Selection is local since there is not an optimal growth rate in the sense that it pays to have a high reproductive potential in the northern gyre under low population densities. The offspring of such a population are inevitably at a disadvantage, however, when advected into the southern oligotrophic reaches of the gyre. Since the resulting genetic and physiological attributes at a location depend upon the past history of all of the subpopulations contributing to the interaction at a given time, this sort of simulation becomes computationally impossible in a Eulerian frame. The population distributions in Figure 4, done in a Lagrangian simulation, takes only an hour on a laptop computer. The details of a suite of such simulations are currently being compared to population density and gene sequences.

## Conclusions

The use of Lagrangian particle-following simulations in modeling population dynamics allows several advantages over Eularian fixed-grid calculations. For simple models the advantage is that the population equations can be simply integrated in time. As new techniques for tracking fluid parcels and therefore planktonic trajectories or individual large pelagic fish or whales become more available, models using real trajectories will become possible. The other advantage that direct Lagrangian simulation of turbulent dispersal of organisms has is that it overcomes the problems that advection/diffusion schemes have with population densities at large distances from their source. Finally, the largest promise in Lagrangian simulations is their use in models that explicitly treat the demographic traits of populations. With the ever-increasing realism in physical models of the marine environment and Lagrangian population models, new insights into marine population dynamics are possible.

## See also

Plankton Viruses. Population Dynamics Models.

## **Further Reading**

- Bucklin A, LaJeunesse TC, Curry E, Wallinga J and Garrison K (1996) Molecular genetic diversity of the copepod, *Nannocalanus minor*: genetic evidence of species and population structure in the N. Atlantic Ocean. *Journal of Marine Research* 54: 285–310.
- Carlotti F (1996) A realistic physical-biological model for *Calanus finmarchicus* in the North Atlantic. A conceptual approach. *Ophelia* 44: 47–58.
- Carlotti F and Wolf KU (1998) A Lagrangian ensemble model of *Calanus finmarchicus* coupled with a 1-D ecosystem model. *Fishers and Oceanography* 7(3/4): 191–204.
- Cowen RK, Lwiza KMM, Sponaugle S, Paris CB and Olson DB (2000) Connectivity of marine populations: Open or closed? *Science* 287: 857–859.
- Flierl G, Grünbaum D, Levin S and Olson DB (1999) From individuals to aggregation: the interplay between behavior and physics. *Journal of Theoretical Biology* 196: 397-454.
- Hoffmann EE, Halstrom KS, Moisan JR, Haidvogel DB and Mackas DL (1991) Use of simulated drifter tracks to investigate general transport patterns and residence times in the coastal transition zone. *Journal of Geophysical Research* 96: 15041–15052.
- Metz JAJ and Diekmann O (eds) (1986) *The Dynamics of Physiologically Structured Populations*, 68. Berlin: Springer-Verlag.
- Okubo A (1980) Diffusion and Ecological Problems: Mathematical Models, 10. Berlin: Springer-Verlag.
- Olson DB and Hood RR (1994) Modelling pelagic biogeography. Progress in Oceanography 34: 161-205.
- Wolf KU and Woods JD (1998) Lagrangian simulation of primary production in the physical environment: The deep chlorophyll maximum and nutricline. In: Rothschild BJ (ed.) *Toward a Theory on Biological-Physical Interactions in the World Ocean*, pp. 51-70. Dordrecht: Kluwer Academic.

# LAND-SEA GLOBAL TRANSFERS

## F. T. Mackenzie and L. M. Ver,

University of Hawaii, Honolulu, HI, USA

Copyright © 2001 Academic Press

doi:10.1006/rwos.2001.0073

## Introduction

The interface between the land and the sea is an important boundary connecting processes operating

on land with those in the ocean. It is a site of rapid population growth, industrial and agricultural practices, and urban development. Large river drainage basins connect the vast interiors of continents with the coastal zone through river and groundwater discharges. The atmosphere is a medium of transport of substances from the land to the sea surface and from that surface back to the land. During the past several centuries, the activities of humankind have significantly modified the exchange of materials between the land and sea on a global scale - humans have become, along with natural processes, agents of environmental change. For example, because of the combustion of the fossil fuels coal, oil, and gas and changes in land use practices including deforestation, shifting cultivation, and urbanization, the direction of net atmospheric transport of carbon (C) and sulfur (S) gases between the land and sea has been reversed. The global ocean prior to these human activities was a source of the gas carbon dioxide  $(CO_2)$  to the atmosphere and hence to the continents. The ocean now absorbs more CO<sub>2</sub> than it releases. In pre-industrial time, the flux of reduced sulfur gases to the atmosphere and their subsequent oxidation and deposition on the continental surface exceeded the transport of oxidized sulfur to the ocean via the atmosphere. The situation is now reversed because of the emissions of sulfur to the atmosphere from the burning of fossil fuels and biomass on land. In addition, river and groundwater fluxes of the bio-essential elements carbon, nitrogen (N), and phosphorus (P), and certain trace elements have increased because of human activities on land. For example, the increased global riverine (and atmospheric) transport of lead (Pb) corresponds with its increased industrial use. Also, recent changes in the concentration of lead in coastal sediments appear to be directly related to changes in the use of leaded gasoline in internal combustion engines. Synthetic substances manufactured by modern society, such as pesticides and pharmaceutical products, are now appearing in river and groundwater flows as they move toward the sea to a greater degree than previously.

# The Changing Picture of Land–Sea Global Transfers

Although the exchange through the atmosphere of certain trace metals and gases between the land and the sea surface is important, rivers are the main purveyors of materials to the ocean. The total water discharge of the major rivers of the world to the ocean is  $36\,000\,\mathrm{km^3y^{-1}}$ . At any time, the world's rivers contain about 0.0001% of the total water volume of  $1459 \times 10^6 \text{ km}^3$  near the surface of the Earth and have a total dissolved and suspended solid concentration of about 110 ppm liter<sup>-1</sup> and 540 ppm liter<sup>-1</sup>, respectively. The residence time of water in the world's rivers calculated with respect to total net precipitation on land is only 18 days. Thus the water in the world rivers is replaced every 18 days by precipitation. The global annual direct discharge to the ocean of groundwater is about 10% of the surface flow, with a recent estimate of  $2400 \,\mathrm{km^3 y^{-1}}$ . The dissolved constituent content of groundwater is poorly known, but one recent estimate of the dissolved salt groundwater flux is  $1300 \times 10^6 \,\mathrm{t y^{-1}}$ .

The chemical composition of average river water is shown in Table 1. Note that the major anion in river water is bicarbonate, HCO<sub>3</sub><sup>-</sup>; the major cation is calcium, Ca2+, and that even the major constituent concentrations of river water on a global scale are influenced by human activities. The dissolved load of the major constituents of the world's rivers is derived from the following sources: about 7% from beds of salt and disseminated salt in sedimentary rocks, 10% from gypsum beds and sulfate salts disseminated in rocks, 38% from carbonates, and 45% from the weathering of silicate minerals. Two-thirds of the HCO<sub>3</sub><sup>-</sup> in river waters are derived from atmospheric CO<sub>2</sub> via the respiration and decomposition of organic matter and subsequent conversion to HCO<sub>3</sub><sup>-</sup> through the chemical weathering of silicate (about 30% of total) or carbonate (about 70% of total) minerals. The other third of the river HCO<sub>3</sub><sup>-</sup> comes directly from carbonate minerals undergoing weathering.

It is estimated that only about 20% of the world's drainage basins have pristine water quality. The organic productivity of coastal aquatic environments has been heavily impacted by changes in the dissolved and particulate river fluxes of three of the major bio-essential elements found in organic matter, C, N, and P (the other three are S, hydrogen (H), and oxygen (O)). Although these elements are considered minor constituents of river water, their fluxes may have doubled over their pristine values on a global scale because of human activities. Excessive riverborne nutrients and the cultural eutrophication of freshwater and coastal marine ecosystems go hand-in-hand. In turn these fluxes have become sensitive indicators of the broader global change issues of population growth and land use change (including water resources engineering works) in the coastal zone and upland drainage basins, climatic change, and sea level rise.

In contrast to the situation for the major elements, delivery of some trace elements from land to the oceans via the atmosphere can rival riverine inputs. The strength of the atmospheric sources strongly depends on geography and meteorology. Hence the North Atlantic, western North Pacific, and Indian Oceans, and their inland seas are subjected to large atmospheric inputs because of their proximity to both deserts and industrial sources. Crustal dust is the primary terrestrial source of these atmospheric inputs to the ocean. Because of the low

By continent	River water concentration <sup>a</sup> (mg/l)												14/- (	
	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	$K^{\scriptscriptstyle +}$	CI-	<i>SO</i> <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> -	SiO <sub>2</sub>	TDS⁵	TOC⁵	TDN⁵	TDP⁵	Water discharge (10 <sup>3</sup> km <sup>3</sup> y <sup>-1</sup> )	Runoff ratio <sup>c</sup>
Africa														
Actual	5.7	2.2	4.4	1.4	4.1	4.2	36.9	12.0	60.5				3.41	0.28
Natural	5.3	2.2	3.8	1.4	3.4	3.2	26.7	12.0	57.8					
Asia														
Actual	17.8	4.6	8.7	1.7	10.0	13.3	67.1	11.0	134.6				12.47	0.54
Natural	16.6	4.3	6.6	1.6	7.6	9.7	66.2	11.0	123.5					
S. America														
Actual	6.3	1.4	3.3	1.0	4.1	3.8	24.4	10.3	54.6				11.04	0.41
Natural	6.3	1.4	3.3	1.0	4.1	3.5	24.4	10.3	54.3					
N. America														
Actual	21.2	4.9	8.4	1.5	9.2	18.0	72.3	7.2	142.6				5.53	0.38
Natural	20.1	4.9	6.5	1.5	7.0	14.9	71.4	7.2	133.5					
Europe														
Actual	31.7	6.7	16.5	1.8	20.0	35.5	86.0	6.8	212.8				2.56	0.42
Natural	24.2	5.2	3.2	1.1	4.7	15.1	80.1	6.8	140.3					
Oceania														
Actual	15.2	3.8	7.6	1.1	6.8	7.7	65.6	16.3	125.3				2.40	
Natural	15.0	3.8	7.0	1.1	5.9	6.5	65.1	16.3	120.3					
World average														
Actual	14.7	3.7	7.2	1.4	8.3	11.5	53.0	10.4	110.1	12.57	0.574	0.053	37.40	0.46
Natural (unpolluted)	13.4	3.4	5.2	1.3	5.8	5.3	52.0	10.4	99.6	9.89	0.386	0.027	37.40	0.46
Pollution	1.3	0.3	2.0	0.1	2.5	6.2	1.0	0.0	10.5	2.67	0.187	0.027		
World % pollutive	9%	8%	28%	7%	30%	54%	2%	0%	10%	21%	33%	50%		

 Table 1
 Chemical composition of average river water

<sup>a</sup>Actual concentrations include pollution. Natural concentrations are corrected for pollution.

<sup>b</sup>TDS = total dissolved solids; TOC = total organic carbon; TDN = total dissolved nitrogen; TDP = total dissolved phosphorus.

<sup>c</sup>Runoff ratio = average runoff per unit area/average rainfall.

Revised after Meybeck M (1979) Concentrations des eaux fluviales en elements majeurs et apports en solution aux oceans, *Revue de Geologie Dynamique et de Geographie Physique* 21: 215–246; Meybeck M (1982) Carbon, nitrogen, and phosphorus transport by world rivers, *American Journal of Science* 282: 401–450; Meybeck M (1983) C, N, P and S in rivers: From sources to global inputs. In: Wollast R, Mackenzie FT and Chou L (eds) Interactions of C, N, P and S Biogeochemical Cycles and Global Change, pp. 163–193. Berlin: Springer-Verlag.

solubility of dust in both atmospheric precipitation and seawater and the overwhelming inputs from river sources, dissolved sources of the elements are generally less important. However, because the oceans contain only trace amounts of iron (Fe), aluminum (Al), and manganese (Mn) (concentrations are in the ppb level), even the small amount of dissolution in seawater (about 10% of the element in the solid phase) results in aeolian dust being the primary source for the dissolved transport of these elements to remote areas of the ocean. Atmospheric transport of the major nutrients N, silicon (Si), and Fe to the ocean has been hypothesized to affect and perhaps limit primary productivity in certain regions of the ocean at certain times. Modern processes of fossil fuel combustion and biomass burning have significantly modified the atmospheric transport from land to the ocean of trace metals like Pb, copper (Cu), and zinc (Zn), C in elemental and organic forms, and nutrient N.

As an example of global land-sea transfers involving gases and the effect of human activities on the exchange, consider the behavior of  $CO_2$  gas. Prior to human influence on the system, there was a net flux of  $CO_2$  out of the ocean owing to organic metabolism (net heterotrophy). This flux was mainly supported by the decay of organic matter produced by phytoplankton in the oceans and part of that transported by rivers to the oceans. An example overall reaction is:

$$C_{106}H_{263}O_{110}N_{16}S_2P + 141O_2$$
  

$$\Rightarrow 106CO_2 + 6HNO_3 \qquad [1]$$
  

$$+ 2H_2SO_4 + H_3PO_4 + 120H_2O$$

Carbon dioxide was also released to the atmosphere due to the precipitation of carbonate minerals in the oceans. The reaction is:

$$Ca^{2^+} + 2HCO_3^- \Rightarrow CaCO_3 + CO_2 + H_2O$$
 [2]

The CO<sub>2</sub> in both reactions initially entered the dissolved inorganic carbon (DIC) pool of seawater and was subsequently released to the atmosphere at an annual rate of about  $0.2 \times 10^9$  tons of carbon as CO<sub>2</sub> gas. It should be recognized that this is a small number compared with the  $200 \times 10^9$  tons of carbon that exchanges between the ocean and atmosphere each year because of primary production of organic matter and its subsequent respiration.

Despite the maintenance of the net heterotrophic status of the ocean and the continued release of  $CO_2$  to the ocean-atmosphere owing to the formation of calcium carbonate in the ocean, the modern

ocean and the atmosphere have become net sinks of anthropogenic CO<sub>2</sub> from the burning of fossil fuels and the practice of deforestation. Over the past 200 years, as CO<sub>2</sub> has accumulated in the atmosphere, the gradient of CO<sub>2</sub> concentration across the atmosphere–ocean interface has changed, favoring uptake of anthropogenic CO<sub>2</sub> into the ocean. The average oceanic carbon uptake for the decade of the 1990s was about  $2 \times 10^9$  tons annually. The waters of the ocean have accumulated about  $130 \times 10^9$  tons of anthropogenic CO<sub>2</sub> over the past 300 years.

## The Coastal Zone and Land–Sea Exchange Fluxes

The global coastal zone environment is an important depositional and recycling site for terrigenous and oceanic biogenic materials. The past three centuries have been the time of well-documented human activities that have become an important geological factor affecting the continental and oceanic surface environment. In particular, historical increases in the global population in the areas of the major river drainage basins and close to oceanic coastlines have been responsible for increasing changes in land use practices and discharges of various substances into oceanic coastal waters. As a consequence the global C cycle and the cycles of N and P that closely interact with the carbon cycle have been greatly affected. Several major perturbations of the past three centuries of the industrial age have affected the processes of transport from land, deposition of terrigenous materials, and in situ production of organic matter in coastal zone environments. In addition, potential future changes in oceanic circulation may have significant effects on the biogeochemistry and CO<sub>2</sub> exchange in the coastal zone.

The coastal zone is that environment of continental shelves, including bays, lagoons, estuaries, and near-shore banks that occupy 7% of the surface area of the ocean  $(36 \times 10^{12} \text{ m}^2)$  or approximately 9% of the volume of the surface mixed layer of the ocean  $(3 \times 10^{15} \text{ m}^3)$ . The continental shelves average 75 km in width, with a bottom slope of  $1.7 \,\mathrm{m\,km^{-1}}$ . They are generally viewed as divisible into the interior or proximal shelf, and the exterior or distal shelf. The mean depth of the global continental shelf is usually taken as the depth of the break between the continental shelf and slope at approximately 200m, although this depth varies considerably throughout the world oceans. In the Atlantic, the median depth of the shelf-slope break is at 120 m, with a range from 80-180 m. The depths of the continental shelf are near 200 m in the

European section of the Atlantic, but they are close to 100 m on the African and North American coasts. Coastal zone environments that have high sedimentation rates, as great as 30-60 cm per 1000 years in active depositional areas, act as traps and filters of natural and human-generated materials transported from continents to the oceans via river and groundwater flows and through the atmosphere. At present a large fraction (about 80%) of the land-derived organic and inorganic materials that are transported to the oceans is trapped on the proximal continental shelves. The coastal zone also accounts for 30-50% of total carbonate and 80% of organic carbon accumulation in the ocean. Coastal zone environments are also regions of higher biological production relative to that of average oceanic surface waters, making them an important factor in the global carbon cycle. The higher primary production is variably attributable to the nutrient inflows from land as well as from coastal upwelling of deeper ocean waters.

Fluvial and atmospheric transport links the coastal zone to the land; gas exchange and deposition are its links with the atmosphere; net advective transport of water, dissolved solids and particles, and coastal upwelling connect it with the open ocean. In addition, coastal marine sediments are repositories for much of the material delivered to the coastal zone. In the last several centuries, human activities on land have become a geologically important agent affecting the land-sea exchange of materials. In particular river and groundwater flows and atmospheric transport of materials to the coastal zone have been substantially altered.

#### **Bio-essential Elements**

Continuous increase in the global population and its industrial and agricultural activities have created four major perturbations on the coupled system of the biogeochemical cycles of the bio-essential elements C, N, P, and S. These changes have led to major alterations in the exchanges of these elements between the land and sea. The perturbations are: (1) emissions of C, N, and S to the atmosphere from fossil fuel burning and subsequent partitioning of anthropogenic C and deposition of N and S; (2) changes in land use practices that affect the recycling of C, N, P, and S on land, their uptake by plants and release from decaying organic matter, and the rates of land surface denudation; (3) additions of N and P in chemical fertilizers to cultivated land area; and (4) releases of organic wastes containing highly reactive C, N, and P that ultimately enter the coastal zone. A fifth major perturbation is a climatic one: (5) the rise in mean global temperature of the lower atmosphere of about  $1^{\circ}$ C in the past 300 years, with a projected increase of about  $1.4-5.8^{\circ}$ C relative to 1990 by the year 2100. Figure 1 shows how the fluxes associated with these activities have changed during the past three centuries with projections to the year 2040.

In part as a result of these activities on land, the fluxes of materials to the coastal zone have changed during historical times. Figure 2 shows the historical and projected future changes in the river fluxes of dissolved inorganic and organic carbon (DIC, DOC), nitrogen (DIN, DON), and phosphorus (DIP, DOP), and fluxes associated with the atmospheric deposition and denitrification of N, and accumulation of C in organic matter in coastal marine sediments. It can be seen in Figure 2 that the riverine fluxes of C, N, and P all increase in the dissolved inorganic and organic phases from about 1850 projected to 2040. For example, for carbon, the total flux (organic + inorganic) increases by about 35% during this period. These increased fluxes are mainly due to changes in land use practices, including deforestation, conversion of forest to grassland, pastureland, and urban centers, and regrowth of forests, and application of fertilizers to croplands and the subsequent leaching of N and P into aquatic systems.

Inputs of nutrient N and P to the coastal zone which support new primary production are from the land by riverine and groundwater flows, from the open ocean by coastal upwelling and onwelling, and to a lesser extent by atmospheric deposition of nitrogen. New primary production depends on the availability of nutrients from these external inputs, without consideration of internal recycling of nutrients. Thus any changes in the supply of nutrients to the coastal zone owing to changes in the magnitude of these source fluxes are likely to affect the cycling pathways and balances of the nutrient elements. In particular, input of nutrients from the open ocean by coastal upwelling is quantitatively greater than the combined inputs from land and the atmosphere. This makes it likely that there could be significant effects on coastal primary production because of changes in ocean circulation. For example, because of global warming, the oceans could become more strongly stratified owing to freshening of polar oceanic waters and warming of the ocean in the tropical zone. This could lead to a reduction in the intensity of the oceanic thermohaline circulation (oceanic circulation owing to differences in density of water masses, also popularly known as the 'conveyor belt') of the ocean and hence the rate at which nutrient-rich waters upwell into coastal environments.

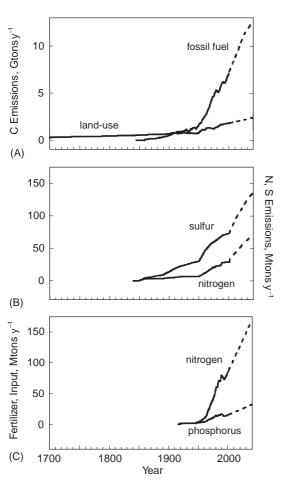
Another potential consequence of the reduction in the rate of nutrient inputs to the coastal zone by upwelling is the change in the CO<sub>2</sub> balance of coastal waters: reduction in the input of DIC to the coastal zone from the deeper ocean means less dissolved CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> coming from that source. With increasing accumulation of anthropogenic  $CO_2$  in the atmosphere, the increased dissolution of atmospheric  $CO_2$  in coastal water is favored. The combined result of a decrease in the upwelling flux of DIC and an enhancement in the transfer of atmospheric CO2 across the air-sea interface of coastal waters is a lower saturation state for coastal waters with respect to the carbonate minerals calcite, aragonite, and a variety of magnesian calcites. The lower saturation state in turn leads to the likelihood of lower rates of inorganic and biological precipitation of carbonate and hence deposition and accumulation of sedimentary carbonate.

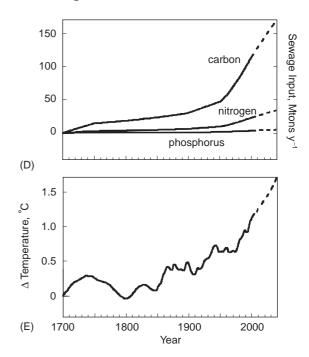
In addition, the present-day burial rate of organic carbon in the ocean may be about double that of the late Holocene flux, supported by increased fluxes of organic carbon to the ocean via rivers and groundwater flows and increased *in situ* new primary production supported by increased inputs of inorganic N and P from land and of N deposited from the atmosphere. The organic carbon flux into sediments may constitute a sink of anthropogenic  $CO_2$  and a minor negative feedback on accumulation of  $CO_2$  in the atmosphere.

The increased flux of land-derived organic carbon delivered to the ocean by rivers may accumulate there or be respired, with subsequent emission of  $CO_2$  back to the atmosphere. This release flux of  $CO_2$  may be great enough to offset the increased burial flux of organic carbon to the seafloor due to enhanced fertilization of the ocean by nutrients derived from human activities. The magnitude of the  $CO_2$  exchange is a poorly constrained flux today. One area for which there is a substantial lack of knowledge is the Asian Pacific region. This is an area of several large seas, a region of important river inputs to the ocean of N, P, organic carbon, and sediments from land, and a region of important  $CO_2$  exchange between the ocean and the atmosphere.

#### **Anticipated Response to Global Warming**

From 1850 to modern times, the direction of the net flux of  $CO_2$  between coastal zone waters and the





**Figure 1** Major perturbations on the Earth system over the past 300 years and projections for the future: (A) emissions of  $CO_2$  and (B) gaseous N and S from fossil fuel burning and land use activities; (C) application of inorganic N and P in chemical fertilizers to cultivated land; (D) loading of highly reactive C, N, and P into rivers and the coastal ocean from municipal sewage and wastewater disposal; and (E) rise in mean global temperature of the lower atmosphere relative to 1700. (Revised after Ver LM et al. 1999.)

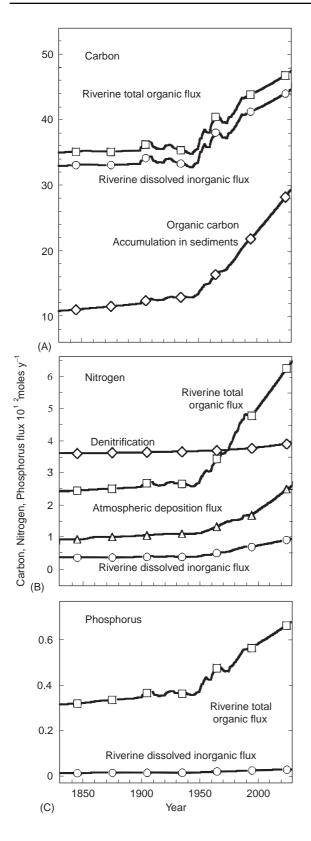
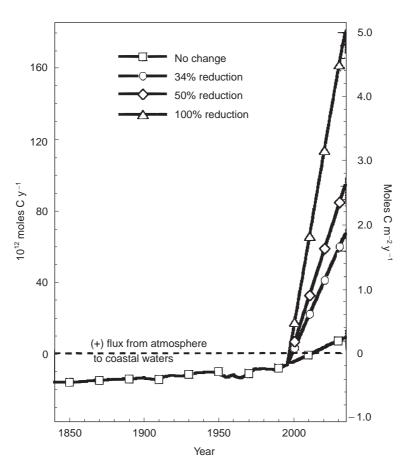


Figure 2 Past, present, and predicted fluxes of carbon, nitrogen, and phosphorus into or out of the global coastal margin, in  $10^{12}$  moles  $y^{-1}$ .

atmosphere due to organic metabolism and calcium carbonate accumulation in coastal marine sediments was from the coastal surface ocean to the atmosphere (negative flux, Figure 3). This flux in 1850 was on the order of  $-0.2 \times 10^9$  tons y<sup>-1</sup>. In a condition not disturbed by changes in the stratification and thermohaline circulation of the ocean brought about by a global warming of the Earth, the direction of this flux is projected to remain negative (flux out of the coastal ocean to the atmosphere) until early in the twenty-first century. The increasing partial pressure of  $CO_2$  in the atmosphere because of emissions from anthropogenic sources leads to a reversal in the gradient of CO<sub>2</sub> across the air-sea interface of coastal zone waters and, hence, invasion of  $CO_2$  into the coastal waters. From that time on the coastal ocean will begin to operate as a net sink (positive flux) of atmospheric  $CO_2$  (Figure 3). The role of the open ocean as a sink for anthropogenic  $CO_2$  is slightly reduced while that of the coastal oceans increases. The net result is the maintenance of the role of the global oceans as a net sink for anthropogenic CO<sub>2</sub>.

The saturation index  $(\Omega)$  for calcite or aragonite (both  $CaCO_3$ ) is the ratio of the ion-activity product IAP in coastal waters to the respective equilibrium constant K at the in situ temperature. For aqueous species,  $IAP = a_{Ca}^{2+} \times a_{CO_3}^{2-}$  (where *a* is the activity; note that for 15 mole% magnesian calcite, the IAP also includes the activity of the magnesium cation, aMg<sup>2+</sup>). Most coastal waters and openocean surface waters currently are supersaturated with respect to aragonite, calcite, and magnesian calcite containing 15 mole% Mg, i.e.  $\Omega_{calcite}$ ,  $\Omega_{aragonite}$ , and  $\Omega_{15\%magnesian \ calcite}$  are >1. Because of global warming and the increasing land-to-atmosphere-to-sea water transport of CO<sub>2</sub> owing to the continuing combustion of fossil fuels and burning of biomass, the concentration of the aqueous  $CO_2$ species in sea water increases and the pH of the water decreases slightly. This results in a decrease in the concentration of the carbonate ion,  $CO_3^{2-}$ , resulting in a decrease in the degree of supersaturation of coastal zone waters. Figure 4 shows how the degree of saturation might change into the next century because of rising atmospheric CO<sub>2</sub> concentrations. The overall reduction in the saturation state of coastal zone waters with respect to aragonite from 1997 projected to 2040 is about 16%, from 3.89 to 3.26.

Modern carbonate sediments deposited in shoalwater ('shallow-water') marine environments (including shelves, banks, lagoons, and coral reef tracts) are predominantly biogenic in origin derived from the skeletons and tests of benthic and pelagic



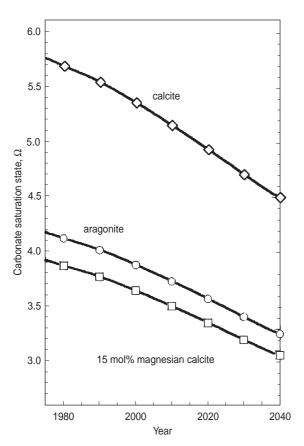
**Figure 3** The net flux of  $CO_2$  between coastal zone waters and the atmosphere due to organic metabolism and calcium carbonate accumulation in coastal marine sediments, under three scenarios of changing thermohaline circulation rate compared to a business-as-usual scenario, in units of  $10^{12}$  moles C y<sup>-1</sup>.

organisms, such as corals, foraminifera, echinoids, mollusks, algae, and sponges. One exception to this statement is some aragonitic muds that may, at least in part, result from the abiotic precipitation of aragonite from seawater in the form of whitings. Another exception is the sand-sized, carbonate ooids composed of either aragonite with a laminated internal structure or magnesian calcite with a radial internal structure. In addition, early diagenetic carbonate cements found in shoal-water marine sediments and in reefs are principally aragonite or magnesian calcite. Thus carbonate production and accumulation in shoal-water environments are dominated by a range of metastable carbonate minerals associated with skeletogenesis and abiotic processes, including calcite, aragonite, and a variety of magnesian calcite compositions.

With little doubt, as has been documented in a number of observational and experimental studies, a reduction in the saturation state of ocean waters will lead to a reduction in the rate of precipitation of both inorganic and skeletal calcium carbonate. Conversely, increases in the degree of supersaturation and in temperature will increase the precipitation rates of calcite and aragonite from seawater. During global warming, rising sea surface temperatures and declining carbonate saturation states due to the absorption of anthropogenic CO<sub>2</sub> by surface ocean waters result in opposing effects. However, experimental evidence suggests that within the range of temperature change predicted for the next century due to global warming, the effect of changes in saturation state will be the predominant factor affecting precipitation rate. Thus decreases in precipitation rates should lead to a decrease in the production and accumulation of shallow-water carbonate sediments and perhaps changes in the types and distribution of calcifying biotic species found in shallow-water environments.

## Anticipated Response to Heightened Human Perturbation: The Asian Scenario

In the preceding sections it was shown that the fluxes of C, N, and P from land to the ocean have



**Figure 4** Changes in saturation state with respect to carbonate minerals of surface waters of the coastal ocean projected from 1999 to 2040. Calculations are for a temperature of 25°C.

increased because of human activities (refer to Table 1 for data comparing the actual and natural concentrations of C, N, P, and other elements in average river water). During the Industrial Era these fluxes mainly had their origin in the present industrialized and developed countries. This is changing as the industrializing and developing countries move into the twenty-first century. A case in point are the countries of Asia.

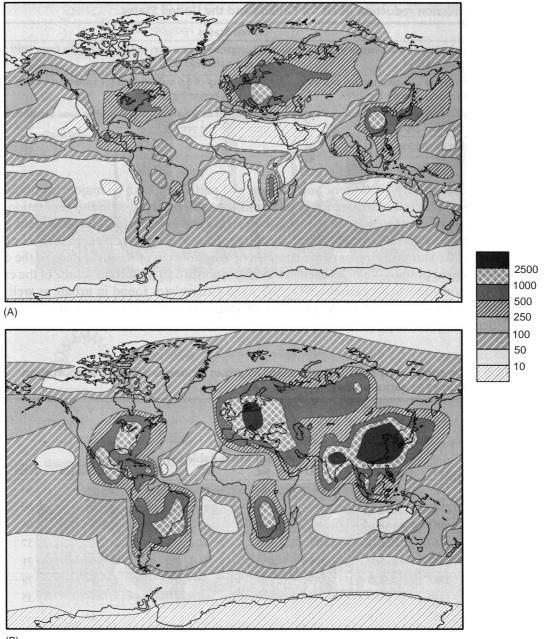
Asia is a continent of potentially increasing contributions to the loading of the environment owing to a combination of such factors as its increasing population, increasing industrialization dependent on fossil fuels, concentration of its population along the major river drainage basins and in coastal urban centers, and expansion of land use practices. It is anticipated that Asia will experience similar, possibly even greater, loss of storage of C and nutrient N and P on land and increased storage in coastal marine sediments per unit area than was shown by the developed countries during their period of industrialization. The relatively rapid growth of Asia's population along the oceanic coastal zone indicates that higher inputs of both dissolved and particulate organic nutrients may be expected to enter coastal waters.

A similar trend of increasing population concentration in agricultural areas inland, within the drainage basins of the main rivers flowing into the ocean, is also expected to result in increased dissolved and particulate organic nutrient loads that may eventually reach the ocean. Inputs from inland regions to the ocean would be relatively more important if no entrapment or depositional storage occurred en route, such as in the dammed sections of rivers or in alluvial plains. In the case of many of China's rivers, the decline in sediment discharge from large rivers such as the Yangtze and the Yellow Rivers is expected to continue due to the increased construction of dams. The average decadal sediment discharge from the Yellow River, for example, has decreased by 50% from the 1950s to the 1980s. If the evidence proposed for the continental United States applies to Asia, the damming of major rivers would not effectively reduce the suspended material flow to the ocean because of the changes in the erosional patterns on land that accompany river damming and more intensive land use practices. These flows on land and into coastal ocean waters are contributing factors to the relative importance of autotrophic and heterotrophic processes, competition between the two, and the consequences for carbon exchange between the atmosphere and land, and the atmosphere and ocean water. The change from the practices of land fertilization by manure to the more recent usage of chemical fertilizers in Asia suggests a shift away from solid organic nutrients and therefore a reduced flow of materials that might promote heterotrophy in coastal environments.

Sulfur is an excellent example of how parts of Asia can play an important role in changing land-sea transfers of materials. Prior to extensive human interference in the global cycle of sulfur, biogenically produced sulfur was emitted from the sea surface mainly in the form of the reduced gas dimethylsulfide (DMS). DMS was the major global natural source of sulfur for the atmosphere, excluding sulfur in sea salt and soil dust. Some of this gas traveled far from its source of origin. During transport the reduced gas was oxidized to micrometersize sulfate aerosol particles and rained out of the atmosphere onto the sea and continental surface. The global sulfur cycle has been dramatically perturbed by the industrial and biomass burning activities of human society. The flux of gaseous sulfur dioxide to the atmosphere from the combustion of fossil fuels in some regions of the world and its conversion to sulfate aerosol greatly exceeds natural fluxes of sulfur gases from the land surface. It is

estimated that this flux for the year 1990 was equivalent to  $73 \times 10^6$  tons y<sup>-1</sup>, nearly four times the natural DMS flux from the ocean. This has led to a net transport of sulfur from the land to the ocean via the atmosphere, completely reversing the flow direction in pre-industrial times. In addition the sulfate aerosol content of the atmosphere derived from human activities has increased. Sulfate aerosols

affect global climate directly as particles that scatter incoming solar radiation and indirectly as cloud condensation nuclei (CCN), which lead to an increased number of cloud droplets and an increase in the solar reflectance of clouds. Both effects cause the cooling of the planetary surface. As can be seen in **Figure 5**, the eastern Asian region is an important regional source of sulfate aerosol because of the





**Figure 5** Comparison of the magnitude of atmospheric sulfur deposition for the years 1990 (A) and 2050 (B). Note the large increases in both spatial extent and intensity of sulfur deposition in both hemispheres and the increase in importance of Asia, Africa, and South America as sites of sulfur deposition between 1990 and 2050. The values on the diagrams are in units of kg S m<sup>-2</sup> y<sup>-1</sup>. (Revised after Mackenzie FT (1998); Rodhe H, Langner J, Gallardo L and Kjellström E (1995) Global transport of acidifying pollutants. *Water, Air and Soil Pollution.* 85: 37–50.)

combustion of fossil fuels, particularly coal. This source is predicted to grow in strength during the early- to mid-twenty-first century (Figure 5).

## Conclusion

Land-sea exchange processes and fluxes of the bioessential elements are critical to life. In several cases documented above, these exchanges have been substantially modified by human activities. These modifications have led to a number of environmental issues including global warming, acid deposition, excess atmospheric nitrogen deposition, and production of photochemical smog. These issues all have consequences for the biosphere - some well known, others not so well known. It is likely that the developing world, with increasing population pressure and industrial development and with no major changes in agricultural technology and energy consumption rates, will become a more important source of airborne gases and aerosols and materials for river and groundwater systems in the future. This will lead to further modification of land-sea global transfers. The region of southern and eastern Asia is particularly well poised to influence significantly these global transfers.

## See also

Aeolian Inputs. Air–Sea Transfer: Dimethyl Sulphide, COS, CS<sub>2</sub>, NH<sub>4</sub>, Non-methane Hydrocarbons, Organo-halogens. Carbon Cycle. Carbon Dioxide (CO<sub>2</sub>) Cycle. Coastal Topography, Human Impact on. Nitrogen Cycle. Ocean Carbon System, Modelling of. Past Climate From Corals. Phosphorus Cycle. Thermohaline Circulation.

#### **Further Reading**

- Berner EA and Berner RA (1996) *Global Environment: Water, Air and Geochemical Cycles.* Upper Saddle River, NJ: Prentice Hall.
- Galloway JN and Melillo JM (eds) (1998) Asian Change in the Context of Global Change. Cambridge: Cambridge University Press.
- Mackenzie FT (1998) Our Changing Planet: An Introduction to Earth System Science and Global Environmental Change. Upper Saddle River, NJ: Prentice-Hall.
- Schlesinger WH (1997) Biogeochemistry: An Analysis of Global Change. San Diego, California: Academic Press.
- Smith SV and Mackenzie FT (1987) The ocean as a net heterotrophic system: Implications from the carbon biogeochemical cycle. *Global Biogeochemical Cycles* 1: 187–198.
- Ver LM, Mackenzie FT and Lerman A (1999) Biogeochemical responses of the carbon cycle to natural and human perturbations: Past, present, and future. *American Journal of Science* 299: 762–801.
- Vitousek PM, Aber JD, Howarth RW *et al.* (1997) Human alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications* 7 (3): 737-750.
- Wollast R and Mackenzie FT (1989) Global biogeochemical cycles and climate. In: Berger A, Schneider S and Duplessy JC (eds) *Climate and Geo-Sciences*, pp. 453–473. Dordrecht: Kluwer Academic Publishers.

## LANGMUIR CIRCULATION AND INSTABILITY

S. Leibovich, Cornell University, Ithaca, NY, USA

Copyright © 2001 Academic Press doi:10.1006/rwos.2001.0141

## Introduction

The surface of a wind-driven sea often is marked by streaks roughly aligned with the wind direction. These streaks, or windrows, are visible manifestations of coherent subsurface motions extending throughout the bulk of the ocean surface mixed layer, extending from the surface down to the seasonal thermocline. These may be regarded as the large scales of the turbulence in the mixed layer. Windrows and their subsurface origins were first systematically studied and described by Irving Langmuir in 1938, and the phenomenon since has become known as Langmuir circulation. The existence of a simple deterministic description making these large scales theoretically accessible distinguishes this problem from coherent structures in other turbulent flows. The theory traces these patterns to a convective instability mechanically driven by the wind waves and currents. Recent advances in instrumentation and computational data analysis have led to field observations of Langmuir circulation of unprecedented detail. Although the body of observational data obtained since Langmuir's own work is mainly qualitative, ocean experiments now can yield quantitative measurements of velocity fields in the near surface region. New measurement