxford University Press, 391 pp.

Cross-references

Capillary Pressure
Conductivity, Hydraulic
Field Water Cycle
Flow Theory
Irrigation
Infiltration
Imbibition
Leaching
Percolation
Permeability
Soil Drainage
Soil Pores
Soil Solution
Soil Water
Tillage
Water Budget in Soil
Water Content and Retention
Wetting Front

WATER POTENTIAL

The potential energy of water per unit mass in a soil measured against a standard state. In a soil there are four component potentials: gravitational, matric, osmotic, and pressure, some of which may be zero. Pure water has a water potential of zero. Presence of a solute lowers this to negative values by an amount equivalent to the osmotic potential.

Cross-references

Conductivity, Hydraulic
Thermodynamics of Soil Water
Water Content and Retention
Water Movement

WATER TABLE

See *Groundwater*.

WATERLOGGED

Saturated with water, the perennial state of a soil below the water table (the phreatic zone) or the temporary state of a soil that is normally unsaturated with respect to water, when that soil is subject to excessive atmospheric precipitation or flooding, or when surface soil thaws while subsoil is frozen. Soil in a waterlogged state is subject to low redox potentials, under which Fe is mobilized in ferrous form, and gleying may occur.

Cross-references

Gleysols
Mires
Planosols
Redox-pH Reactions and Diagrams in Soils
Stagnosols
Wetland

WATERSHED

The line separating the waters flowing into different rivers or river basins; a narrow elevated tract of ground between two drainage areas. Also the whole gathering ground of a river system, the area drained by a river system.

WEATHERING SYSTEMS IN SOIL SCIENCE

Materials at or close to the Earth's surface respond to ambient conditions by undergoing a complex set of transformations called weathering. Weathering is driven by the energy of the sun and involves exchanges between lithosphere, atmosphere, hydrosphere and biosphere, at low temperature and atmospheric pressure, and with many interacting factors influencing its course (see Figure F1 of *Factors of Soil Formation*). As the proximate cause by which most of the land surface of the Earth acquires its mantle of soil, weathering is of supreme importance in maintaining the biosphere (see *Soil*). To make the same point in anthropocentric terms, the provision of ecological goods and services through the medium of soil is the fundamental way by which the biosphere, and human society embedded in it, is sustained (Daily, 1997).

The principal physical and mechanical processes that take place during weathering are the abrasion and comminution of rocks and minerals as a result of erosive forces (see *Mechanical Weatheing; Wind erosion*; *Water erosion*; *Ice erosion*) and hydration along grain boundaries. A suite of fragment and particle sizes is produced, which depends on macrofeatures (bedding and jointing for example) and microfeatures (chemistry, mineralogy, texture and structure in particular) of the parent materials, and on the type, intensity and duration of weathering. Prolonged weathering increases the percentage of finer materials in the product. By virtue of their large surface area, the finer materials become the most chemically reactive part of the system, and the principal locus for the formation of clay minerals and hydroxy crystalline and amorphous compounds.

Forcing factors

Anderson et al. (2004) emphasize three forcing factors for the Earth's weathering engine: climatic, tectonic and anthropogenic.

Climatic. As the term "weathering" implies, weather or climate is a principal forcing factor in the process, especially in terms of temperature and the water cycle (Tardy and Roquin,

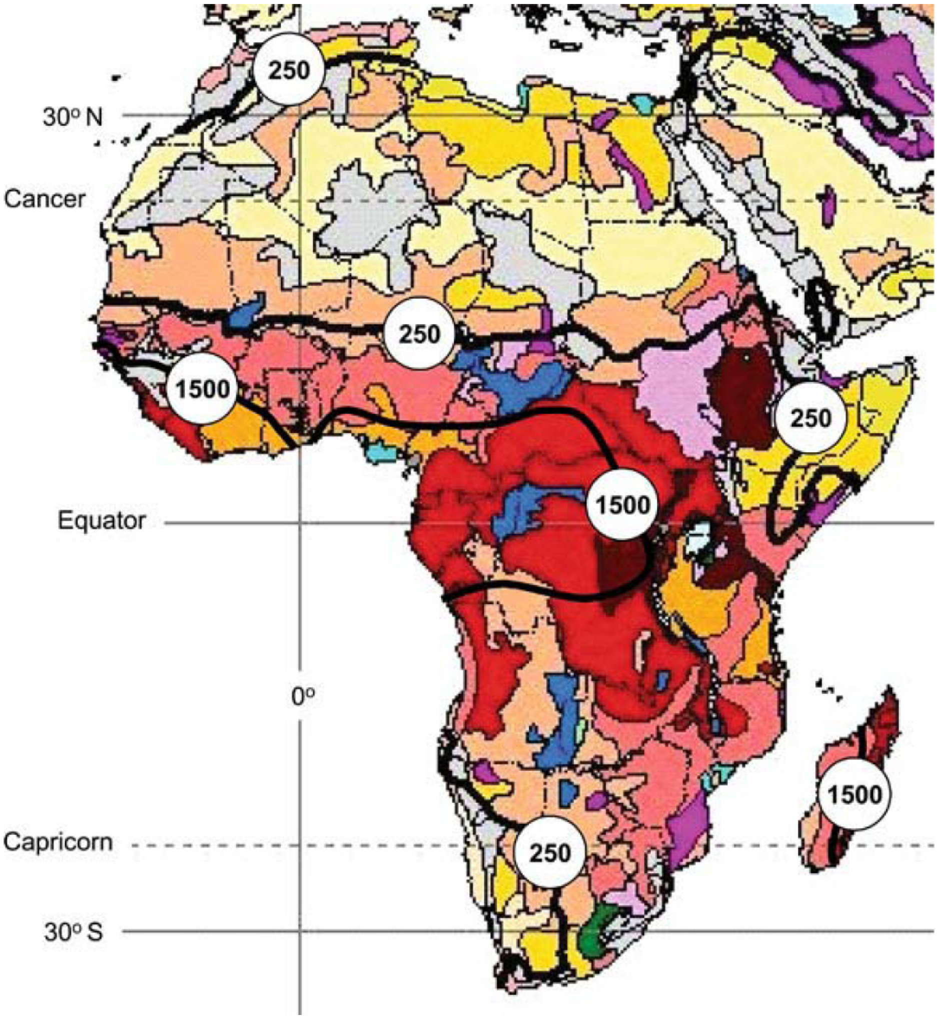


Figure W8 FAO soils map of Africa with climatic zonation, represented by annual precipitation values, superimposed. The isohyets are labeled in terms of mm rainfall per year. Below 250 mm, arid and semi-arid zone soils are found (Calcisols, Gypsisols and salt-affected soils). Above 1500 mm, ferrallitic soils, with kaolinite ± gibbsite, occur (Ferralsols, Alisols, Plinthosols for example). Between the 250 and 1500 mm isohyets ferrallitic soils also occur, since the region of higher rainfall once extended into this area, but they are accompanied by soils that have been later modified by more recent, drier conditions such as Lixisols (additional soils data from Zech and Hintermaier-Erhard, 2007).

1986). The effect of climate is clearly seen in the way in which the distribution of soil types on the African continent follows climatic zones (Figure W8). It was explicitly recognized in the designation ‘zonal soils’ introduced by American pedologists in the early 20th century. As a forcing factor, climate is closely bound to variations in vegetation regime worldwide. Vegetation has a profound effect on weathering within the solum, and upon the development of diversity among soils, and it might be worthwhile for the purposes of pedology, to recognize a *biotic* forcing factor separately from the climatic one. The climate of the recent past must also be taken into consideration. The Pleistocene was a period of recurrent glaciation, and as a result of the extensive development of ice sheets, new, weatherable materials has been added and exposed to the Earth’s surface in the form of glacigene sediments and fresh rock surfaces. Without the moraine, outwash and other deposits, there would be negligible weathering and soil cover in the glaciated regions of the northern hemisphere, as the striae and chatter-marks on exposed rock in the Canadian Shield, still generally well-preserved after several thousand years of exposure to weathering processes, clearly indicate. Only where glacigene sediments occur, original and reworked, is there any significant weathering and soil formation.

Tectonic. A second important forcing factor comes into play where endogenic processes such as volcanism and orogeny impact upon the exogenic cycle. In Africa, it is most obvious in the case of the Ethiopian Highlands, where volcanic additions essentially reset the weathering system back to time zero during the Cenozoic. In the Americas and Eurasia, orogeny has had a similar, though more dramatic effect in resetting the weathering clock in the young fold belts of the late Mesozoic and early Cenozoic. New additions of rock to the weathering regime as a result of tectonism and volcanism (together with glaciation) are

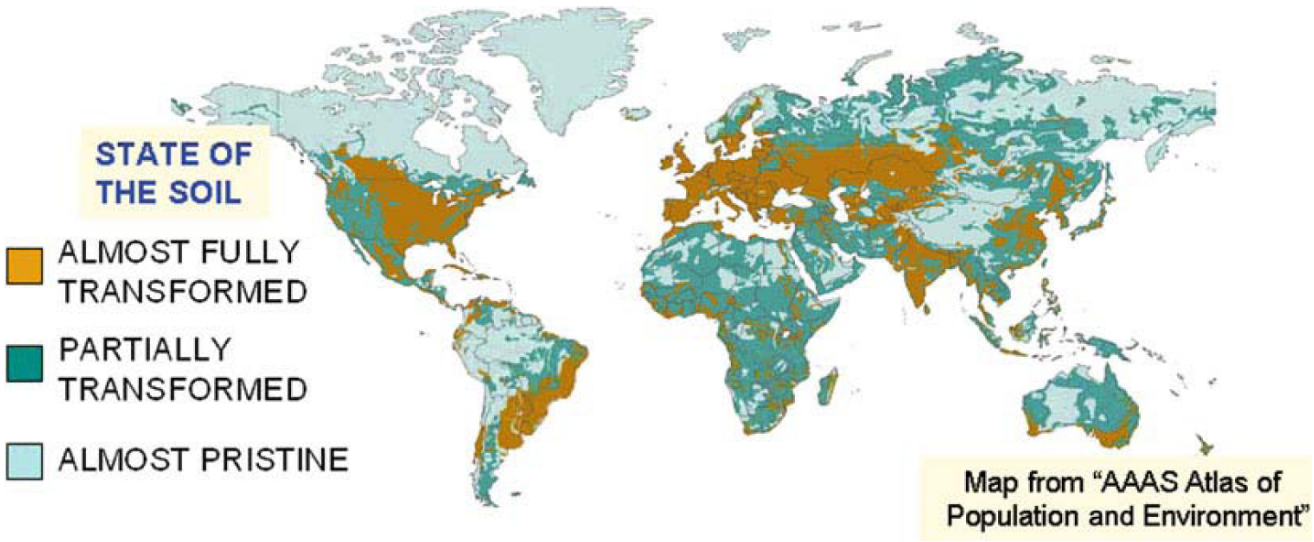


Figure W9 The extent to which human activity has transformed the soil. The most affected areas have been called the Anthrobleme, or human scar (Chesworth, 2006).

important in fertilizing the biosphere (Chesworth, 2006), and the most inherently fertile soils are found where these processes have been most recently active (Chesworth, 1982).

Human. Within the last 300 years (that is, since the beginnings of the Industrial Revolution) a third forcing factor has come to dominate the world's weathering system, including the soil. This is the human, or anthropogenic factor (Vitousek et al., 1997), with agricultural activities being predominant (Chesworth, 1996, 2006). Figure W9 illustrates the point. It is interesting to note that human forcing of the Earth machine has to a considerable degree followed a deeper, geological imperative (Figure W10).

Weathering rates

The problem of determining weathering rates has been attacked in the field and in the laboratory. Field studies depend upon finding a datable surface that has undergone weathering for a measurable time. Estimates are dependent upon all the interacting soil forming factors referred to in the first paragraph and are therefore site specific and without general significance. Laboratory studies of weathering, are misleading as regards to absolute rates (White and Brantley, 2003), but throw light on mechanism. The rate-limiting step appears to be via surface controlled reactions in most cases (Grandstaff, 1986), though the weathering of glass may be diffusion controlled.

Different minerals weather at different rates, but, as Eggleton (1986) points out, no adequate general explanation exists. The susceptibility of a mineral to weathering may possibly be related to its position in Bowen's reaction series (Goldich, 1938) or to its free energy of formation (Keller, 1954). Ultimately, "*weathering rate will depend on the mechanism whereby the weathering agents break the bonds between the atoms of the crystal*" (Eggleton, 1986).

Colman and Dethier (1986) and Lerman and Meybeck (1988) provide two collections of papers containing much information about weathering rates. Again they confirm the view that rate is site specific and generalizations are difficult to draw. Judged in terms of soil production, rates range generally from 1 to about 500 mm per thousand years, with most soils forming at rates less than 100 mm per thousand years. It seems reasonable to state that in regions with a temperate, humid climate the rate of soil formation on aluminosilicate parent materials will be less than 50 mm per thousand years (Colman and Dethier, 1986), with soils on carbonate parent materials forming at rates between 50 and 100 mm per thousand years (Reynolds et al., 1987). The actual depth of weathering says nothing about soil type of course, the rate of formation of which will depend upon how long it takes for a specific diagnostic horizon to form. Regosols, with no diagnostic horizons may form in less than a hundred years. Podzols have formed on unconsolidated glacial deposits in Northern Canada with well-developed Ae and Bs horizons in 8 000 years or less. Ferralsols, which require the formation of a ferralic horizon, take the longest time to develop i.e., times of the order of 10^6 years. These figures for the rates of formation of horizons are from Porta et al. (1994, p. 496).

Weathering trends

Weathering involves reaction between solid and amorphous phases and an aqueous solution. Oxygen and CO_2, of atmospheric or biospheric provenance, are actively involved, as also are acids and complexants produced by the breakdown of organic matter. All this is mediated by microorganisms, with bacteria as the dominant influence. Acid-base, and redox reactions are characteristic, and singly or in combination they produce three overall trends in the weathering soil mantle (Figure W11):

- an *acid trend*: caused by over-titration, as for example in humid regions where atmospheric precipitations and rotting vegetation produce a continuous supply of hydrogen ions to the soil;
- an *alkali trend*: caused by under-titration, as for example in semi-arid and arid regions where the supply of hydrogen ions is inadequate and bases predominate, particularly the carbonates of Ca, Mg and Na;

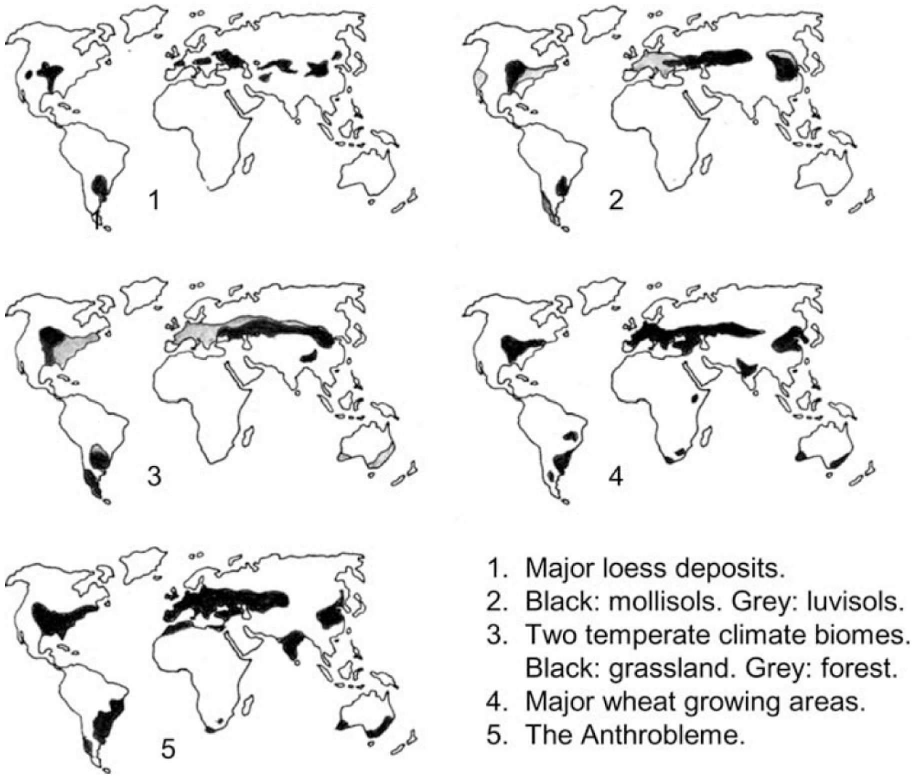


Figure W10 The bottom layer of the ecological palimpsest is loess, the parent material of most grassland soils and many soils of the temperate forest biome. These are the most extensive areas of soil that have been taken over for agricultural purposes, so that they mark the most humanly modified regions of the Earth (Chesworth, 2006).

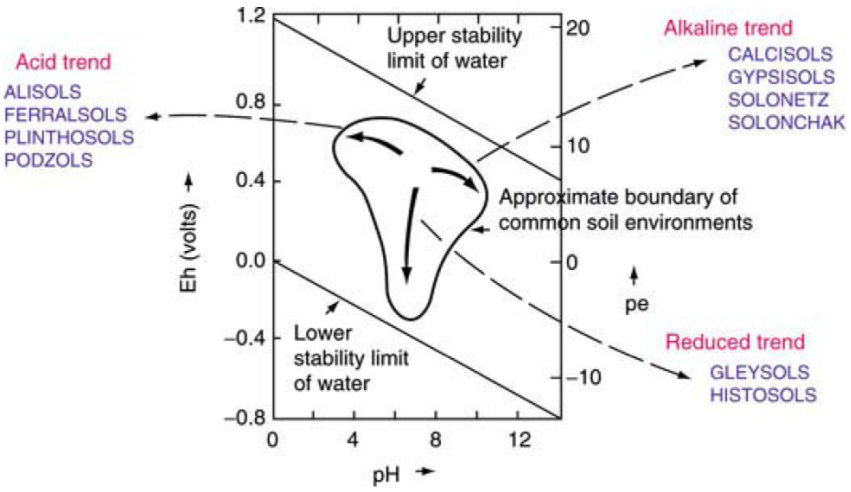


Figure W11 The three main trends in the evolution of the common soils (diagram modified from Chesworth, 1992). See *Redox Reactions and Diagrams in Soil*.

- a *reduced trend*: caused by the exclusion or diminution of free oxygen in the weathering system by virtue of water-saturation, or by the excessive oxygen demand of the bacterial breakdown of organic matter, or by both.

The global picture

Jackson and Sherman (1953) maintain that there are two compartments of the weathering zone: an upper (pedochemical) part, where organic acids and complexants are significantly

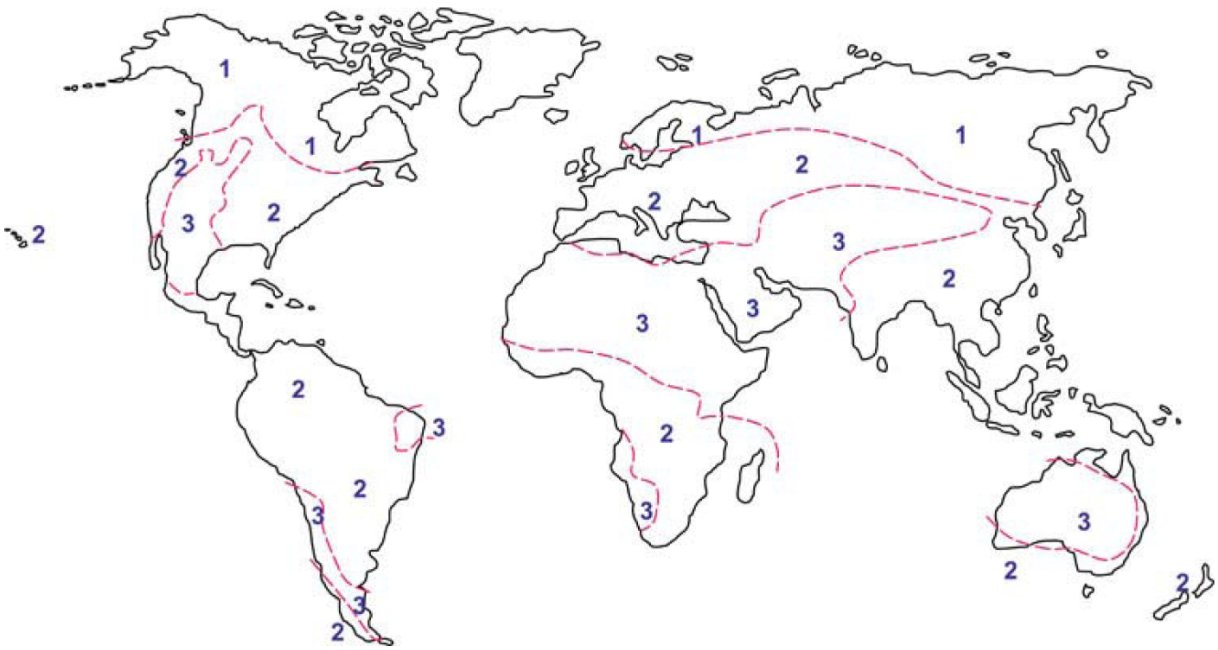


Figure W12 The global weathering system partitioned into 3 zones. *Zone 1:* typical environment of acidolysis; *Zone 2:* environment of hydrolysis in the strict sense; *Zone 3:* arid and semi-arid regions within which isolated areas of salinolysis and alkalinolysis are found (modified from Pedro and Siefferman, 1979).

present, and a lower (geochemical) one, where they are absent or greatly attenuated. At depth, weathering will be largely determined by the ability of the system $H_2O–CO_2$ to produce protons, and will be much the same worldwide (rate differences apart). In the upper compartment however, regional variations in weathering chemistry occur, reflecting geographical changes in the coupled factors of climate and vegetation, and the organic degradation products of the latter. How many distinctly different weathering environments this will result in, and therefore how many distinctly different soil types will form, is a debatable point. Pedro and Sieffermann (1979) for example recognize four environments (or processes): acidolysis: Al_2O_3 more mobile than SiO_2; hydrolysis: SiO_2 more mobile than Al_2O_3; alkalinolysis: mobility sequence $SiO_2 > Al_2O_3 >$Na, Ca, Mg; salinolysis: mobility sequence $Al_2O_3 \gg SiO_2 >$Na, Ca, Mg. Brinkmann (1970) added a fifth to these - ferrolysis: a two step redox process of acidification in waterlogged soils. Gaucher (1977) on the other hand itemizes ten different types of soil-chemical environment on the basis of differing geochemical mobilities of major components. Macias and Chesworth (1992) discuss the matter further.

Regardless of how many separate types are recognized the acid end points of weathering differ with latitude. Thus the Podzol is typical of humid temperate climates, and the Ferralsol of humid tropical ones. The former is the prototypical system for demonstrating the effect of organic constituents on weathering, while the latter, since organic debris breaks down rapidly in the tropics, is not basically different from a weathering regime dominated by the $H_2O–CO_2$ system. Stated differently, the pedochemical compartment of the weathering zone becomes indistinguishable from the geochemical compartment in the humid tropics. Despite this chemical convergence however, physical differences remain (Macias and Chesworth, 1992).

Considerations such as these are incorporated in Figure W12, a highly generalized map showing the distribution of weathering systems and soil forming environments on a global scale.

Ward Chesworth

Bibliography

Anderson, S.P., Blum, J., Brantley, S.L., Chadwick, O., Chorover, J., Derry, L.A., Drever, J.I., Hering, J.G., Kirchner, J.W., Kump, L.R., Richter, D., and White, A.F., 2004. Proposed initiative would study Earth's weathering engine. *EOS*, **85**: 265–272.

Brinkmann, R., 1970. Ferrolysis, a hydromorphic soil-forming process. *Geoderma*, **3**: 199–206.

Chesworth, W., 1982. Late Cenozoic geology and the second oldest profession. *Geosci. Canada*, **9**: 54–61.

Chesworth, W., 1992. Weathering systems, Chapter 2. In Martini, I.P., and Chesworth, W., eds., *Weathering, Soils and Paleosols.* Amsterdam: Elsevier, pp. 19–40.

Chesworth, W., 1996. Agriculture as a Holocene process and its bearing on sustainability. In Perez Alberti, A., ed., *Dinamica y Evolucion de Medios Cuarternarios.* Santiago de Compostela, Spain: Xunta de Galicia, pp. 31–36.

Chesworth, W., 2006. The enemy within, Chaper 3. In Lavigne, D.M., ed., *Gaining Ground: in Pursuit of Ecological Sustainability.* IFAW, University of Limerick, pp. 31–42.

Colman, S.M., and Dethier, D.P. (eds.), 1986. *Rate of Chemical Weathering of Rocks and Minerals.* London: Academic press, 603 pp.

Daily, Gretchen C. (ed.), 1997. *Nature's Services: societal dependence on natural ecosystems*. Washington, DC: Island Press. 392, pp.

Eggleton, R.A., 1986. In Colman, and Dethier, eds., *The Relation Between Crystal Structure and Silicate Weathering Rates*, pp. 21–40.

Gaucher, G., 1977. Vers une classification pedologique naturelle base sur la geochimie de la pedogenese. *Catena*, **4**: 1–27.

Goldich, S.S., 1938. A study in rock weathering. *J. Geol.*, **46**: 17–58.

Grandstaff, D.E., 1986. In Colman, and Dethier, eds., *The Dissolution Rate of Forsteritic Olivine from Hawaiian Beach Sand,* pp. 41–59.

Jackson, M.L., and Sherman, G.D., 1953. Chemical weathering of minerals in soils. *Adv. Agron.*, **5**: 219–318.

Keller, W.D., 1954. Bonding energies of some silicate minerals. *Am. Mineral.*, **39**: 783–793.

Lerman, A., and Meybeck, M., 1988. Physical and geochemical weathering in geochemical cycles. *NATO Adv. Study Inst. Ser. C*, 251–275.

Macias, F., and Chesworth, W., 1992. Weathering in humid regions, with emphasis on igneous rocks and their metamorphic equivalents. Chapter 12. In Martini, I.P., and Chesworth, W., eds., *Weathering, Soils and Paleosols.* Amsterdam: Elsevier, pp. 283–306.

Pedro, G., and Sieffermann, G., 1979. Weathering of rocks and formation of soils. *Earth Sci.*, **16**: 39–55.

Porta, J., Lopez-Acevedo, M., and Roquero, C., 1994. Edafología: para la agricultura y el medio ambiente. Madrid: Ediciones Mundi-Prensa, 807 pp.

Reynolds, B., Hornung, M., and Stevens, P.A., 1987. Solute budgets and denudation rate estimates for a mid-Wales catchment. *Catena*, **14**: 13–23.

Tardy, Y., and Roquin, C., 1986. Geochemistry and evolution of lateritic landscapes, Chapter 16. In Martini, I.P., and Chesworth, W., eds., *Weathering, Soils and Paleosols.* Amsterdam: Elsevier, pp. 407–443.

Vitousek, P.M., Mooney, H.A., Lubchenko, J., and Melillo, J.M., 1997. Human dominanation of Earth's ecosystems. *Science*, **277**: 494–499.

White, A.F., and Brantley, S.L., 2003. The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field. *Chem. Geol.*, **202**: 479–506.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer. 130 pp.

Cross-references

Classification of Soils: World Reference Base (WRB) for Soil Resources
Factors of Soil Formation
Ferrolysis
Ice Erosion
Redox Reactions and Diagrams in Soil
Soil
Water Erosion
Wind Erosion

WENTWORTH SCALE

Also the Udden Wentworth Scale. A classification of loose, particulate material based on particle size diameter. In nature the range of particle sizes is so great that a logarithmic scale of this nature is more practical than a linear scale. Krumbein made the logarithmic base explicit in his Φ scale, where $\Phi = -\log 2$ (grain size in mm) (see Table W2).

Table W2 Wentworth scale

Φ	Size (mm)	Size class
		Boulders
−8	256	Cobbles
−6	64	Pebbles
−2	4	Granules
−1	2	Very coarse sand
0	1	Coarse sand
1	1/2	Medium sand
2	1/4	Fine sand
3	1/8	Very fine sand
4	1/16	Silt
8	1/256	Clay

WETLAND

An area of land that is usually saturated with water. Several classifications exist; the Canadian system is illustrated (Figure W13) as one that makes clear distinctions on the basis of ecosystem (rather than engineering, or simply hydrological) characteristics.

Cross-references

Mires
Peat

WETTABILITY

The property of forming a liquid film over a surface by virtue of the attraction of the surface for the liquid being greater than the cohesive force between molecules within the liquid.

Cross-reference

Hydrophilicity, Hydrophobicity

WETTING FRONT

As water penetrates a dry soil, the wetted soil takes a darker color in contrast to its original light appearance. Because of this change in color, the transition zone between the dry soil and the moistened soil can be appreciated visually. For a number of soils the transition is quite sharp, and the propagation of this color change, as more water moves into the soil, can be followed by eye readily. The region of rapid change in color resulting from an increased water content is called the wetting front.

From this clear visual separation between the light dry soil and the dark moist soil, one might infer that ahead of the wetting front, the soil is in its original state of dryness and that behind the wetting front, water now fully occupies the pore space vacated by the displaced air. But this is not the case. If one were to measure water content as a function of distance away from the water source, one would obtain a profile as shown in Figure W14. Though there is no discernible difference in color behind the wetting front, the water content behind it is far from uniform. In fact, it reaches its maximum value $\tilde{\theta}$, that is, a state of full saturation except for a certain amount of trapped residual air, only close to the source of water.

Whereas the phenomenon of propagation of the wetting front must have been known to primitive man as a matter of daily observation, the mechanism by which water actually invades the soil was not elucidated until the seventeenth century. Certainly if water is poured on top of a soil column, one expects water to percolate through the soil by gravity. On the other hand, if a thin layer of water and a soil sample lie side by side as shown in Figure W15a, in contact, on top of a horizontal tray, why would water, at atmospheric pressure, penetrate the porous medium and displace air, also at atmospheric pressure? Yet, apparently for no reason, it does. It is as though it were sucked in!

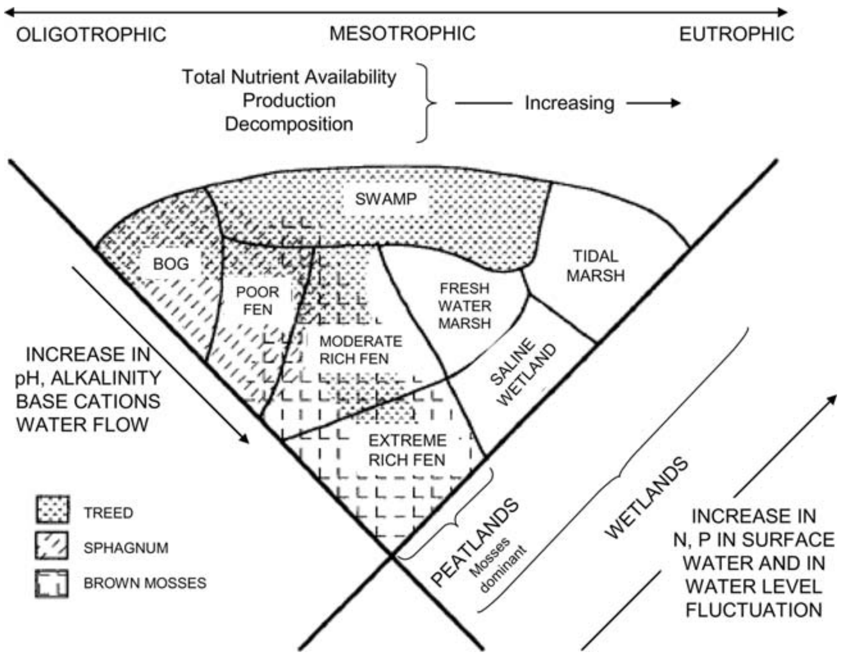


Figure W13 Terminology and ecological characteristics of wetlands (adapted from Zoltai, S.C., and Vitt, D.H., 1995. Canadian wetlands: environmental gradients and classification. *Vegetatio*, **118**: 131–137. Bogs and fens are also classed as mires: bogs are ombrotrophic mires, while fens are minerotrophic. See *Mires*.

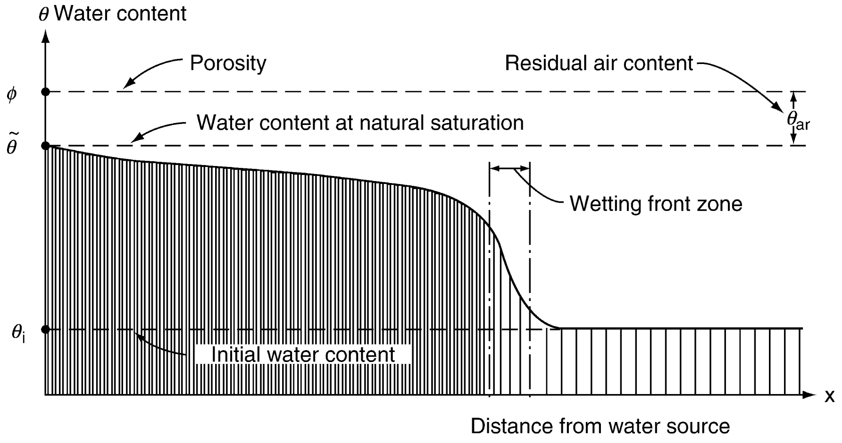


Figure W14 Variation of water content and soil color with distance from water source.

Propagation in a tube

The thorough understanding of the reason why water, at atmospheric pressure, will penetrate a porous medium and displace another fluid such as air also at atmospheric pressure, is of capital importance for a sound physical understanding of *water movement* (*q.v.*) in soils. To the extent that a porous medium, as a first rough approximation, can be visualized as a bundle of unconnected cylindric tubes, some small, some large, there is merit in the study of the wetting of a tube. This highly idealized model of the porous medium is an obviously inaccurate picture of an extremely complex reality. Its merits as a model of reality are almost null. Nevertheless, it provides a convenient and simple introduction to ulterior, more complicated developments.

Consider a preferentially water-wet tube of small diameter initially filled with air. The tube is brought in contact with an ample supply of water at atmospheric pressure (Figure W15). The initial water-air interface or wetting front may be considered to be the plane αb. For an infinitesimal amount of time the force diagram will be as shown on Figure W15b. The interface will be in equilibrium except at the contact with the solid. There, a net impulse of magnitude proportional to $\sigma_{as}-\sigma_{ws}$ causes the point a of the interface to move into the tube. The

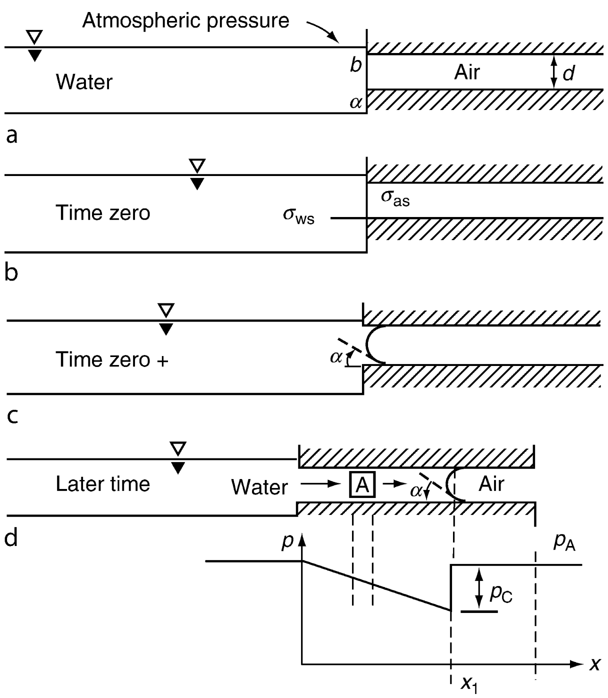


Figure W15 Stages of penetration of wetting front in a tube.

air-solid surface tension is σ_{as} (see *Capillary pressure* for a definition of surface tension), and σ_{ws} is the water-solid surface tension. Because the other points of the interface are in equilibrium, the interface curves in, and it very quickly assumes the shape shown in Figure W15c, where α is the equilibrium wetting angle. The interface is now in equilibrium because the surface tension force and the capillary pressure force balance one another. Because the pressure drop in the moving air phase is essentially negligible compared to that in water, the pressure in the air just ahead of the interface is essentially atmospheric p_A. Just behind the interface, the pressure in the water p_w is less than atmospheric by an amount equal to the capillary pressure p_c. At the inlet the pressure is atmospheric. As a result, there exists an unbalanced pressure gradient in the water phase that causes the water to flow and that sustains the motion initially created by unbalanced surface-tension forces. Viscous shear (particle A, Figure W15d) will resist the driving force tending to enforce a uniform flow. Actually, flow is constantly retarded because the pressure gradient in the water phase p_c/x_i itself decreases with time. In summary, motion is originated by preferential wettability and later sustained by the induced pressure gradient in the wetting phase.

From this qualitative physical understanding of the mechanism of wetting, a quantitative prediction for the rate of propagation (or celerity) of the wetting front can be developed. Let the position of the wetting front be located at x_f at time t. The pressure distribution in the tube is indicated in Figure W16. Application of Poiseuille's Equation for laminar flow in a cylindrical tube (Morel-Seytoux, 1969) in the water and in the air phase yields for the water and air velocities in the tube, respectively,

$$u_w = \frac{dx_f}{dt} = \frac{R^2}{8\mu_w}\frac{(p_a - p_w)}{x_f} \tag{1}$$

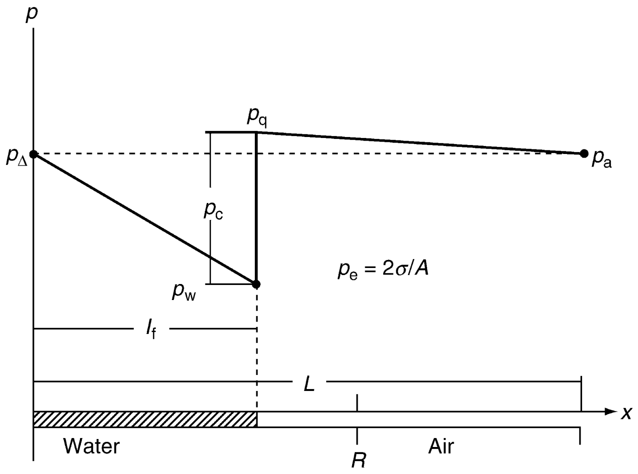


Figure W16 Fluid pressure distribution in a wetting tube.

and

$$u_a = \frac{dx_f}{dt} = \frac{R^2}{8\mu_a}\frac{(p_a - p_A)}{(L - x_f)} \tag{2}$$

where L is the length of the tube and μ_w and μ_a are the viscosities of water and air. As the two velocities must be equal, it follows by equating μ_w and μ_a, that the unknowns p_w and p_a must be related by the equalities,

$$\frac{p_a - p_A}{\mu_a(L - x_f)} = \frac{p_A - p_w}{\mu_w x_f} = \frac{p_c}{\mu_a(L - x_f) + \mu_w x_f} \tag{3}$$

from which the velocity dx_f/dt can be obtained as a function of the wetting-front position, namely,

$$\frac{dx_f}{dt} = \frac{R^2}{8}\frac{p_c}{x_f(\mu_w - \mu_a)\mu_a L} \tag{4}$$

If the viscosity of air is neglected compared to that of water and if one expresses the capillary pressure as an equivalent water height h_c, Equation (4) takes the simpler form

$$\frac{dx_f}{dt} = \frac{R^2\rho_w g}{8\mu_w}\frac{h_c}{x_f} \tag{5}$$

After integration one obtains

$$x_f = \left(\frac{R^2\rho_w g h_c}{4\mu_w}\right)^{0.5\sqrt{t}} \tag{6}$$

from which the imbibition rate, $I = (dx_f/dt)$, (that is, volumetric water inflow rate per unit cross-section area) can be deduced as an explicit function of time

$$I = \frac{1}{2}\frac{S_p}{\sqrt{t}} \tag{7}$$

where

$$S_p = \sqrt{\frac{R^2\rho_w g h_c}{4\mu_w}} \tag{8}$$

can be called the Poiseuille sorptivity. This sorptivity characterizes the ability of the tube to imbibe water. Alternately the imbibition rate can be expressed as a function of position of the wetting front, namely,

$$I = \frac{1}{2}\frac{S_p^2}{x_f} \tag{9}$$

Equations (9) and (7) are equivalent since $x_f = S_p\sqrt{t}$. Assuming that the interface has the shape of a spherical cap, the capillary pressure at the wetting front is

$$h_c = \frac{2\sigma\cos\alpha}{R\rho_w g} \tag{10}$$

from which a more explicit form of the Poiseuille sorptivity is obtained

$$S_p = \sqrt{\frac{R\sigma\cos\alpha}{2\mu_w}} \tag{11}$$

Propagation in a soil

If one assumes that in the soil, as in the capillary tube, the wetting front separates the dry soil from a fully saturated soil (Figure W17), then the imbibition rate in a horizontal soil is given by the application of Darcy's Law for saturated soil between the soil-entry face and the wetting front, namely,

$$I = \overline{K}\frac{[H_A - (H_A - H_f)]}{x_f - 0} = \overline{K}\frac{H_f}{x_f} \tag{12}$$

since the water is at atmospheric pressure at the entry face and is below atmospheric pressure just behind the wetting front. The term $\overline{K}$ is the *hydraulic conductivity* (*q.v.*) at natural saturation. The term H_f is the so-called wetting-front suction. Whereas the capillary pressure across a meniscus in a capillary tube is well defined by Equation (10), the wetting-front suction is not. For, clearly, there are as many capillary-suction values as there are menisci in all the complex-shaped interconnected capillaries that constitute the real soil. Proceeding by analogy, one can, at best, say that the wetting-front suction is an average capillary suction in some sense across a representative pore radius.

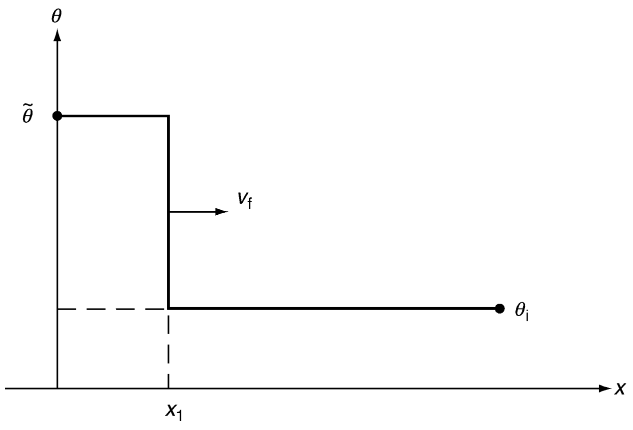


Figure W17 The piston displacement model of Green and Ampt.

For flow in the vertical direction, the imbibition (or infiltration) rate is given, again by application of Darcy's Law, by the slightly different formula

$$I = \overline{K}\frac{(H_f + z_f)}{z_f} = \overline{K} + \overline{K}\frac{H_f}{z_f} \tag{13}$$

which shows the additive effects of the gravity and capillarity forces on the infiltration rate. The celerity of the wetting front is related to the infiltration rate by the equation

$$I = \left(\tilde{\theta} - \theta_i\right)\frac{dz_f}{dt} \tag{14}$$

since only the volume change from θ_i to $\overline{\theta}$ is available to water rather than the total bulk volume of soil. Combining Equations (13) and (14) and integrating leads to a relation between the wetting-front position and time in the form

$$\frac{\overline{K}t}{\overline{\theta} - \theta_i} = z_f - H_f \ln\left(1 + \frac{z_f}{H_f}\right) \tag{15}$$

known as the Green and Ampt Equation (Green and Ampt, 1911). The Green and Ampt Equation cannot be used for prediction purposes since the wetting-front suction is not known. However, if an experiment is performed in which the various positions of the wetting front are visually recorded as a function of time, one can deduce indirectly from the observations the value of H_f. The best value of H_f is that value which when used in Equation (15) gives predicted positions of the wetting front at given times closest to the actual observations. The wetting-front suction, in spite of its impressive name, has been reduced to the low status of an empirical constant (Childs, 1969).

Bouwer's wetting-front suction

The rather good fit between actual observations of cumulative infiltration W and those predicted by a slightly modified form of Equation (15), namely,

$$\overline{K}t = W - H_f\left(\overline{\theta} - \theta_i\right)\ln\left[1 + \frac{W}{H_f\left(\overline{\theta} - \theta_i\right)}\right] \tag{16}$$

since for a full displacement of air by water $W = z_f(\theta - \theta_i)$, led several investigators to suspect that Equation (16) might be valid without the assumption of complete saturation (piston displacement) behind the wetting front. The undiscovered relation between the wetting-front suction and the soil characteristic curves such as capillary pressure (see *Capillary pressure*) and water relative permeabilities (see *Permeability*) kept teasing the brains of various scientists.

Bouwer (1964, p. 142) suggested an approximate determination of H_f by substituting for it what he called the critical pressure head, defined by the relation

$$H_b = \int_0^\infty k_{rw} dh_c \tag{17}$$

where k_{rw} is the relative permeability to water (that is, relative to the wetting permeability at natural saturation), and hc is the capillary pressure (expressed as a water height). Intuitively, viewing the porous medium as an ensemble of capillaries, the use of a weighted average of capillary pressure across the wetting front is appealing. The problem is of course the choice of the weight. The treatment of a different problem, that of unsaturated flow above mildly sloping water tables (Bouwer, 1964, p. 130) suggested naturally k_{rw} as the weighting function. By comparison with observations, it was found that the use of H_{b} yielded accurate predictions of infiltration rates from a canal in sand.

A two-fluid formulation

As water penetrates the soil, it displaces the air. The problem of water movement is therefore also a problem of air movement. Traditionally, the description of the air movement has been neglected. The resulting mathematical simplification is secured at the expense of physical significance.

Darcy's Law for two immiscible fluids (Morel-Seytoux, 1969) such as air and water can be written in the form

$$v_{\mathrm{w}} = -\frac{kk_{\mathrm{rw}}}{\mu_{\mathrm{w}}}\left(\frac{\partial p_{\mathrm{w}}}{\partial z} - \rho_{\mathrm{w}}\mathrm{g}\right) \tag{18}$$

$$v_{\mathrm{a}} = -\frac{kk_{\mathrm{ra}}}{\mu_{\mathrm{a}}}\left(\frac{\partial p_{\mathrm{a}}}{\partial z} - \rho_{\mathrm{a}}\mathrm{g}\right) \tag{19}$$

where v_{w} and v_{a} are the fluid velocities (in the Darcy sense), k is the intrinsic permeability, k_{rw} and k_{ra} are the fluid relative permeabilities, ρ_{w} and ρ_{a} their specific masses, g is the acceleration of gravity, and z is the vertical coordinate oriented positive downward. The law of conservation for both fluids yields

$$\frac{\partial\theta}{\partial t} + \frac{\partial}{\partial z}(v_{\mathrm{w}}) = 0 \tag{20}$$

and

$$\frac{\partial\theta_{\mathrm{a}}}{\partial t} + \frac{\partial v_{\mathrm{a}}}{\partial z} = 0 \tag{21}$$

where θ is water content, and θ_{a} is air content. Adding Equations (18) and (19) gives

$$\begin{aligned} v_{\mathrm{w}} + v_{\mathrm{a}} &= v \\ &= -(\lambda_{\mathrm{w}} + \lambda_{\mathrm{a}})\frac{\partial p_{\mathrm{w}}}{\partial z} - \lambda_{\mathrm{a}}\frac{\partial p_{\mathrm{c}}}{\partial z} + \lambda_{\mathrm{w}}\rho_{\mathrm{w}}\mathrm{g} + \lambda_{\mathrm{a}}\rho_{\mathrm{a}}\mathrm{g} \end{aligned} \tag{22}$$

where v (the sum of v_{w} and v_{a}) is defined as the total velocity and λ_{w} and λ_{a} (short notations for $kk_{\mathrm{rw}}/\mu_{\mathrm{w}}$ and $kk_{\mathrm{ra}}/\mu_{\mathrm{a}}$) are the fluid mobilities. Equation (22) can be rewritten as

$$\frac{v}{\Lambda} = -\frac{\partial p_{\mathrm{a}}}{\partial z} + f_{\mathrm{w}}\rho_{\mathrm{w}}\mathrm{g}\frac{\partial h_{\mathrm{c}}}{\partial z} + \rho_{\mathrm{w}}\mathrm{g}f_{\mathrm{w}} + \rho_{\mathrm{a}}\mathrm{g} \tag{23}$$

where Λ (sum of the mobilities) is the total mobility, and f_{w} is a function of water content θ defined as

$$f_{\mathrm{w}} = \frac{\lambda_{\mathrm{w}}}{\Lambda} \tag{24}$$

Integration of Equation (24) between the water-entry face and just below the wetting front yields

$$\int_0^{zf}\frac{\mathrm{d}z}{\Lambda} = \rho_{\mathrm{w}}\mathrm{g}\int_0^{h_{\mathrm{ci}}} f_{\mathrm{w}}\mathrm{d}h_{\mathrm{c}} + \rho_{\mathrm{w}}\mathrm{g}\int_0^{zf} f_{\mathrm{w}}\mathrm{d}z + \rho_{\mathrm{a}}\mathrm{g}z_{\mathrm{f}} \tag{25}$$

Adding similarly Equations (20) and (21), one obtains

$$\frac{\partial(\theta_{\mathrm{w}} + \theta_{\mathrm{a}})}{\partial t} + \frac{\partial v}{\partial z} = \frac{\partial\phi}{\partial t} + \frac{\partial v}{\partial z} = \frac{\partial v}{\partial z} = 0 \tag{26}$$

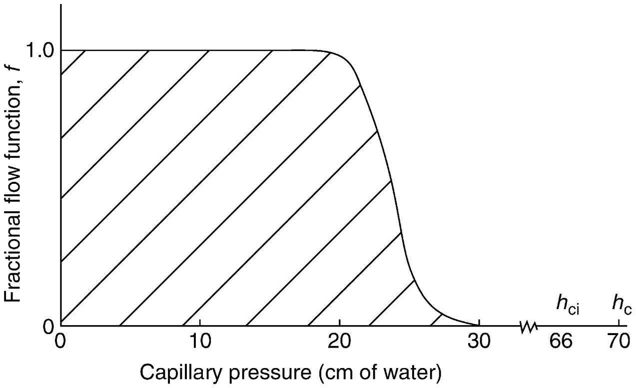


Figure W18 Fractional flow function versus capillary pressure (expressed as a water height). *Crosshatched area* expresses the effective capillary drive in centimeters of water.

since the porosity does not vary with time if the medium is undeforming and stable. Since v does not vary with z, it can be taken outside the integral sign in Equation (25) and one obtains for v the expression

$$v = \frac{\rho_{\mathrm{w}}\mathrm{g}\left(\int_0^{h_{\mathrm{ci}}} f_{\mathrm{w}}\mathrm{d}h_{\mathrm{c}} + \int_0^{zf} f_{\mathrm{w}}\mathrm{d}z\right)}{\int_0^{zf}\frac{\mathrm{d}z}{\mu_{\mathrm{w}}\Lambda_{\mathrm{r}}}} \tag{27}$$

having neglected the weight of air. Or with minor changes in notations

$$v = \frac{\overline{K}\left(H_{\mathrm{c}} + \int_0^{zf} f_{\mathrm{w}}\mathrm{d}z\right)}{\int_0^{zf}\frac{\mathrm{d}z}{\mu_{\mathrm{w}}\Lambda_{\mathrm{r}}}} \tag{28}$$

where Λ_{r} is the relative total mobility (i.e., the sum of $(k_{\mathrm{rw}}/\mu_{\mathrm{w}}) + (k_{\mathrm{ra}}/\mu_{\mathrm{a}})$, and H_{c} is the effective capillary drive defined by the relation

$$H_{\mathrm{c}} = \int_0^{h_{\mathrm{ci}}} f_{\mathrm{w}}\mathrm{d}h_{\mathrm{c}} \tag{29}$$

The relevance of Equation (28) to the problem of Green and Ampt is clearly understood if one rewrites Equation (13) in the form

$$I = \frac{\overline{K}\left(H_{\mathrm{f}} + \int_0^{zf}\mathrm{d}z\right)}{\int_0^{zf}\frac{\mathrm{d}z}{\mu_{\mathrm{w}}(1/\mu_{\mathrm{w}}+0)}} \tag{30}$$

and if one recognizes that at the water-entry face $v = I$. Indeed, if one assumes full saturation behind the wetting front in Equation (27), it transforms into

$$I = \overline{K}\left(\frac{H_{\mathrm{c}} + z_{\mathrm{f}}}{z_{\mathrm{f}}}\right) \tag{31}$$

which by comparison with Equation (13) yields the result that the wetting-front suction H_{f} is identical to the effective capillary drive H_{c}. The empirical wetting-front suction turns out to be a well-defined theoretically derivable quantity, namely,

$$H_f = H_c = \int_0^{h_{ci}} f_w \mathrm{d}h_c \tag{32}$$

Figure W18 shows a typical f_w versus h_c curve for a sand. For $h_{ci} = 66$ cm of water, H_c (surface of crosshatched area) = 24 cm.

H. J. Morel-Seytoux

Bibliography

Bouwer, H., 1964. Unsaturated flow in ground-water hydraulics. *J. Hydraul. Div., Am. Soc. Civil Eng.*, **90**(HY5): 121–144.

Childs, E.C., 1969. *The Physical Basis of Soil Water Phenomena.* New York: Wiley, 439 pp.

Green, W.H., and Ampt, C.A., 1911. Studies on soil physics. 1. Flow of air and water through soils, *J. Agric. Sci.*, **4**: 1–24.

Morel-Seytoux, H.J., 1969. Introduction to flow of immiscible liquids in porous media. In de Wiest, R., ed., *Flow Through Porous Meida.* New York: Academic Press, pp. 455–516.

Morel-Seytoux, H.J., and Khanji, J., 1974. Derivation of an equation of infiltration. *Water Resour. Res. J.*, **10**(4): 795–800.

Cross-references

Capillary Pressure
Conductivity, Hydraulic
Flow Theory
Imbibition
Infiltration
Permeability
Soil Water and Its Management
Water Budget in Soil
Water Movement

WILTING POINT

The point at which, through heat or drought, a plant loses turgidity and becomes limp or flaccid. A permanent wilting point may be defined in terms of standard test plants, as the point beyond which, the plant will not recover, when adverse conditions of heat or drought ameliorate.

WIND EROSION

Wind erosion is a serious problem in many parts of the world. It occurs where land surfaces are unprotected from the direct impact of the wind and is worse in semi-arid and arid areas (Figure W19). In these areas, vegetation cover is inadequate to protect the surface, especially when agricultural procedures of crop cultivation and grazing further reduce this cover. And losing topsoil lowers the quality and fertility of soils. For example, in the Great Plains of western North America, about 70 million ha are eroded by combined water (60%) and wind (40%) at twice the rates required for sustainable agriculture (United States Department of Agriculture, 1989). In the Sahel fringe of the Sahara, overgrazing by cattle and other processes (including natural ones) are causing increasing desertification (Bielders et al., 2000; Mainguet, 1995). Large-scale modeling

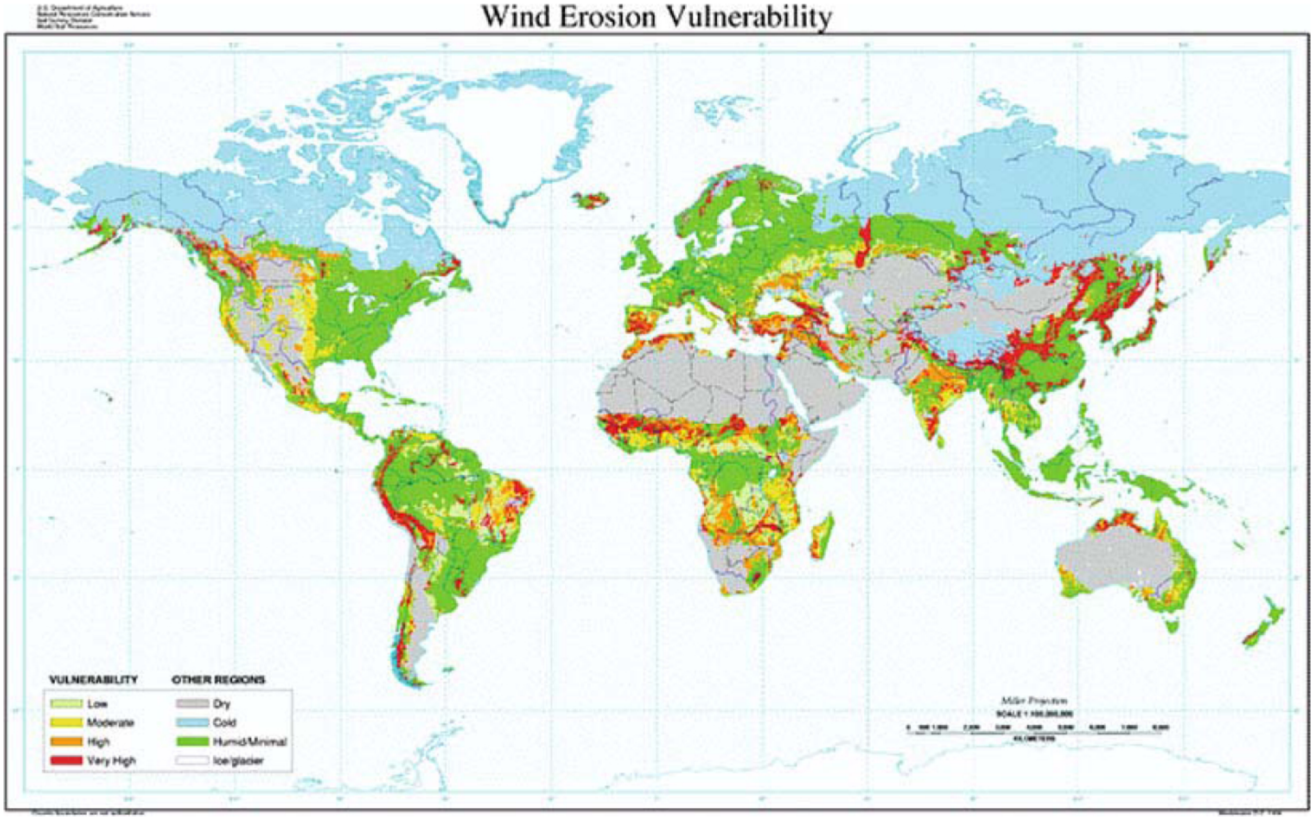


Figure W19 World wind erosion susceptibility: highest vulnerabilities are along the margins of the world's deserts. Courtesy USDA.

of wind erosion and transport are now done on a global scale, but their accuracy ultimately depends on understanding the smaller-scale processes of wind erosion and transportation (Raupach and Lu, 2004).

Process

Wind erodes by picking up particles from exposed sediment surfaces and by sandblasting solid rock with these particles. Sandblasting is an intermittent and slow process, which is relatively unimportant and will not be considered further here. Erosion of softer sediments and soils can be, however, a rapid process and is extremely important and effective. Generally, wind erosion increases as rainfall decreases and the soils become sandier (Leys, 1999).

The erosion of sediment depends on the type of material exposed and the speed of the wind (Nickling, 1994). The minimum force required to move particles of a given grain size is the threshold (or critical) shear force (τ). Because of the problems of measuring this surface shear force directly, it is more usual to use the threshold velocity (u_t) or the threshold shear velocity (u_t^*) which can be calculated or measured from wind velocity profiles. The fluid threshold is the wind velocity required to erode surface grains; while the impact threshold is the wind velocity required for sand grains already in the wind to impact and erode surface grains (Figure W20). Below a diameter of about 0.06 mm, grains form a smooth surface, which requires greater wind velocity to remove than sand, which forms small protuberances that initiate erosive microvortices. So the sand fluid threshold is higher, though sand is easily eroded by impacting grains. Once erosion starts, it is the bombardment by entrained particles that keeps sediment moving, so that less overall energy is needed at lower wind velocity to keep the process going, and the dynamic threshold velocity is about 80% of the static threshold. Also, the system can end up saturated with sand so that only transport, without erosion occurs. These concepts apply to uniform well-sorted grain sizes (Livingstone and Warren, 1996, chapter 2). More poorly sorted sediments have a greater separation between the start of movement (fluid threshold) and overall movement (impact threshold) (Goossens and Gross, 2002; Nickling, 1988). Particles move as creep or bed load (by being trundled along the surface), by saltation (where particles are splashed up by impacts and then fall back to rebound again), or in suspension (where fluid turbulence keeps the particles 'floating' in the main windflow) (Figure W21). All other factors being equal, the grain sizes decreases from creep through saltation and into suspension. Moisture content greatly reduces wind erosion. A crude estimate is that soils must dry to 4% water content (when their pores are about 15% filled) before erosion starts. Vegetation restricts the movement of sediment either by trapping already entrained material of by reducing the wind velocity at the surface, though stresses are higher at the top of the vegetation and the gustiness of the wind can be increased.

The transport rate (q) of sand can be estimated from (Namikas and Sherman, 1997):

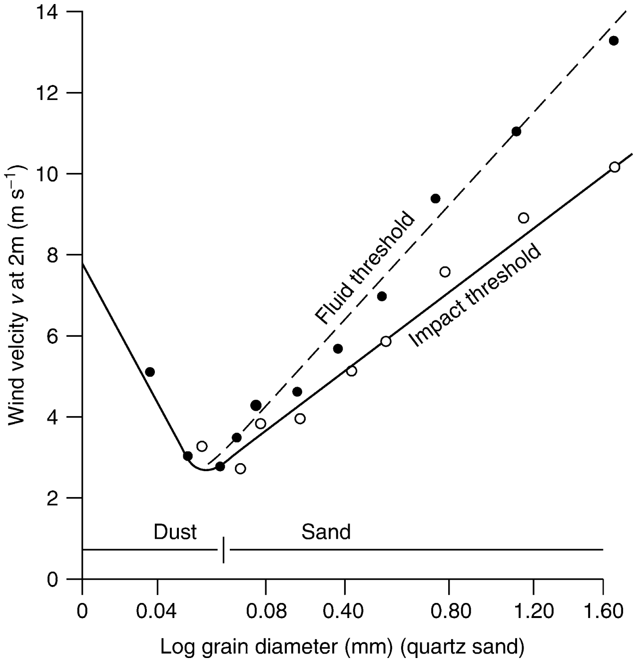


Figure W20 Fluid and impact threshold velocities for sand and dust (dust includes silt and clay) (from Livingstone and Warren, 1996, Figure 2.6).

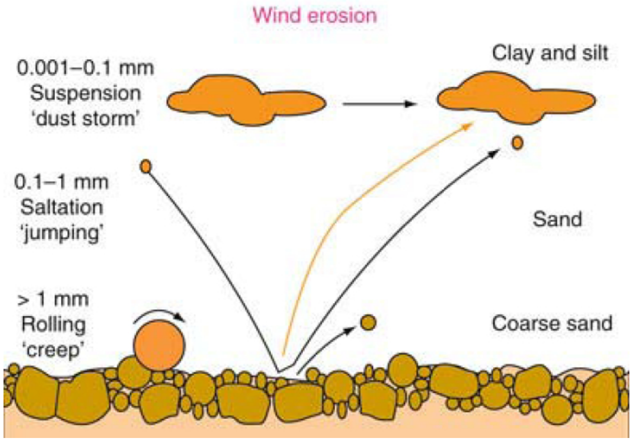


Figure W21 Processes of wind erosion and transportation: 'creep', saltation and suspension.

Figure W22 Angular pebble lag after sand has been removed: Gilf Kebir Plateau, SW Egypt. Camera cover is 5 cm diameter.

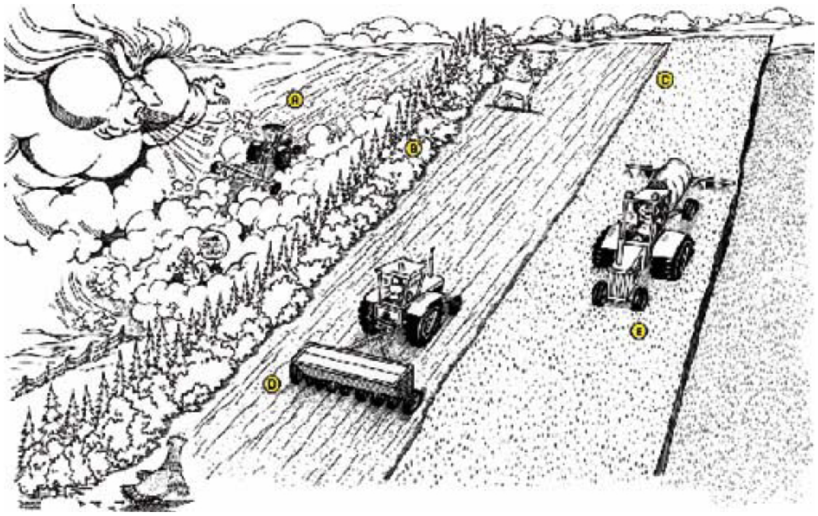


Figure W23 Wind erosion prevention (from SWCS): (*A*) too much tillage breaks down soils and plant residues into small particles that can be removed by the wind; (*B*) tree and shrub shelter belts reduce wind action at the surface of adjacent fields; (*C*) strip planting perpendicular to the prevailing wind reduces erosion even if alternate strips are left fallow; (*D*) leaving plant residues (straw, dead plant) reduces wind velocity at the surface; (*E*) killing weeds on fallow fields with weedkiller and leaving residue prevents wind erosion.

$$q = \mathrm{K}\frac{\rho}{\mathrm{g}}(u^* - u_t^*)(u^* + u_t^*)^2$$

where K is a dimensionless constant (2.78 from Kawamura's wind tunnel experiments), ρ is air density, g is gravitational acceleration.

But the predictions of various and transport formulae vary greatly and in any case few surfaces outside sand dunes consist only of sand. For less uniform surfaces, various attempts at quantifying wind erosion have been made – none of them very satisfactory. A further problem is that an armored stony lag layer eventually forms on most sediments and reduces wind erosion to zero (Figure W22). Such lag layers are usually disturbed from time to time by desert floods, which sporadically occur even in the most arid regions, exposing finer sediment for reworking. Estimates of wind erosion from models are often much more than actually takes place (Hagen, 2004; Warren, 2000). A typical formula used to calculate wind erosion of fields is of the type:

$$E = f(I, K, C, L, V)$$

where E is erosion in t $\mathrm{ha}^{-1}\ \mathrm{yr}^{-1}$; I is soil erodability (from 0 for stones up to 300 for dust), K is surface roughness ranging from 0.5 (rough) to 1, C is climate (wind speed and moisture), L is field size from 0 (small, protected) to 1 (open), and V is equivalent quantity of vegetative cover, including crop residues such as standing wheat stubbles (weight × 6). Such estimates from formulae, however, need careful checking and validation with actual field measurements (Funk et al., 2004; Zoback et al., 2003).

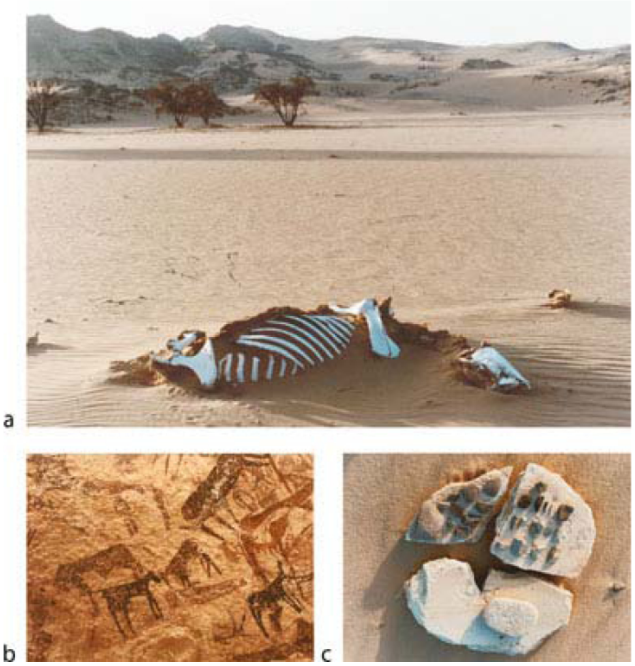


Figure W24 Jebel Uweinat, NW Sudan; (a) present dead and wind-scoured uninhabited landscape: between about 8000 and 5000 years ago the climate was wet enough for various hunting, cattle grazing and grain-growing cultures to live in the area as shown by cave paintings (b) and remains of grain grinding querns and flint implements (c).

Mitigation

Things that affect the amount of wind erosion include soil erodability, roughness, climate and weather, the unsheltered distance across a field along the prevailing wind erosion direction and residue or plant cover (Hayes and Fenster, 1980). Reducing wind erosion can be done in three ways (Figure W23):

- First, reduce the wind velocity at the soil surface. This can be done with windbreaks, crop residues, cover crops, and strip cropping.
- Second, trap soil particles once they have started moving. This can be done with ridging or roughening the soil surface.

- Third, increase the size of soil aggregates, which means that it takes a stronger wind to move the soil. This can be done by using crop rotations that include grasses and legumes, by growing high-residue crops and returning crop residues to the soil, and by emergency tillage, which creates clods on the soil surface.

Though climatic data is often limited in semi-arid and arid areas (Lynch and Edwards, 1980), obtaining accurate estimates and models of wind erosion is becoming increasingly important. With the current trend towards global warming, the threshold of landscape stability can easily be crossed in the fertile plains belts of both North America and Eurasia, even under present climatic regimes (Arbogast, 1996). Desertification is a historical and continuing problem in Africa (Figure W24) and Asia: it may soon become even more important in North America and Europe.

Michael Brookfield

Bibliography

Arbogast, A.F., 1996. Stratigraphic evidence for late-Holocene aeolian sand mobilization and soil formation in south-central Kansas, U.S.A. *J. Arid Environ.*, **34**: 403–414.
Bielders, C.L., Alvey, S., and Cronin, N., 2001. Wind erosion: the perspectives of grass-roots communities in the Sahel. *Land Degrad. Devel.*, **12**: 57–70.
Funk, R., Skidmore, E.L., and Hagen, L.J., 2004. Comparison of wind erosion measurements in Germany with simulated soil losses by WEPS. *Environ. Model. Softw.*, **19**: 177–183.
Goossens, D., and Gross, J., 2002. Similarities and dissimilarities between the dynamics of sand and dust during wind erosion of loamy sandy soils. *Catena*, **47**: 269–289.
Hagen, L.J., 2004. Evaluation of the wind erosion prediction system (WEPS) erosion submodel on cropland fields. *Environ. Model. Softw.*, **19**: 171–176.
Hayes, W.A., and Fenster, C.R., 1980. Understanding wind erosion and its control. University of Nebraska-Lincoln Extension Report G79-474-A.
Leys, J., 1999. Wind erosion on agricultural land. In Goudie, A.S., Livingstone, I., and Stokes, S., eds., *Aeolian Environments, Sediments and Landforms.* Chichester: Wiley, pp. 143–166.
Livingstone, I., and Warren, A., 1996. *Aeolian Geomorphology: An Introduction.* Singapore: Addison-Wesley, 211 pp.
Lynch, L.G., and Edwards, K., 1980. The analysis of limited climatic data with reference to wind erosion risk in semi-arid to arid regions. *Agric. Meteorol.*, **21**: 37–47.
Mainguet, M., 1995. *Homme et la Sécheresse.* Paris: Masson, 335 pp.
Namikas, S., and Shearman, D.J., 1997. Predicting aeolian transport: revisiting the White model. *Earth Surface Processes. Landforms*, **22**: 601–604.
Nickling, W.G., 1988. The initiation of particle movement by wind. *Sedimentology*, **35**: 499–511.
Nickling, W.G., 1994. Aeolian sediment transport and deposition. In Pye, K., ed., *Sediment Transport and Depositional Processes.* London: Blackwell, pp. 293–350.
Raupach, M.R., and Lu, H., 2004. Representation of land-surface processes in aeolian transport models. *Environ. Model. Softw.*, **19**: 93–112.
SWCS (Alberta Chapter), 1997. Wind erosion prevention poster (online at http://www.soils.rr.ualberta.ca/SoilPosters/fortex.htm).
United States Department of Agriculture, 1989. The second RCA appraisal: soil, water, and related resources on non-federal land in the United States. Washington, D.C.: U.S. Government Printing Office.
Warren, A. (ed.), 2000. Wind erosion on European light soils (WEELS). Final report to the European Union Commission, Brussels.
Zoback, T.M., Sterk, G., Funk, R., Rajot, J.L., Stout, J.E., and van Pelt, R.S., 2003. Measurement and data analysis methods for field-scale wind erosion studies and model validation. *Earth Surface Processes. Landforms*, **28**: 1163–1188.

Cross-references

Conservation
Erosion
Mechanical Weathering
Micrometeorology

WIND EROSION EQUATION

An equation for predicting E, the amount of soil erosion from a given area in a given time period, due to wind:

$$E = I\,K\,C\,L\,V$$

I is the soil erodability factor in mass/area/unit time (usually a year) for a flat bare soil
K is the ridge roughness factor
C is a factor representing the influence of climate
L is a function of the fetch length
V is the vegetative factor

The Revised Wind Erosion Equation (RWEQ) makes annual or period estimates of wind erosion based on a single event wind erosion model that includes factors for wind and rainfall, soil roughness, the erodible fraction of soil, crusting, and surface residues (see also Figure W25).

Cross-references

Erosion
Wind Erosion

WINDTHROW

The uprooting and blowing down of trees by the wind. Also used as a descriptor of the soil thrown up in this event.

WOODLAND

A wooded region or piece of ground. Also the name of a culture that existed in eastern North America between approximately 1000 B.C. and A.D. 1000, characterized by agriculture, hunting, burial mounds, and a distinctive style of pottery.

Cross-reference

Biomes and their Soils

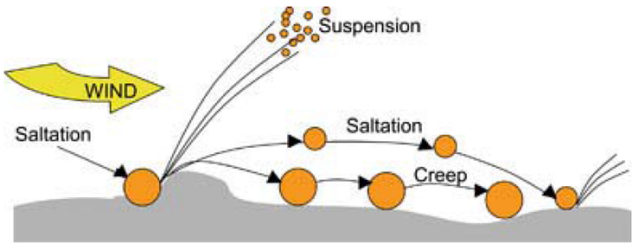


Figure W25 Wind erosion.

Y

YIELD

The amount of a crop or other biological product obtained from a particular tract such as a farm or specific field, expressed in terms of mass per unit area (kg ha^{-1} for example).

Bibliography

Lobell. D.B., and Field, C.B., 2007. Global scale climate–crop yield relationships and the impacts of recent warming. *Environ. Res. Lett*. 2: 014002.

Rosenzweig, C., Iglesias, A., Yang, X.B., Epstein, P.R., and Chivian, E., 2000. *Climate Change and U.S. Agriculture: The Impacts of Warming and Extreme Weather Events on Productivity, Plant Diseases, and Pests.* Cambridge, MA: Center for Health and the Global Environment, Harvard Medical School, 46 pp.

Cross-references

Fertilizers, Inorganic
Fertilizers, Organic

Z

ZETA POTENTIAL

A charged colloidal particle suspended in an aqueous solution develops an electrical double layer that is dependent upon solution and particle characteristics. Imposition of an electric field in a suspension allows the visualization of the particle charge as these materials migrate towards the electrodes. Figure Z1 shows a schematic diagram of a negatively charged particle suspended in electrolyte solution. The particle is migrating in response to an imposed electric field. As this particle migrates the highly structured water and ions near the particle moves with the particle.

Zeta potential (ζ) is defined as the average potential (ψ) in the electrical double layer at the zone of shear between a mobile charged particle and the immobile liquid phase in which a particle is suspended. In colloidal systems, charge arises from ionization of surface groups, from adsorption of surface-active materials, from permanent charge associated with crystal structure, or from a combination of these mechanisms. Particle charge is satisfied by ions of opposite sign (counter ions), which are attracted to the charged interface between the particle and the solution phase.

Historical introduction

Electrokinetic behavior, especially electrophoretic mobility and zeta potential measurements, have been an important theoretical and applied tool in colloid and interface science since the late nineteenth century. Flocculation and dispersion of colloids (colloidal stability), ion exchange, adsorption phenomena and models of ion and potential distribution at the charged interface are rooted in the research of early colloidal scientists, many of whom used electrokinetic techniques. In the classic 1952 publication *Colloid Science*, Kruyt (1952) presented historical aspects of colloidal systems research. According to his account, in the late nineteenth century and early twentieth century, "*attention was drawn to the fact that colloids moved in an electrical field*" and the "*stability of these sols is closely connected with their electrophoretic mobility.*" Early developments in electrokinetic research were also discussed by Sennett and Oliver (1965). They reported that in 1808 Reuss observed what is now called electro-osmosis. Additional experimental work with charged colloidal particles appeared in a number of publications during the nineteenth century (Sennett and Oliver, 1965). These included the studies of Dorn published in 1880 on sedimentation potential, and colloid stability investigations of Schultz published in 1882 and 1883. Hardy's work on colloid stability appeared in 1900 and Perrin's extensive studies of electro-osmotic flow and streaming potential were published in 1904. In 1892 Linder and Picton observed the migration of sols in an electrical field, indicating that they were charged.

The theory of the electrical double layer dates from the work of Helmholtz published in 1879 (Sennett and Oliver, 1965; Wiklander, 1964). In the early part of the twentieth century Gouy (1910, cited in Overbeek, 1952) and Chapman in (1913, cited in Overbeek, 1952) independently proposed a theoretical treatment of the plane-electrified interface. Their work gave rise to the Gouy-Chapman model. Interestingly, this treatment preceded the similar theory of Debye and Hückel for electrolyte solutions which was published in 1923 (Overbeek, 1952). A rigorous quantitative treatment of the electrical double layer presents some difficulties that have not been completely resolved, however useful approximations have been advanced (Carnie and Torrie, 1984; Sennett and Oliver, 1965).

Work on zeta potential of soil colloids predated our information on the structure of layer silicate clay and was an important tool used to describe soil behavior. Early work by Mattson (1928, 1929, 1931) examined dispersion exchange and flocculation of sols and gels of iron, aluminum and silicates and related changes in zeta potential to differences in clay composition. Later, Jenny and Reitemeier (1935) showed that the energy of adsorption determined the potential of the particle and the stability of the suspension. This stability was related to the zeta potential. Since these early soils investigations, the concept of zeta potential, electrophoretic mobility and the point of zero charge have been an indispensable aspect of soil and colloidal chemistry investigations in spite of the fact that the relationship between electrophoretic mobility and zeta potential is not adequately worked out for all situations.

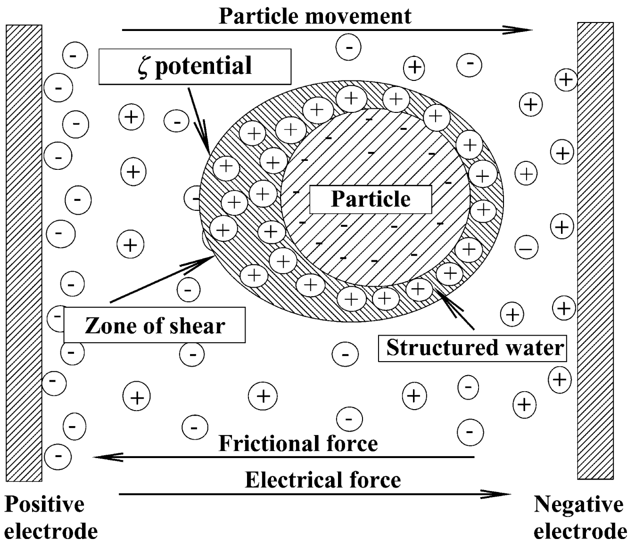


Figure Z1 A representation of a negatively charge colloid suspended in electrolyte solution migrating toward the positive electrode. The zone of rapidly changing viscosity defines the shear zone and the location of the zeta potential.

Concepts

The Gouy-Chapman model predicts an approximately exponential decay of potential with distance away from the interface as thermal and electrical energies interact. Similarly, counter-ion concentration decreases in nearly exponential fashion away from the particle. The Gouy-Chapman approach assumed point charges interacting with a uniformly charged, infinitely flat plate. The field is described by Poisson's Equation and ion distribution in the electrical field follows the Boltzmann distribution law. Modifications by Stern (Stern, 1924 in Shaw, 1969) and Grahame (1947) incorporated a layer (Stern Layer) of strongly adsorbed ions of finite size similar to a molecular capacitor. The resulting Stern-Grahame model gives a representation as shown in Figure Z2a. In this model, sometimes referred to as the Gouy-Chapman-Grahame-Stern or GCGS Model, the charge at the surface is distributed in two distinct regions. Next to the surface, counter ions are strongly adsorbed. In the Stern layer ions are specifically adsorbed and the electrical potential decreases linearly (Overbeek, 1952). Potential at the outer edge of the Stern layer is called the Stern potential (ψ_δ). Outside of the Stern layer, ion distribution follows the Gouy and Chapman model. In this diffuse layer, potential (ψ_D) decreases in a nearly exponential fashion. Some models of the double layer include a layer of hydrated ions that have been termed the Outer Helmholtz

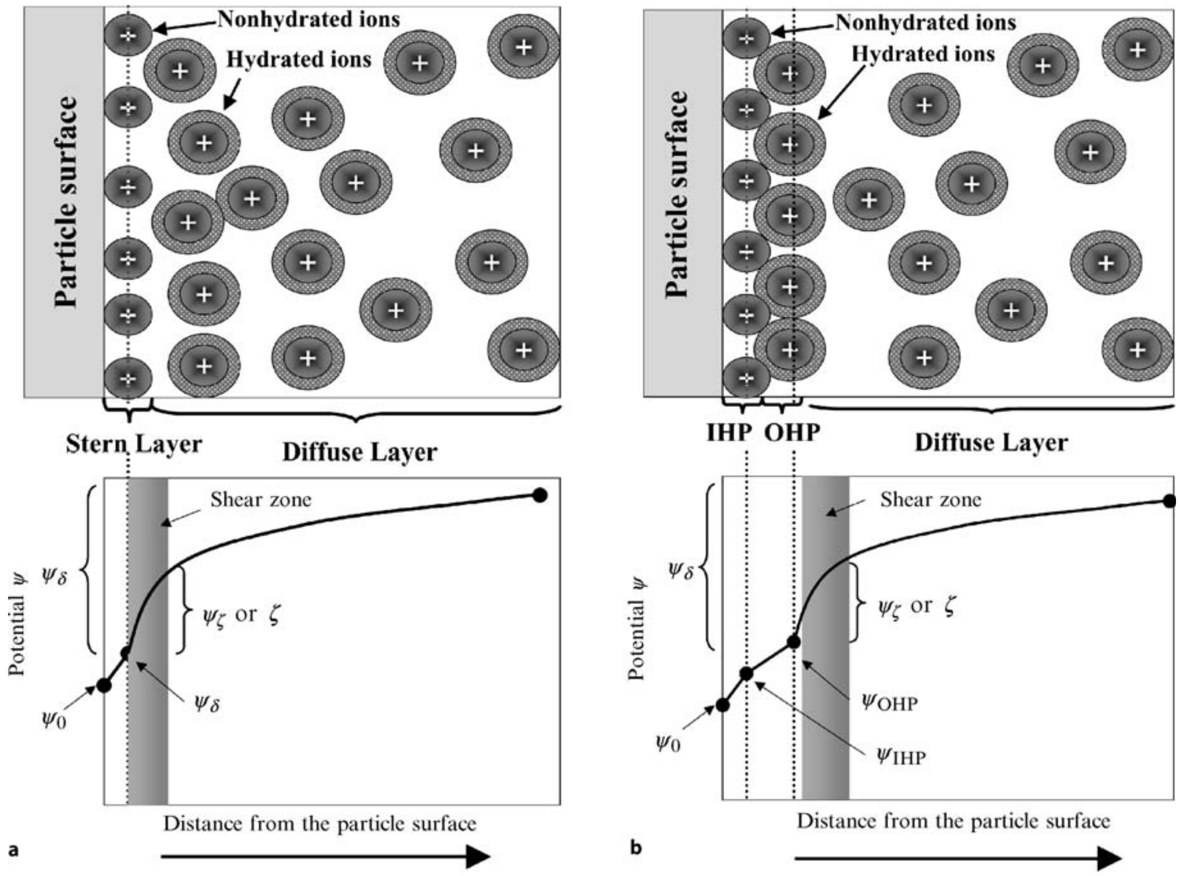


Figure Z2 A generalized representation of a charged particle (infinite flat plate) and the spatial location of various potentials and the shear plane normal to the particle for; (**a**) A representation of the Stern model; (**b**) a model including an inner and outer Helmholtz layers at the solid-solution interface.

Plane (OHP) (Hunter, 1981). A slightly more complex model defines both an inner and outer Helmholtz plane (IHP and OHP) that are the plane of closest approach for non-hydrated ions (~0.1–0.2 nm) and ions that retain their primary hydration shell (~0.6 nm) (Figure Z2b) (Hunter, 1981; Attard et al., 2000). Potential drop across the Stern and or Helmholtz layers is considered to be linear and the potential outside of these layers is again described by the Gouy-Chapman model.

As an electrical potential is applied charged particles migrate in the electrical field. Ions and water in the Stern layer or Helmholtz layers are thought to move with the particle while those in the diffuse layer move with the liquid phase. Therefore the shear plane and location of the zeta potential (ψ_ζ or ζ) is assumed to be in the diffuse layer outside of or adjacent to the Stern layer or outer Helmoltz plane (Hunter, 1981).

More recently, a number of surface complexation models have been advanced to describe adsorption on charged particle surfaces (Hayes et al., 1991). In addition sophisticated statistical mechanical treatments have been applied to the electrified interface that include electrostatic correlations and excluded volumes corrections (Attard et al., 2000; Martín-Molina et al., 2003). The newer models refine the concepts and ideas proposed in earlier formulations and provide important corrections to the GCSG model, but more refined calculations still do not provide an exact location for the shear plane. None of the potentials depicted in Figure Z2 can be determined by direct experimentation. However, zeta potential (and others) can be inferred from electrokinetic measurements of particle suspensions.

Electrophoretic mobility and zeta potential

Electrophoretic mobility (EM) measurements are the most common electrokinetic technique used to collect data for the calculation of zeta potential (Harsh and Xu, 1990; Hunter, 1981; Shaw, 1969). Less commonly, techniques such as streaming potential and moving boundary methods have been used to estimate particle charge and potential (Bousse et al., 1991; Shaw, 1969). Electroacoustic (Miller and Berg, 1991) and plane interface techniques (Sasaki et al., 1991) have also been reported. Light scattering methods including Laser Doppler electrophoresis offers advantages over the conventional methods (Goff and Luner, 1984; McFadyen, 1987; Thompson, 1992, Martín-Molina et al., 2003).

Electrophoretic measurements determine the velocity of particles in relation to an applied electrical gradient. As the electrical potential of the particle increases in a uniform field, particle velocity or electrophoretic mobility (EM) increases. Ions located between the particle surface and the “slipping plane” within the zone of immobile water migrate with the particle (van Olphen, 1977). The potential at this “slipping plane” or “shear plane” is the appropriate average potential which determines the particle mobility. As the particle moves in relation to an applied field, frictional forces retard the migration resulting in a zero net force and a constant velocity. As depicted in Figure Z1, a spherical particle with charge (Q) uniformly distributed over the surface and immersed in an aqueous salt solution with a uniform electric field (E) will travel with a velocity of v_e determined by the balance between the electrical forces ($f_e = QE$) and the Stokes frictional forces exerted by the liquid ($f_v = 6\pi v_e a\eta$). Equating these forces gives a first approximation of particle velocity (Hunter, 1981; Stigter, 1975):

$$QE - g\pi a v_e = 0$$

or

$$v_e = \frac{QE}{6\pi\eta a}$$

In more detailed examinations of the phenomena, additional forces, which oppose the electrical force, must be considered (c.f., Harsh and Xu, 1990; Hunter, 1981; Overbeek, 1952; Shaw, 1969; van Olphen, 1977). An electrophoretic retardation arises because the counter ions and water in the ion atmosphere are attracted in the direction opposite to particle velocity. The applied field constantly distorts the diffuse layer ions and the distortion and reformation of the diffuse layer ions results in a relaxation force (Harsh and Xu, 1990; Hunter, 1981; Overbeek, 1952; Shaw, 1969; Stigter, 1975; van Olphen, 1977). If these forces are taken into consideration the equation proposed by Henry (1931, reported in Hunter, 1981) gives:

$$u_e = \frac{2\varepsilon_0 D\zeta}{3\eta} f(\kappa, a)$$

In this equation ε_0 is the permittivity of a vacuum, D is the dielectric constant of liquid water, u_e is the electrophoretic mobility $= v_e/E$ where v_e is the measured velocity and E is the applied field, and η is the viscosity of liquid water.

The Debye-Hückel term, κ is a convenience parameter, which contains an electrolyte concentration term. The particle radius is a. Kappa has units of m^{-1} and the reciprocal $(1/\kappa)$ is thought of as the thickness of the double layer surrounding the particle. Since κ is related to ionic strength and a is particle radius, the formulation in Equation (2) shows that both salt content and particle size affect the calculation of zeta potential from electrophoretic mobility.

If the particle is small relative to the size of the double layer $f(\kappa,a) = 1$, then resulting equation is:

$$u_e = \frac{2\varepsilon_0 D\zeta}{3\eta}$$

If the particle is large relative to the double layer distance, $f(\kappa,a) = 1.5$ and the more familiar Smoluchowski Equation results (Harsh and Xu, 1990; Hunter, 1981)

$$u_e = \frac{\varepsilon_0 D\zeta}{\eta}$$

For intermediate values of κa, several alternative solutions are available (cf. Hunter, 1981; O’Brien and White, 1978). Hunter (1981) also suggests that particle conduction can affect results; however, he concludes that except for metallic dispersions particles should be treated as insulators unless there is evidence to the contrary.

Discussion

As can be imagined, the interplay of the liquid, ions and molecules at the particle interface is complex and a number of assumptions about the interfacial system must be made to calculate the zeta potential or other electrical properties of the colloid from EM or other electrokinetic techniques (Harsh and Xu, 1990). Sposito (1984) points out that the application of Equation (3) or (4) implies that ζ and ψ_x are solutions of the Poisson Equation that contains the dielectric constant of the media. If the charge at the shear plane is to be calculated, the assumption of the Poisson-Boltzmann distribution must be considered (Harsh and Xu, 1990; Sposito, 1984). In the classical double layer theory, the particle is a flat infinite plate, ions are point charges without volume, the liquid permittivity is assumed to be constant everywhere, and only long range electrical forces act on the ions (Harsh and Xu, 1990). Many of these assumptions are not realistic, however when considered *in toto*, corrections for several factors tend to compensate and the diffuse double layer model is a reasonable approach for low potential and ionic strengths, particularly in the diffuse layer outside of the Stern plane (Bolt, 1955; Shaw, 1969; Overbeek, 1952; Hunter, 1981). As Hunter (1981) points out, at concentrations $<10^{-2}$ M for 1:1 electrolytes with potentials $|\psi_D| < 100$ mV the corrections are less than 2%. The reader is referred to the discussions of Harsh and Xu (1990), Hunter (1981) and O'Brien and White (1978) for additional refinements for systems with varying particle size, shape, and electrolyte concentrations. A statistical mechanical descriptions and comparison to the classical double layer has been presented by Carnie and Torrie (1984) and others (Attard et al., 2000; Martín-Molina, 2003).

In spite of many refinements in our models and theories, the location of the shear plane is not known. Dzombak and Morel (1990) suggest that the location of the shear plane changes as ionic strength and particle charge increase. Differences in the location of the shear plane are implicit in the diagram of charge distribution for different surface complexation models (cf. Figure 2 in Hayes et al., 1991). Harsh and Xu (1990) also mention the possibility of variation in the position of the shear plane as does Shaw (1969).

This long-standing problem lead van Olphen (1977) to suggest that it is advisable to report electrophoretic results in terms of observed mobilities rather than zeta potentials calculated from simpler formulas. In clay suspensions, Delgado et al. (1986) found that the more elaborate technique of O'Brien and White (1978) gave results similar to those derived for the Smoluchowski Equation at electrolyte concentrations above 1 and 10 mM for $Ca(NO_3)_2$ and NaCl respectively. At lower electrolyte concentrations, calculated zeta potential varied between the two approaches by a factor of two in $Ca(NO_3)_2$ suspensions. Harsh and Xu (1990) presented evidence that for Li-saturated Wyoming bentonite the Smoluchowski Equation and O'Brien and White's approach converge as electrolyte concentration increases. Calculated charge density at the shear plane was also similar at higher ionic strengths.

In addition, it must be remembered that EM and zeta potential are macroscopic property of the particle. Zeta potential is the average potential of the particle at the shear plane and imparts no information about the distribution of positive and negative charge. Charge distribution characteristics must be derived from independent measurements. Clay particles may also have both permanent and pH-dependent charge on the planar surface and edges respectively that react differently to electrolyte and pH changes.

With these caveats in mind, zeta potential and electrokinetic phenomena of charge particles have been a very important tool for the elucidation of reactions and mechanisms at the particle-solution interface. Zeta potential has been very successful at estimating coagulation rates of colloidal suspensions (Wiese and Healy, 1975 as cited in Davis and Kent, 1990). Changes in EM and hence zeta potential have been used extensively to determine the point of zero charge (P2C), charge reversal, changes in potential with pH, ionic strength, and the influence of ion and molecular adsorption on expressed charge and potential. Since the net charge on the particle and the electrical field vanish at the pzc, many of the assumptions and physical limitations confounding the calculation of zeta potential from electrophoretic mobility measurements also vanish. The interested reader is referred to any of the cited references for a more extended discussion of the theory and application of electrokinetic properties to soil colloids.

Note: The term zeta potential occurs in a different usage in J. Willard Gibbs' classic paper *On the equilibrium of heterogeneous substances* (1876–1878). We now call his form of the term the Gibbs Free Energy.

R. J. Zasoski

Bibliography

Attard, P., Antelmi, D., and Larson, I., 2000. Comparison of the zeta potential with the diffuse layer potential from charge titration. *Langmuir*, **16**: 1542–1552.

Bolt, G.N., 1955. Analysis of the validity of the Gouy–Chapman theory of the electric double layer. *J. Colloid Sci.*, **10**: 206–218.

Bousse, L., Mostarshed, S., van der Shoot, B., Rooij, N.F., and Göpel, W., 1991. Zeta potential measurements of Ta_2O_5 and SiO_2 thin films. *J. Colloid. Interface Sci.*, **147**: 22–32.

Carnie, S.L., and Torrie, G.M., 1984. The statistical mechanics of the electrical double layer. *Adv. Chem. Phys.*, **56**: 141–253.

Davis, J.A., and Kent, D.B., 1990. Surface complex modeling in aqueous geochemistry, In Hochella, Jr., M.F., and White, A.F., eds., *Rev. Mineral. 23: Mineral–Water Interface Chemistry.* Washington, DC. Mineralogical Society of America, Chapter 5. pp. 177–260.

Delgado, A., Gonzalez-Caballero, F., and Bruque, J.M., 1986. On the zeta potential and surface charge density of montmorillonite in aqueous electrolyte solutions. *J. Colloid. Interface Sci.*, **113**: 203–211.

Dzombak, D.A., and Morel, F.M.M., 1990. *Surface Complex Modeling, Hydrous Ferric Oxide.* New York: Wiley.

Goff, J.R., and Luner, P., 1984. Measurement of colloid mobility by laser Doppler electrophoresis: the effect of salt concentration on particle mobility. *J. Colloid Interface Sci.*, **99**: 468–483.

Grahame, D.C., 1947. The electrical double layer and the theory of electrocapillarity. *Chem. Rev.*, **41**: 441–501.

Harsh, J.B., and Xu, S., 1990. Microelectrophoresis applied to the surface chemistry of clay minerals. *Adv. Soil Sci.*, **14**: 131–165.

Hayes, K.F., Redden, G., Ela, W., Leckie, J.O., 1991. Surface complexation models: an evaluation of model parameter estimation using FITEQL and oxide mineral titration data. *J. Colloid Interface Sci.*, **142**: 448–469.

Hunter, R.J., 1981. *Zeta Potential in Colloid Science. Principles and Applications.* New York: Academic Press, p. 386.

Jenny, H., and Reitemeier, R.F., 1935. Ionic exchange in relation to the stability of colloidal systems. *J. Phys. Chem.*, **39**: 593–604.

Kruyt, H.R., 1952. General introduction, Chapter I. In Kruyt, H.R., ed., *Colloid Science.* Amsterdam, The Netherlands. Elsevier, pp. 1–57.

Martín-Molina, A., Quesada-Pérez, M., Galisteo-González, F., and Hidalgo-Álvarez, 2003. Looking into overcharging in model colloids through electrophoresis: asymmetric electrolytes. *J. Chem. Phys.* **118**: 4183–4189.

Mattson, S., 1928. The electrokinetic and chemical behavior of the alumino-silicates. *Soil Sci.*, **25**: 289–311.

Mattson, S., 1929. The laws of soil colloidal behavior: II. Cataphoresis, flocculation and dispersion. *Soil Sci.*, **28**: 373–409.

Mattson, S., 1931. The laws of colloidal behavior: VI. Amphoteric behavior. *Soil Sci.*, **32**: 343–365.

McFadyen, P., 1987. Electrophoretic mobility and zeta potential of colloidal particles. *Am. Lab.*, **Apr**: 64–75.

Miller, M.P., and Berg, J.C., 1991. A comparison of electroacoustic and microelectrophoretic zeta potential data for titania in the absence and presence of a poly(vinyl alcohol) adlayer. *Colloid Surface*, **59**: 119–128.

O'Brien, R.W., and White, L.R., 1978. Electrophoretic mobility of a spherical colloidal particle. *J. Chem Soc. Faraday Trans. II.*, **74**: 1607–1627.

van Olphen, H., 1977. *An Introduction to Clay Colloidal Chemistry*, 2nd edn. New York: Wiley.

Overbeek, J.Th.G., 1952. Electrokinetic phenomena, Chapter V. In Kruyt, H.R., ed., *Colloid Science.* Amsterdam, The Netherlands: Elsevier, pp. 194–244.

Sasaki, H., Muramatsu, A., Arakatsu, H., and Usui, S., 1991. ζ potential measurement by means of the plane interface technique. *J. Colloid Interface Sci.*, **142**: 266–271.

Sennett, P., and Oliver, J.P., 1965. Colloidal dispersions electrokinetic effects and the concept of zeta potential. In Ross, S., ed., *The Chemistry and Physics of Interfaces.* Washington, DC: ACS.

Shaw, D.J., 1969. *Electrophoresis.* New York: Academic Press.

Sposito, G., 1984. *The Surface Chemistry of Soils.* New York: Oxford University Press.

Stigter, D., 1975. Electrophoresis, Chapter 20. In van Olphen, H., and Mysels, K.J., eds., *Physical Chemistry: Enriching Topics from Colloid and Surface Science.* La Jolla, CA: Theorex, pp. 293–307.

Thompson, R.G., 1992. Practical zeta potential determination using electrophoretic light scattering. *Am. Lab.*, **Aug**: 48–53.

Wiklander, L., 1964. Cation and anion exchange phenomena, Chapter 4. In Bear, F.E., ed., *Chemistry of the Soil*, 2nd edn. New York: Rehinhold Publishing Company, pp. 163–205.

ZONAL SOIL

See *Order*.

ZONE

Word applied to a large geographical region defined in terms of some special quality. Climate is a common property used for this purpose, and has been employed to delineate a total of five zones or belts that encircle the globe latitudinally. These are: the Frigid (frozen or cold) Zones encircling the poles, the Torrid (burning or hot) Zone between the tropics of Cancer and Capricorn, and the Temperate Zones, north and south, between Frigid and Torrid Zones.

Author Index

Subject Index