33 Trace Metal Accumulation, Movement, and Remediation in Soils Receiving Animal Manure

Karamat R. Sistani and Jeffrey M. Novak

CONTENTS

ABSTRACT

Trace metals are important components in an animal's daily food rations because they are essential for maintaining various physiological processes. Because some animal feeds contain inadequate supplies, trace metals are added into feeds to ensure an optimal supply and to minimize health disorders. Unfortunately, trace metal levels in feeds are frequently fortified to amounts greater than recommended to ensure adequate uptake. Trace metals not retained by the animal are excreted in manure. The return of manure to the land completes a natural recycling process. However, trace metals from manure are also known to be a potential source of pollution to the environment.

The application of animal manures on agricultural lands as a fertilizer has the benefit of resource recycling and waste minimization from livestock production facilities. Research from around the world has shown, however, that continuous manure applications can cause their accumulation in soils because crop uptake of trace metals is small. Although trace metals are accumulating in manure-treated soils, there are few reports of levels reaching phytotoxic threshold concentrations. High levels of trace metals in soils, however, can potentially pose a water quality risk when runoff or leaching transports trace metals into surface water sources. Research has shown that the risk of trace metals causing environmental problems depends upon the element's solubility and binding affinity to organic matter and minerals.

Countermeasures to reduce trace metal concentrations in soils include phytoremediation and additions of soil chemical amendments. It is recommended that trace metal accumulation in soils may be avoided and/or reduced by optimizing their concentration in feed stocks, improving animal trace metal uptake efficiencies, and reducing application rates onto the same fields.

33.1 INTRODUCTION

The well-being of humankind is inflexibly linked to the stock of nutrient elements, including trace metals in the biogeosphere and their capacity for cycling and manipulation. The capacity to produce usable plant biomass depends upon the adequacy and balance of nutrient elements. The uptake of nutrients by plants has been well-researched for over three centuries by European scientists. Early colonial farmers in America knew that some soils were more fertile than others and that the soil nutrients' status depended upon the chemical composition of the geologic strata.

Soils are composed of various rocks and minerals that, after weathering by physical and chemical agents, will release metals into the soil solution, mostly as cations and anions [1,2]. Metals released by these solid phases can be used by plants as nutrients. The quantity of metals required by plants depends on the metabolic functions of the metal in question [3]. Because the amount of metal assimilated by plants varies widely, their essentiality in the plant nutrient cycle has been conveniently classified into groups called macro- and micronutrients (Table 33.1). Macronutrients are required in larger amounts and are utilized for the formation of amino acids, cell membrane components, maintaining electrochemical balances, and formation of enzymes (Table 33.1). Although micronutrients are required in smaller quantities, they still have essential roles in plant physiological reactions (Table 33.1). In this chapter, micronutrients will be referred to as trace metals.

TABLE 33.1
Grouping of Elements into Macro- and Micronutrient Categories and Physiological Functofunctions of Each Trace Metal in Plant Growth

Element	Physiological function in plant
Macro	
N	Structural component of cell wall, amino acid formation
P	Transfer of energy, formation of genetic material
K	Electrochemical balance, nutrient translocation
Ca	Structural component of cell wall
Mg	Core molecule in chlorophyll
S	Component of amino acids, enzymes
Micro	
B	Component of enzymes
Co	Nitrogen fixation
Cl	Electrochemical balance
Cu	Coenzyme, component of chlorophyll
Fe	Chlorophyll component, some enzyme functions
Mn	Chlorophyll component, some enzyme functions
Mo	Nitrogen fixation, conversion of N into amines
Zn	Protein formation, chlorophyll production

Source: Thompson, L.M. and Troeh, F.R., *Soils and Soil Fertility*. 4th ed. McGraw–Hill Publishing Co., New York.

Trace metal concentrations in soils can vary widely because of chemical compositional differences in soil parent materials and geologic deposits. Literature has shown that soils formed over serpentine geologic deposits are high in Cr and Ni [4] and rock deposits containing cinnabar contribute to a high level of soil Hg [5]. Anthropogenic factors are, however, frequently more responsible for high soil trace metal concentrations. For instance, excessively high trace metal concentrations in soils can also occur as a result of additions of fertilizers, sewage sludges, animal manure, irrigation waters, and mine spoils. In localized areas, such as those contaminated by mining or industrial wastes, other non-nutrient elements like Cd, Pb, and Hg may also occur in soils.

Application of animal manures to fields is another recognized pathway for the introduction of trace metals to soils. Cattle, poultry, and swine feeds are frequently fortified with various levels of trace metals in order to maintain various physiological processes and to avoid animal health disorders [6–8]. In some cases, trace metals are supplemented in amounts that exceed the daily recommended allowances because some metals are not easily sorbed by the animal's digestive tract. Trace metals that pass through the animal's gut are excreted in the manure. Literature often reports a close relationship between trace metal intake by livestock and the manure's trace metal concentrations [9–11].

Optimum use of trace metal-enriched animal manures as a beneficial fertilizer requires that application rates be balanced with crop nutritional uptake rates. Agronomic crops assimilate much smaller amounts of trace metals compared to macronutrients [12]. Consequently, if trace metal application rates exceed plant removal rates, it is highly probable that they will accumulate in soil. Studies in Asia, Europe, and the U.S. [10,13–16] have reported trace metal accumulation in soils that receive continuous long-term applications of animal manure.

Trace element accumulation in soil poses serious animal health, environmental, and agronomic issues [17]. Alonso et al. [18] investigated the effects of Cu-enriched pig slurry additions to cattle grazing pastures in Galicia, Spain. They reported that more than 20% of the cattle grazing in the field had liver Cu concentrations that exceeded the potential Cu toxic concentration of 150 mg/kg fresh weight. Cu toxicity has also been reported in sheep and cattle that have been grazing on pastures contaminated with pig slurry [19–21]. Soils with high trace metal concentrations can be a point source of contamination for surface water bodies [22,23] and can cause occurrences of crop phytotoxicity [24]. Trace metals can be transported offsite by runoff [25] and by leaching [26,27].

Soil chemical and physical features have a large influence on the solubility and thus offsite transport potential of trace metals. For example, trace metal bioavailability, mobility, and toxicity are regulated by soil pH, texture, and the kinetic distribution between solution and solid phases [28]. Soil pH is probably the most important intrinsic soil property influencing trace metal mobility [28]. Additionally, binding of trace metals to organic matter is known to control their mobility and leaching potential [29–32].

Remediation strategies to reduce trace metals concentrations in soils and sediments are available. Conventional treatment strategies like soil washing and incineration are destructive to the background matrix. Destruction of key soil quality factors (e.g., organic matter, cation exchange capacity, etc.) in the soil matrix lowers the potential reuse of the material. On the other hand, in some examples, nondestructive remediation technologies can reduce trace metal concentrations or create compounds that render trace metals immobile.

Phytoremediation is a plant-based technology that can reduce trace metal concentrations in contaminated soils and sediments [33–35]. In phytoremediation, specific plants are used to phytoextract target trace metals and then translocate the metal to above-ground plant biomass [34]. After harvesting, the target trace metal is removed from the system. A disadvantage of using phytoremediation is that hyperaccumulator plant growth is slow and production of above-ground biomass is limited. This means that considerable time may be required for plants to reduce trace metal concentrations. Time estimates to remove trace metals from soils have been modeled by examining relationships between target metal concentrations and the quantity of metal removed in the harvested crop. These projected time estimates can vary from a few to several hundred years depending on the reduction level required, yield, bioavailability, leaching potential, and plant uptake [36–38].

Because trace metal accumulation in soils will probably have a long residence time, it is important to understand reasons for the accumulation and to determine soil factors controlling mobility. An understanding of these factors is critical for the development of physical or chemical remediation strategies or adjustments in manure management practices to reduce trace metal accumulation. This review has been designed initially to determine sources and distributions of metals in various animal manure types. Then, an analysis between metal uptake rates by plants vs. manure application rates is examined to determine potential imbalances and accumulation to phytotoxic levels. Pathways that influence trace metal transport offsite into water bodies are then examined. Finally, the chapter concludes with the plant- and chemical-based remediation strategies available as countermeasures to reduce soil trace metal concentrations.

33.2 SOURCES AND DISTRIBUTIONS OF TRACE METALS IN MANURE

Trace metal assimilation by animals is important for the proper functioning of many physiological processes, including reproduction, enzymatic catalysis, and electron transport reactions (Table 33.2) [39,40]. If the supply of trace metals is inadequate in the livestock's diet, then growth and/or health of the animal species can be adversely affected [39].

Animals ingest trace metals through consuming plant materials; however, dietary metal requirements may not be met because of low metal concentrations in the feed sources. In many cases, the absorption and bioavailability of the trace metals by livestock are low; consequently, trace minerals have traditionally been supplemented to animal diets to ensure an adequate supply. Unfortunately, trace metals are frequently supplemented in amounts that exceed the daily recommended intake amount [41]. For example, daily dietary concentrations of 150 to 250 mg/kg Cu_2SO_4 and 2500 to 3000 mg/kg $ZnSO_4$ (more than 25 times the minimum requirement) have been reported to stimulate swine growth [42,43]. On an international scale, the U.S. National Research Council recommends between 3.5 and 6.0 mg Cu/kg in the daily diet of swine (piglets to finishing pigs). However, Europe's current recommendation through Directive 70/534/EEC allows maximum Cu levels between 35 and 175 mg/kg [41]. Current European regulations for the maximum daily Zn content in swine diets are also higher than NRC recommendations.

The reduction of Cu and Zn in dietary supplies is one of the avenues available to limit trace metal accumulations. Jondreville et al. [41] reported that annual Cu and Zn accumulation could be reduced by 35% if Cu and Zn concentrations were reduced in swine feed rations from 100

TABLE 33.2
Physiological Role of Selected Trace Metals in Animal Diets

Trace element	Physiological role in animals
B	Increase bone strength and feed efficiency in swine
Co	Vitamin formation
Cu	Enzyme formation, reproductive processes
Fe	Cytochrome functions and electron transport process
Mn	Enzyme formation, reproductive process
Mo	Enzyme formation
Zn	Enzyme formation, fetus development

Sources: Hostetler, C.E. et al., *Vet. J.*, 166, 125, 2003; Bolan, N.S. and Adriano, D.C., *Crit. Rev. Environ. Sci. Technol.* 34(3): 291-338, 2004.

TABLE 33.3
Trace Metal Concentration Ranges in Cattle, Poultry, and Swine Manure

Trace element	Cattle manures	Poultry manures mg/kg dry weight	Swine manure
B	0.3 to 24	—	—
Co	0.3 to 24	1.2 to 5.0	11
Cu	2 to 62	4.4 to 31	13
Mn	30 to 550	166 to 242	168
Fe	—	80 to 560	—
Mo	0.05 to 49	5 to 42	34
Zn	15 to 250	36 to 158	198

Sources: Kabata–Pendias, A. and Pendias, H., *Trace Elements in Soils and Plants*, CRC Press, Boca Raton, FL, 1984; Edwards, D.R. and Daniels, T.C., *Bioresour. Technol.*, 41, 9, 1992; Arora, C.L. et al., *Indian J. Agric. Sci.*, 45, 80, 1975; Adriano, D.C., Trace Elements in the Terrestrial Environment. Springer-Verlag, Berlin, 1986.

to 20 mg/kg and from 250 to 100 mg/kg, respectively. Spears et al. [44] evaluated the effects of lowering Cu and Zn supplementation from 15 to 5 mg/kg and from 100 to 25 mg/kg, respectively, on trace metal concentrations in swine feces. Results demonstrated that lower Cu and Zn concentrations in dietary intake reduced Cu and Zn excretions in feces by 40% without negatively affecting carcass characteristics or carcass value. Van Heugten et al. [8] demonstrated similar results. Reducing trace metal intake by animals is a possibility, but the lack of relevant information on possible health side-effects (e.g., impairment of immune system [45]) could limit acceptance of this practice.

Not all of the trace metals consumed by animals are absorbed by the animal's digestive tract; consequently, the manure is often trace metal enriched (Table 33.3). For example, swine can excrete approximately 80 to 95% of the total daily Cu and Zn contained in dietary supplements [19,42,46]. Kunkle et al. [9] found that Cu concentrations in poultry litter were linearly related to that in feed and that the litter Cu concentration was about 3.25-fold higher than values measured in the feed. Edwards and Daniels [47] reported that poultry manures were enriched in trace metals like Mn, Fe, Cu, and Zn. From numerous poultry manure compositional investigations, they summarized that the mean Mn, Fe, Cu, and Zn concentrations were 304, 320, 53, and 354 mg/kg, respectively [47]. Barker and Zublena [48] conducted a Cu and Zn concentration assessment in swine manure measured from several swine operations in North Carolina and reported that the mean concentrations were 15 and 62 mg/kg, respectively. These results suggest that animal manures are a significant source of several trace metals and that lack of ruminant assimilation and subsequent deposition of excreta in fields allows these trace metals to accumulate in soils.

Trace metal concentrations in animal manures vary greatly (Table 33.3). This should not be unexpected, considering the large number of management variables associated with manure management systems [49,50]. As shown in Table 33.5, trace metal concentrations like Cu, Fe, Mn, and Zn will vary depending upon source (broiler cake vs. poultry litter vs. feed). The large variation in trace metal concentration is probably a result of animal age, type of feed source, trace metal supplements, bedding differences, and manure storage practices [40]. Because of this large variation in trace metal concentrations, it is difficult to imply that manures from certain livestock types will have a specific trace metal compositional signature.

33.3 TRACE METAL ACCUMULATION IN MANURE-TREATED SOILS

Because some soils can have fertility levels that are out of balance (Table 33.6), animal manures have historically been applied to soils as a fertilizer and to improve the soil's physicochemical properties [51,52]. A large portion of the approximately 10 million Mg of broiler litter (a mixture of manure, wasted feed, feather, and bedding materials such as wood shavings) produced annually in the southeastern U.S. is applied to hay field, pasture, and row crops [53]. After applications of poultry litter to low-fertility soils (Table 33.7), monthly monitoring of trace metal concentrations in topsoils shows that levels do not change dramatically within 1 year after application. Although manures contain essential micronutrients and organic matter, their high trace metal concentration is recognized as a significant source for trace metal accumulation in soils [7,10,14,26].

Brink et al. [54] reported that application of swine effluent (annual mean of 10 ha cm) to Bermuda grass pasture added annual averages of 0.6 kg ha^{-1} Cu, 2.2 kg ha^{-1} Fe, 0.3 kg ha^{-1} Mn, and 0.86 kg ha^{-1} Zn to the soil. Evers [55] also reported application of 9 Mg ha^{-1} broiler litter added averages of 5.85 kg ha^{-1} Zn, 5.0 kg ha^{-1} Fe, 9.4 kg ha^{-1} Cu, and 6.55 kg ha^{-1} Mn to soil. In another study, it was reported [56] that high Cd levels in soils and vegetables across Sydney, Australia, were due to repeated applications of poultry manures. Animal manure applications to agricultural lands in England and Wales accounted for 25 to 45% of the total annual Cu and Zn inputs [7].

Kingery et al. [26] examined long-term application (15 to 28 years) of poultry litter on nutrient levels in several Ultisols in Alabama. They reported that topsoil Cu and Zn concentrations (2.5 and 10 mg kg^{-1}) in poultry litter-treated soils were higher than topsoil Cu and Zn concentrations (0.75 and 2.2 mg kg^{-1}, respectively) measured in control soils (no history of manure application). Nicholson et al. [7] modeled potential annual trace metal loadings in soil treated with 250 kg N ha^{-1} yr^{-1} from various manure sources. The quantities of trace metals were based on the manure dry matter and typical metal concentrations in manures. Significant quantities of Cu and Zn were added to soil through the application of swine (2.2 and 1.6 kg ha^{-1}), poultry (1.1 and 0.5 kg ha^{-1}), and cattle (1.0 and 0.3 kg ha^{-1}) manures, respectively. These researchers noted that the modeled trace metal loading rates may be higher in areas where Cu- and Zn-enriched swine and poultry manures have been applied for many years [7].

Many studies have suggested additional reasons for trace metal accumulation in manure-treated soils. These reasons include repeated applications of manure to the same field and a low trace metal crop nutrient requirement. Repeated manure applications to the same fields occur because manure transportation costs are high and land availability for manure disposal is limited. Frequently, animal manures are not transported very far, and they are often applied close to the production facility. Land available for manure application continues to decline because of high real estate prices, encroachment of urban sprawl, zoning restriction, and exhaustion of the soil's nutrition assimilation capacity. Expecting some animal producers to locate more land available for manure application may not be economically feasible. Unless directed to cease by a restrictive nutrient management plan, some fields will probably continue to receive trace metal-enriched animal manures.

The low trace metal requirement by crops is also an important reason for their accumulation. Researchers have conducted experiments to determine the sufficiency level of trace metals utilized by agronomic crops (Table 33.4). Data in this table exemplify that the sufficiency range of trace metals in crop tissue is much smaller than for macronutrients (Table 33.4). For example, the nutrient sufficiency range for trace metals like Co and Mo are orders of magnitude smaller than for macronutrients like N and K. Through field experiments, researchers have measured the amount of trace metals removed by harvesting crops. For example, Bermuda grass (*Cynodon dactylon* L.), legumes, and other temperate annual and perennials grasses are commonly used in southern and southeastern U.S. pasture systems to assimilate nutrients contained in animal manures [51,54,55,57,58]. The grass can remove 0.009 and 0.218 kg of Cu and Zn, respectively, per 7.3 Mg/ha yield of above-ground biomass [59].

TABLE 33.4
Sufficiency Range of Macro- and Micronutrients Assimilated by Agronomic Crops

Element	Sufficiency range (mg/kg, dry weight)	Plant part measured in
Macro		
N	1000 to 6000	Leaf tissue
P	200 to 500	Mature leaves
K	1500 to 4000	Recent and mature leaves
Ca	500 to 1500	Mature leaves
Mg	150 to 400	Dry matter
S	150 to 500	Leaf tissue
Micro		
B	20	Dry matter
Co	0.021 to 0.55	Dry matter
Cl	50 to 200	Dry matter
Cu	2 to 20	Leaf tissue
Fe	50 to 75	Leaf tissue
Mn	10 to 200	Leaf tissue
Mo	0.15 to 0.30	Dry matter
Zn	15 to 20	Leaf tissue

Source: Jones Jr., J.B., *Agronomic Handbook, Management of Crops, Soils and their Fertility*. CRC Press, Boca Raton, FL, 2003.

TABLE 33.5
Calcium, Magnesium, Potassium, Copper, Iron, Manganese, and Zinc Content of Broiler Cake, Litter, and Feed

Variables	Ca	Mg	K	Cu	Fe	Mn	Zn
	g kg^{-1}			mg kg^{-1}			
Broiler cake	99.1 (8.7)a	24.4 (2.1)a	125.7 (8.9)a	2763 (72)a	3818 (119)a	2307 (102)a	1848 (92)a
Broiler litter	26.2 (2.4)b	6.1 (0.9)b	30.3 (1.5)b	662 (43)b	1055 (57)b	556 (23)b	36 (27)b
Broiler feed	10.1 (1.3)	1.8 (0.3)	9.0 (1.1)	210 (19)	202 (18)	169 (14)	139 (11)

Notes: Standard error in parentheses; means followed by the same letter in each column (excluding feed) were not significantly different at a 0.05 probability level according to Tukey's test.

Source: Sistani, K.R. et al., *Bioresour. Technol.*, 90(1), 27, 2003.

Novak and Watts [38] examined the effects of applying swine manure effluent to a 1-ha field in North Carolina cropped with coastal Bermuda grass. They estimated that approximately 10.5 and 15.6 kg of Cu and Zn, respectively, were applied annually after spraying 4.32×10^6 L ha^{-1} of swine manure effluent. Performing a mass balance revealed that, after grass Cu and Zn removal with harvested above-ground biomass, approximately 10.49 and 15.38 kg of Cu and Zn, respectively, would remain in the 1-ha field. This shows that the annual rate of Cu and Zn additions wase much higher than the grasses' Cu and Zn removal rate.

The investigation by Novak and Watts [38] is an important demonstration of why trace metals accumulate in soils. If trace metals accumulate to phytotoxic levels, sensitive crops can potentially suffer serious yield declines [24,60,61]. Although agronomic crops vary in their sensitivity to trace

TABLE 33.6
Initial Soil Chemical Analyses[a] and Nutrient Composition of Broiler Litter Applied in 2000 and 2001

	pH	N	P	K	Ca	Mg	Cu	Fe	Mn	Zn
	g kg^{-1}				mg kg^{-1}					
Soil										
0–5 cm depth	6.2	1.59	0.74	0.30	1.09	0.13	29	283	160	35
5–10 cm depth	6.4	0.56	0.35	0.17	0.59	0.09	10	231	192	7
Litter										
May (2000)	7.7	34.9	22.5	29.6	30.1	6.1	687	837	631	416
July (2000)	7.8	32.7	19.8	28.7	29.8	6.5	632	795	703	456
May (2001)	7.4	32.5	20.8	29.1	30.9	6.4	541	1040	657	455
July (2001)	7.6	30.7	18.1	28.3	26.2	5.8	457	702	559	380

[a] Mehlich 3, except for pH and N.

Source: Sistani, K.R. et al., *Agron. J.,* 96, 525, 2004.

TABLE 33.7
Soil Concentrations of Copper, Iron, Manganese, and Zinc at Different Sampling Times in 2000 and 2001

Sampling dates	Soil depth (cm)	Cu	Fe	Mn	Zn
		Mg/kg			
Jan 2000	0–10	19.8 ± 7.2[a]	257.7 ± 36.3	176.5 ± 30.5	21.2 ± 15.3
Feb 2000	0–10	20.7 ± 7.3	236.7 ± 42.3	172.6 ± 29.6	26.8 ± 18.2
Mar 2000	0–10	32.5 ± 6.9	287.1 ± 10.4	153.4 ± 16.1	40.9 ± 11.1
Apr 2000	0–10	43.6 ± 13.2	511.8 ± 70.5	284.5 ± 54.7	57.6 ± 19.5
May 2000	0–10	36.3 ± 8.6	459.2 ± 43.1	250.9 ± 46.4	46.6 ± 16.8
Jun 2000	0–10	50.3 ± 13.6	483.2 ± 29.8	260.6 ± 32.8	56.4 ± 19.3
Jul 2000	0–10	38.2 ± 7.6	321.4 ± 27.2	160.6 ± 23.8	43.0 ± 12.6
Aug 2000	0–10	21.9 ± 6.9	499.5 ± 66.6	239.4 ± 41.1	37.3 ± 10.4
Sep 2000	0–10	27.3 ± 7.7	301.9 ± 31.3	132.9 ± 20.2	31.7 ± 12.5
Oct 2000	0–10	34.7 ± 7.7	423.5 ± 26.2	172.4 ± 21.9	35.7 ± 10.7
Nov 2000	0–10	33.3 ± 7.4	372.4 ± 23.3	156.4 ± 25.8	34.9 ± 10.6
Dec 2000	0–10	25.8 ± 8.9	118.8 ± 1.6	182.2 ± 30.8	39.6 ± 14.2
Mar 2001	0–10	31.0 ± 6.3	421.0 ± 46.8	145.4 ± 17.9	41.0 ± 12.1
Jun 2001	0–10	31.3 ± 6.2	109.6 ± 3.0	125.3 ± 12.5	32.6 ± 10.1
Sep 2001	0–10	37.2 ± 7.2	302.8 ± 36.7	108.1 ± 14.5	47.2 ± 15.8
Dec 2001	0–10	32.8 ± 6.1	220.3 ± 14.9	85.0 ± 11.9	46.0 ± 14.0

[a] Data points are averages of 24 values, ± standard deviations, and extracted by Mehlich 3.

Source: Sistani, K.R. et al., *Bioresour. Technol.*, 90(1), 27, 2003.

metal phytotoxicity [3,62], critical plant available (Mehlich 3 extractable) concentrations in North Carolina soils for sensitive plants have been reported as >120 mg kg^{-1} for Zn and >60 mg kg^{-1} for Cu [62]. Some crops, however, are sensitive to soil Zn concentrations far below 120 mg kg^{-1}. For instance, peanuts (*Arachis hypogaea* L.) are sensitive to Zn concentrations as low as 12 mg kg^{-1} [63]. Because peanuts are sensitive to low soil Zn concentrations, fields used for their production have a Zn concentration limit of 20 mg kg^{-1} [62].

The concern about possible trace metal phytotoxicity and a subsequent decline in crop yields due to manure applications has been previously investigated. These studies have shown that agronomic crops grown in soils treated with animal manure can cause an increase in trace metal concentration in pasture grasses [64], in corn leaves (*Zea mays* L.) [65,66], and in corn ear leaf tissue [67]. In the study by Batey et al. [64], pasture grasses treated with Cu-enriched pig slurry had elevated Cu concentrations, but not to a phytotoxic level. Much of the increase in Cu concentration was attributed to direct foliar contamination during manure application [64]. Korneagy et al. [66] applied approximately 103 kg Cu ha^{-1} as Cu-enriched pig manure over a 3-year period to a corn crop; this resulted in a doubling of the Cu level in corn roots and slight increases in the ear leaves, but did not influence grain yield or Cu concentration in leaves.

Mullins et al. [68] reported similar Cu concentration results in corn ear leaves following application of Cu-enriched swine manure to three Virginia soils. In this study, corn yields did not decline in spite of the high Cu uptake concentrations. Sutton et al. [69] reported that four annual applications of Cu-enriched swine manure (15.3 kg Cu ha^{-1}) neither decreased corn grain yield nor increased Cu concentrations in corn tissues. These studies show that although Cu-enriched manure applied to soils can increase crop tissue Cu concentrations, the increase in Cu uptake is insufficient to influence yields adversely. Except for the sensitivity of peanuts to soil Zn concentrations, examination of the literature suggests a minimal number of reports of decreased crop yields caused by trace metal accumulations in manure-treated soils.

33.4 PATHWAYS FOR OFFSITE METAL TRANSPORT

There are many physically and chemically based pathways for offsite trace metal transport from manure-treated soils. This review will focus on two common pathways: trace metal movement in runoff and leaching through soils. A few field runoff simulation studies have shown high Cu, Fe, and Zn concentrations in runoff from poultry litter-treated soils. Less information exists in the literature documenting runoff metal losses from swine and cattle manure-treated soils, however. With regards to leaching risks, some long-term field studies show limited migration of metals in the soil profile because of strong metal binding by topsoil organic matter.

In contrast to these reports, other field sites treated with manures have revealed that Cu and Zn can leach to subsoil depths. Leaching of trace metals in manure-treated soils is facilitated by dissolved organic carbon compounds [40]. It is important that the ability of offsite trace metal transport into water bodies and aquatic ecosystems be known because studies have reported that metal enrichment can pose a significant threat to water quality [23] and can cause detrimental impacts on aquatic plants, shellfish, and other wildlife [70].

33.4.1 RUNOFF

The few investigations of trace metal movement via runoff from manure-treated soils have reported that runoff losses from fields treated with poultry litter can contain measurable concentrations of trace metals such as Cu, Fe, and Zn [25,71]. Moore et al. [25] reported that runoff collected from plots in Arkansas treated with 2 to 9 Mg ha^{-1} of poultry litter contained an average soluble Cu concentration of 0.93 mg L^{-1} and that runoff from control plots averaged 0.01 mg Cu L^{-1}. In a similar study, runoff samples from plots in Arkansas treated with 5 Mg ha^{-1} of poultry litter had average concentrations of Fe (0.2 mg L^{-1}) and Zn (0.06 mg L^{-1}) that were not high enough to be a direct threat to aquatic life [71]. Concentrations above 0.3 mg L^{-1} and 0.18 mg L^{-1} of Fe [72] and Zn [73], respectively, are judged to be potentially harmful to freshwater fish.

On the other hand, Cu concentrations (mean of 0.45 mg L^{-1}) in runoff samples were high enough to be of environmental concern [71]. Elevated Cu concentrations in streams can be toxic to algae [70] and maximum concentrations of 0.02 mg L^{-1} are recommended to protect freshwater fish. These studies show that runoff samples collected from plots treated with poultry litter can contain elevated Cu concentrations that, if not diluted, can be a concern for fish in freshwater surface water systems. It can also be perceived that the risk of trace metal contamination of water bodies might not be as great as considered, despite elevated concentrations at the soil surface, because interaction of trace metals with topsoil organic matter may limit transport of trace metals across the landscape. Further studies are needed to evaluate trace metal movement in runoff, particularly using several different manure types (e.g., swine, cattle, etc.).

33.4.2 Leaching

Leaching of trace metals in manure-treated fields is commonly investigated by sampling topsoil and subsoil depths and extracting for available trace metals using various reagents (e.g., double acids, Mehlich 3, chelating reagents, etc.). This approach has been used in several studies in which soils were treated with poultry litter [26], swine manure [13,38,64], and cattle manure [74,75]. These investigations have reported contrasting results concerning trace metal leaching to subsoil depths.

Trace metals are generally regarded as relatively immobile in most soils because they are bound to soil organic matter [30,76] and are sorbed by Fe–Mn oxides and clays, and precipitated as carbonates, hydroxides, and phosphates [77]. Batey et al. [64] applied up to 12.1 kg ha^{-1} of Cu-enriched hog manure slurry onto a field containing a mixture of perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.). Analyses of soil profile samples taken from this field showed that trace metal accumulation was limited to the top several centimeters of the soil profile [64]. Lack of leaching to subsoil depths supports the contention that Cu will mostly accumulate in topsoil by forming strong bonds with various soil organic and inorganic components. Other manure application studies related to Cu accumulation or leaching in soil reported similar results [67,74,75].

Few investigations have reported trace metal leaching to subsoil depths in fields treated with swine manure [13,38] and poultry litter [26]. King et al.[13] treated two North Carolina Ultisols with swine lagoon effluent (1340 kg N ha^{-1} yr^{-1}) and reported significantly different Cu concentrations between control and treated soils in samples collected between 15 and 30 cm deep. In this study, swine manure treatment on topsoil and subsoil Zn and Mn concentrations had no significant effects.

Novak and Watts [38] collected topsoil (0 to 15 cm) and subsoil samples (15 to 45 cm deep) in North Carolina Ultisols treated for 10 years with swine manure effluent. Nearby soils without a history of swine manure effluent application were collected in a similar manner to that used for controls. Copper and Zn were extracted from the soils using Mehlich 3 extractant that contains the chelating agent ethylenediaminetetraacetic acid (EDTA) [78]. After 10 years of swine effluent application, topsoil and subsoil mean Cu concentrations in the treated soils were similar to those of controls (Table 33.8). Novak and Watts [38] found higher mean Zn concentrations in treated topsoils than in those of the controls. In subsoil depths (15 to 45 cm), however, the Mehlich 3 extractable mean Cu and Zn concentrations in treated vs. control soils showed no differences, indicating very minimal leaching (Table 33.8).

In a similar study, Kingery et al. [26] examined the effects of long-term (15 to 28 years) poultry litter applications (6 and 22 Mg/ha/yr) to some Ultisols in the Sand Mountain region of Alabama. They collected topsoils and subsoils and extracted for available Cu and Zn, using a double acid extractant [79]. These workers found the highest Cu concentrations in topsoils (0 to 15 cm deep) treated with litter compared to samples without litter application. Additionally, litter-treated soils collected at 30 cm had higher mean Cu concentrations than in samples without litter application. Below 45 cm, the mean Cu concentrations showed no differences among treatments [26]. Similarly, the greatest Zn concentrations were measured in topsoils treated with poultry litter. There were minimal differences in mean Zn concentrations between treatments measured in subsoil samples (30 to 45 cm deep). In work done with cattle manure applications, Chang et al. [75] found Zn accumulations to a depth of 30 cm.

TABLE 33.8
Mean Cu and Zn Concentrations Extracted Using Mehlich 3 Reagent from Control Soils (0 years) and from Soils after 10 years of Swine Manure Effluent Application

Metal	Depth (cm)	Control soils (0 yrs)[a] (mg/kg)	Soils treated for 10 years (mg/kg)
Cu	0 to 15	0.48 (0.30)a	3.59 (2.77)a
	15 to 45	0.27 (0.10)a	0.86 (0.46)a
Zn	0 to 15	1.69 (1.39)b	7.87 (4.67)c
	15 to 45	1.39 (0.78)d	1.33 (0.41)d

[a] Mean Cu and Zn concentrations after 0 vs. 10 years' effluent application were tested by depth using a *t*-test and means followed by a different letter were significantly different at a $P < 0.05$ level of rejection.

Source: Novak, J.M. and Watts, D.W., *Trans. ASAE* (in review), 2004.

The leaching of Cu and Zn to subsoil depths has been explained by metal chelation with soluble organic compounds from the litter [80,81]. It appears that the highest trace metal concentrations in manure-treated fields are measured in topsoil. By extracting subsoils and finding an increase in Cu and Zn concentrations, scientists have suggested that some downward leaching of Cu and Zn can occur in manure-treated soils. Measured subsoil concentration increases are, however, small. Nevertheless, lack of substantial Cu and Zn concentrations in subsoil depths cannot exclude the fact that soluble forms of trace metals can leach through the soil profile and could cause enrichment in shallow ground water. Trace metal enrichment of shallow ground water as a result of leaching has not been sufficiently documented in soils treated with animal manures. Additional studies examining trace metal concentrations in shallow ground water beneath manure-treated fields should be conducted to determine whether trace metal leaching is a significant water quality issue.

33.5 REMEDIATION STRATEGIES

When trace metals accumulate in soils to threshold concentrations that pose a detrimental agronomic or environmental effect, a number of remediation strategies are available to reduce or immobilize their concentrations. This review will focus on two nondestructive remediation strategies: phytoremediation and *in situ* chemical immobilization using chemical amendments. Conventional remediation strategies like incineration, soil washing, solidification, or removal of contaminated soil are costly and often harmful to desirable soil properties like organic matter, cation exchange capacity, and texture. More recently, nondestructive remediation technologies have been employed that do not require offsite transport of contaminated materials; instead, metals are removed by growing crops or immobilized as insoluble metal forms by adding a chemical amendment.

33.5.1 PHYTOREMEDIATION

The development of phytoremediation, employing a plant-based approach to remediate metals, has previously been reviewed [33–35,37]. Crops utilized in phytoremediation can extract the target metal from soil and then hyperaccumulate the metal in above-ground plant biomass [35]. The metal-enriched plant biomass can be harvested and removed from the contaminated site, thus avoiding extensive excavation and disposal costs, and loss of topsoil through removal [82]. Plants capable of hyperaccumulating metals are usually specific to one target metal [83]. Because of this trait, maximizing metal removal through phytoremediation probably will require growth and cultivation of several sequential plants to reduce soil metal concentrations to acceptable levels [33].

The success of the phytoremediation process depends on adequate plant yields, high metal concentration in above-ground plant biomass, and harvesting of plant biomass to ensure metal removal from the contaminated site [35]. Hyperaccumulator plants possess an ability to take up abnormally high amounts of metals in their shoots [35]. Baker and Brooks [84] have reported a number of plant species capable of accumulating exceptionally high concentrations (usually > 0.1% in leaf dry matter) of Ni, Zn, Cu, Co, and Pb in their above-ground plant parts. These metal hyperaccumulator plant species have been recognized on the basis of dry leaf matter metal concentrations, often growing in mine waste areas with high metal concentrations.

Baker et al. [83] reported that a few plants in the genera *Thlaspi* and *Cardaminopsis* in the Brassicaceae family are capable of accumulating Zn to 1.0% (dry weight). Several other *Thlaspi* species isolated from lead/zinc-mineralized soils in central European countries have been reported with up to 2% Zn in leaf tissue [85]. High Cu concentrations (up to 13,700 $\mu g\ g^{-1}$) have been measured in leaf tissue of *Aeollanthus biformifolius* De Wild. (Lamiaceae), a dwarf perennial herb endemic to the southern part of Zaire [86]. Baker and Brooks [84] have identified 26 hyperaccumulator plants for Co (> 1000 $\mu g\ g^{-1}$), all of which are native to Zaire. The majority are slow growing herbs in a range of families including Lamiaceae, Scrophulariaceae, Asteraceae, and Fabaceae [83]. Baker et al. [83] reported that the highest Co concentration measured in a hyperaccumulator was 10, 200 $\mu g\ g^{-1}$ in *Haumaniastrum robertii* (Robyns) Duvign. Et Plancke (Lamiaceae).

Hyperaccumulator plant species are slow growing with low biomass production, so their utilization without some form of trait modification is limited. Therefore, using plant species with high biomass production, such as pea (*Pisum sativum* L.), oat (*Avena sativa* L.), canola, (*Brassica napus* L.), and Indian mustard (*Brassica juncea* L. Czern.), has been suggested to enhance metal uptake and removal from the contaminated site [82,87]. These plants can produce more above-ground biomass; however, they have other limitations, such as their lower metal uptake amount and need for high amounts of macronutrients like N and P.

Another geochemical factor that limits the success of phytoremediation is the metal's bioavailability [88,89]. Metal bioavailability can be increased by adding a chelating agent like EDTA to the metal-contaminated soils. This approach was employed by Shen et al. [90], who treated Pb-contaminated soil with EDTA. They reported that cabbage (*Brassica rapa* L.) shoots had elevated Pb concentrations between 4620 and 5010 mg/kg dry matter compared to controls with only 126 and 101 mg/kg at days 7 and 14, respectively, after treatment. Other investigations have added chelating agents such as HEDTA (hydroethylenediaminetriacetic acid) and NTA (nitrilotriacetic acid) to enhance metal uptake by plants in pot and field experiments [82,91].

Although it has been recognized since the 1990s that metal uptake by hyperaccumulator plants could be a useful technology for metal remediation, slow growth coupled with some soil ediphatic conditions has limited its successful application. Phytoremediation is limited by soil ediphatic conditions that inherently limit plant growth, e.g., lack of water, low/high soil pH values, and availability of nutrients [35]. If growth conditions are improved by adjusting soil pH, optimizing soil moisture, and supplying micronutrients, phytoremediation may be a viable technology for trace metal reduction. To date, the utilization of phytoremediation has not proved to be an economically viable solution to reduce soil trace metal concentrations.

33.5.2 Immobilization Using Chemical Amendments

It has been mentioned previously that some conventional trace metal remediation technologies can reduce metal concentrations, but can also be destructive to the background media. These forms of metal remediation technologies may be unsuitable in situations in which the background material may be used to support subsequent plant growth for recreational purposes. Recent studies have demonstrated that *in situ* contaminant immobilization may be the preferred approach to remediate metals in soils and shallow sediments [92,93].

In situ immobilization methods typically reduce the mobility and bioavailability of the target metal by redirecting solid-phase speciation in favor of less labile phases through sorption or precipitation modes [94,95]. This type of technology requires the addition of a chemical amendment to the contaminated media that has a higher affinity for the metal than the background matrix. The amendment, however, should not impair ediphatic processes responsible for maintaining good soil quality. Otherwise, other chemical and physical problems may be created by adding chemical amendments to contaminated soil or sediments.

Many additives have been screened for their potential to immobilize heavy metals in soils. Many of these additives are alkaline materials such as lime [96,97], zeolites [80], incinerator ashes [98], Fe-rich byproducts from TiO_2 pigment production [99], and hydroxyapatite [100]. In addition to the amendment fixing the metal, additions of alkaline amendments will increase soil pH values, thus causing other exchange sites (present on clay surfaces, iron oxides, and organic matter) to be more reactive to metal binding [80]. Applications of chemical amendments have been shown to bind significant amounts of Co, Cu, and Zn in contaminated soils and sediments. For example, apatite was effective at binding Co, Cu, and Zn in contaminated media [92,93]. Additionally, significant binding of Zn in contaminated materials by Fe-oxides [99], and by zeolites [80,92] has been reported.

Some problems have been noted with the use of chemical amendments to immobilize metals. The amendment may contain trace metal impurities that may exceed environmental limits if applied at sufficiently high concentrations. Additionally, because the same metal sorption mechanisms will also bind nontarget macronutrients such as P and Fe, amendment may reduce the concentrations of essential plant nutrients [92].

33.6 CONCLUSIONS

Trace elements are inorganic components in feeds and are part of the chemical makeup of the animal's body. They are essential for maintaining various physiological processes and are required in sufficient amounts to avoid health disorders, reproductive problems, or disruption in the production of animal products for consumers (milk, wool, eggs, etc.). Consequently, to reduce the incidence of animal health problems and disruption in product generation, trace metals are supplemented in the animal's daily rations. Unfortunately, in some cases, trace elements are supplemented in amounts that exceed the daily recommendations. Under these scenarios, trace metals not assimilated by the animal digestive system resulted in the production of trace metal-rich manures. Crops do not require large amounts of trace metals, and the scientific literature has shown that continual application of trace metal-enriched manures to the same fields results in their accumulation.

Trace metal accumulation in soils is not an isolated incident, but rather is a worldwide issue because it has been reported in Europe, Asia, and the U.S. Agronomic and environmental issues concerning trace metal accumulation have been discussed in this review. Few studies have shown a phytotoxic effect of trace metals causing a serious crop yield decline. One study showed that high soil Zn contents can be phytotoxic to sensitive crops like peanuts. Except for peanuts, trace metal accumulation in manure-treated soils has not caused widespread crop yield declines.

As a matter of fact, some investigations have shown that Cu-enriched manure applications to corn have not resulted in elevated Cu concentrations in tissue samples. Nevertheless, low trace metal uptake by agronomic crops implies that metals will continue to accumulate in manure-treated soils. If current manure management protocols do not change for the next 100 years, some fields in Europe may contain soils with sufficient trace metal concentrations for crop growth of sensitive crops to be adversely affected [10].

The buildup of trace metals in soils probably should be a concern because it may contribute to future environmental issues. For instance, studies have shown that runoff from manure-treated fields had elevated Cu concentrations that, if undiluted prior to entry into a water body, could be toxic to fish. Data on the long-term consequences of trace metal accumulation in soils with respect to ground- and surface water enrichment are lacking. Long-term monitoring of Cu and Zn concentrations in ground- and surface water systems in watersheds high in animal production may be needed to address potential issues of water quality impairment by trace metals.

Countermeasures to reduce trace metal concentrations in soils include plant removal (phytoremediation) and immobilizing the metal using chemical amendments. Both of these technologies have been shown to be effective at reducing metal concentrations, but they have inherent limitations. Areas where phytoremediation could be used may be inhospitable for plant growth, thereby requiring additional management inputs to produce a harvestable crop. Chemical amendments added to soils may bind nontarget plant nutrients and can contain trace metals as contaminants.

Perhaps the most significant countermeasure to reduce trace metal accumulation is simply by a reduction in the trace metal supplementation in feedstuffs [41]. A possible mechanism to achieve this is to lower the maximum permitted trace metal levels in feedstuffs and feed additives. A problem with this approach is that some animals may suffer health problems because of a reduction in trace metal uptake. Further measures, such as improved trace metal assimilation through reformulating the organic/inorganic compounds that carry the trace elements or the addition of phytase, can complement the reduction or even make the reduction feasible.

REFERENCES

1. Kabata–Pendias, A. and Pendias, H., *Trace Elements in Soils and Plants*, CRC Press, Boca Raton, FL, 1984.
2. Pierzynski, G.M., Sims, J.T., and Vance, G.F., *Soils and Environmental Quality.* Lewis Publ., Boca Raton, FL, 1994.
3. Marschner, H., *Mineral Nutrition of Higher Plants*, 2nd ed., Academic Press, New York, 1995.
4. Proctor, J. and Woodell, S.R.J., The ecology of serpentine soils. *Adv. Ecol. Res*., 9, 255, 1975.
5. Harsh, J.B. and Doner, H.E., Characterization of mercury in a river-wash soil. *J. Environ. Qual.,* 10, 333, 1981.
6. Capar, S.G., Tanner, Friedman, and Boyer, Multielement analysis of animal feed, animal wastes, and sewage sludge. *Environ.Sci. Technol*., 7, 785, 1978.
7. Nicholson, F.A., Chambers, Williams, and Unwin, Heavy metal contents of livestock feeds and animal manures in England and Wales. *Bioresources Technology.,* 23, 23, 1999.
8. Van Heugten, E., O'Quinn, Funderburke, Flowers, and Spears, Effects of supplemental trace mineral levels on growth performance, carcass characteristics, and fecal mineral excretion in growing-finishing swine. Available at: (http://mark.asci.ncsu.edu/SwineReports/2002/vanheugten1.htm), 2002.
9. Kunkle, W.E., Carr, Carter, and Bossard, Effects of flock and floor type on the levels of nutrient and heavy metals in broiler litter. *Poultry Sci*., 60, 1160, 1981.
10. Van Driel, W. and Smilde, K.W., Micronutrients and heavy metals in Dutch agriculture. *Fertilizer Res.*, 25, 115, 1990.
11. Miller, R.E., Lei, X., and Ullrey, D.E., Trace elements in animal nutrition. In: *Micronutrients in Agriculture,* 2nd ed., J.J. Mortvedt (Ed.), Soil Science Society America, Madison, WI, 1991, 593.
12. Jones Jr., J.B., *Agronomic Handbook, Management of Crops, Soils and their Fertility.* CRC Press, Boca Raton, FL, 2003.
13. King, L.D. et al., Westerman, Cummings, Overcash, and Burns, Swine lagoon effluent applied to "coastal" Bermuda grass: II. Effects on soil. *J. Environ. Qual.,* 14, 14, 1985.
14. Eneji, A.E., Honna, T., and Yamamoto, S., Manuring effect on rice grain yield and extractable trace elements in soils. *J. Plant Nutr.*, 24, 967, 2001.
15. Hansen, M.N., Risk of heavy metal accumulation in agricultural soil when livestock manure and organic waste is used for fertilizer. In *Proc. Global Perspective in Livestock Waste Management, 4th International Livestock Waste Management Symposium and Technology Expo*., Penang, Malaysia, 2002, 269.
16. Franzluebbers, A.J., Wilkinson, S.R., and Stuedemann, J.A., Bermuda grass management in the southern Piedmont, USA: IX. Trace elements in soil with broiler litter application. *J. Environ. Qual*., 33, 778, 2004.

17. Senesi, G.S., Baldassarre, Senesi, and Radina, Trace element inputs into soils by anthropogenic activities and implications for human health. *Chemosphere,* 39, 343, 1999.
18. Alonso, M.L., Benedito, Miranda, Castillo, Hernandez, and Shore, The effect of pig farming on copper and zinc accumulation in cattle in Galicia (Northwestern Spain). *Vet. J.*, 160, 259, 2000.
19. Parkinson, R.J. and Yells, R., Copper content in soil and herbage following pig slurry application to grassland. *J. Agric. Sci.*, 105, 183, 1985.
20. Christie, P. and Beattie, J.M., Grassland soil microbial biomass and accumulation of potentially toxic metals from long-term slurry application. *J. Appl. Ecol.*, 26,597, 1989.
21. Poole, D.B., McGrath, Fleming, and Moore, Effects of applying copper-rich pig slurry to grassland. *Irish J. Agric. Res.*, 29, 34, 1990.
22. Pierzynski, G.M., Sims, J.T., and Vance, G.F., *Soils and Environmental Quality.* 2nd ed. CRC Press, Boca Raton, FL, 1990.
23. Xue, W., Nhat, Gachter, and Hooda, The transport of Cu and Zn from agricultural soils to surface water in small catchment. *Adv. Environ. Res.,* 8, 69, 2003.
24. Wong, M.H. and Bradshaw A.D., A comparison of the toxicity of heavy metals, using root elongation of rye grass (*Lolium prenne.*). *New Phytol.,* 91, 255, 1982.
25. Moore, P.A., Jr., Daniels, Gilmour, Shreve, Edwards, and Wood, Decreasing metal runoff from poultry litter with aluminum sulfate. *J. Environ. Qual.*, 27, 92, 1998.
26. Kingery, W.L., Wood, Delaney, Williams, and Mullins, Impact of long-term land application of broiler litter on environmentally related soil properties. *J. Environ. Qual.*, 23, 139, 1994.
27. Li, Z. and Shuman, L.M., Mobility of Zn, Cd, and Pb in soils as affected by poultry litter extract I. leaching in soil columns. *Environ. Pollut.*, 95, 219, 1997.
28. Hesterberg, D., Biogeochemical cycles and processes leading to changes in mobility of chemicals in soils. *Agric, Ecosyst. Environ.,* 67, 121, 1998.
29. del Castilho, P., Chardon, W.J., and Salomons, W., Influence of cattle-manure slurry application on the solubility of cadmium, copper, and zinc in manured acidic, loamy-sand soil. *J. Environ. Qual.*, 22, 689, 1993.
30. Stevenson, F.J., *Humus Chemistry.* 2nd ed. John Wiley & Sons, New York, 1994.
31. Chowdhury, A.K., McLaren, Cameron, and Swift, Fractionation of zinc in some New Zealand soils. *Commun. Soil Sci. Plant. Anal.*, 28, 301, 1997.
32. Yin, Y., Impellitteri, You, and Allen, The importance of organic matter distribution and extract soil:solution ratio on the desorption of heavy metals from soils. *Sci. Total Environ.*, 287, 107, 2002.
33. Raskin, I., Kumar, Dushenkov, and Salt, Bioconcentration of heavy metals by plants. *Curr. Opin. Biotechnol.*, 5, 285, 1994.
34. Salt. D.E., Baylock, Kumar, Dushenkov, Ensley, Chet, and Raskin, Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. *Biotechnology,* 13, 468, 1995.
35. Wenzel, W.W., Adriano, Salt, and Smith, Phytoremediation: a plant-microbe-based remediation system, In *Bioremediation of Contaminated Soils.* D.C. Adriano, J.M. Bollag, W.R. Frankenburg, and R.C. Sims (Eds.), American Society of Agronomy Monograph 37. ASA, Madison, WI, 1999, 457.
36. Alloway, B.J., *Heavy Metals in Soils*. 2nd ed. Blackie, Glasgow, Scotland, 1995.
37. McGrath, S.P., Dunham, S.J., and Correll, R.L., Potential for phytoextraction of zinc and cadmium form soils using hyperaccumulator plants. In *Phytoremediation of Contaminated Soil and Water.* N. Terry and G.S. Banuelos (Eds.), CRC Press, Boca Raton, FL, 2000, 110.
38. Novak, J.M. and Watts, D.W., Copper and zinc accumulation, profile distribution, and crop removal in coastal plain soils receiving long-term, intensive applications of swine manure. *Trans. ASAE* (in review), 2004.
39. Hostetler, C.E., Kincaid, R.L., and Mirando, M.A., The role of essential trace elements in embryonic and fetal development in livestock. *Vet. J.*, 166, 125, 2003.
40. Bolan, N.S. and Adriano, D.C., Distribution and bioavailability of trace elements in livestock and poultry manure byproducts. *Crit. Rev. Environ. Sci. Technol.* 34(3): 291–338, 2004.
41. Jondreville, C., Revy, P.S., and Dourmad, J.Y., Dietary means to better control the environmental impact of copper and zinc by pigs from weaning to slaughter. *Livestock Prod. Sci.,* 84, 147, 2003.
42. Brumm, M.C., Sources of manure: swine. In *Animal Waste Utilization*, *Effective Use of Manure as a Soil Resource*. J.L. Hatfield and B.A. Stewart (Eds.), Ann Arbor Press, MI, 1998, 49.

43. Poulsen, H.D., Zinc and copper as feed additives, growth factors or unwanted environmental factors. *J. Anim. Feed Sci.,* 7, 135, 1998.
44. Spears, J.W., Creech, B.A., and Flowers, W.L., in *Proc. Reducing Copper and Zinc in Swine Waste through Dietary Manipulation*, *Anim. Waste Manage. Symp.* G.B. Havenstein (Ed.), 1999, 179.
45. Dorton, K.L., Engle, Hamar, Sicilano, and Yemm, Effects of copper source and concentration on copper status and immune functions in growing and finishing steers. *Anim. Feed Sci. Tech.,* 110, 31, 2003.
46. Unwin, R.J., Copper in pig slurry: some effects and consequences of spreading on grassland. In *Inorganic Pollution in Agriculture*, MAFE reference book no. 326. London, 1977, 306.
47. Edwards, D.R. and Daniels, T.C., Environmental impacts of on-farm poultry waste disposal — a review. *Bioresour. Technol*., 41, 9, 1992.
48. Barker, J.C. and Zublena, J.P., Livestock manure nutrient assessment in North Carolina, In *Proc. 7th International Symposium Agricultural Wastes*. American Society of Agricultural Engineers, St. Joseph, MO, 1995, 98.
49. Sistani, K.R., Adeli, Brink, Tewolde, and Rowe, Seasonal and management impact on broiler cake nutrient composition. *J. Sustainable Agric.,* 24(1): 27–37, 2003.
50. Sistani, K.R., Brink, McGowen, Rowe, and Oldham, A change of management practice among broiler producers: broiler cake vs. broiler litter. *Bioresour. Technol*., 90(1), 27, 2003.
51. Sistani, K.R., Pederson, Brink, and Rowe, Nutrient uptake by ryegrass cultivars and crabgrass from a highly phosphorus-enriched soil. *J. Plant Nutr.,* 26(12), 2521, 2003.
52. Tewolde, H., Sistani, K.R., and Rowe, D.E, Broiler litter as a complete nutrient source for cotton. In *Proceedings of the Beltwide Cotton Conferences*, D.A. Richter (Ed.), San Antonio, 2004.
53. Bagley, C.P., Evans, R.R., and Burdine, W.B., Jr., Broiler litter as a fertilizer or livestock feed. *J. Prod. Agric*., 9, 342, 1996.
54. Brink, G.E., Rowe, Sistani, and Adeli, Bermudagrass cultivar response to swine effluent application. *Agron. J.,* 95(3), 597, 2003.
55. Evers, G.W., Ryegrass-Bermuda grass production and nutrient uptake when combining nitrogen fertilizer with broiler litter. *Agron. J*., 94, 905, 2002.
56. Jinadasa, K.B., Milham, Hawkins, Cornish, Williams, Kaldor, and Conroy, Survey of cadmium in vegetables and soils of greater Sydney, Australia. *J. Environ. Qual.,* 26, 924, 1997.
57. Brink, G.E., Pederson, Sistani, and Fairbrother, Uptake of selected nutrients by temperate grasses and legumes. *Agron. J*., 93, 887, 2001.
58. Brink, G.E., Rowe, D.E., and Sistani, K.R. Broiler litter application effects on yield and nutrient uptake of "Alicia" Bermuda grass. *Agron. J*., 94, 911, 2002.
59. Zublena, J.P., Soil facts: nutrient removed by crops in North Carolina. *North Carolina Cooperative Extension Service Bulletin. AG-439-16*. Available at: (http://www.soils.ncsu.edu/publications/soilfacts/AG-439-16/), 1991
60. Brady, N.C., *The Nature and Properties of Soils*. 9th ed. Macmillian, New York, 1984.
61. Whitehead, D.C., *Nutrient Elements in Grassland: Soil–Plant Relationships*. CABI Publishers, New York, 2000.
62. Tucker, M.R., Stokes, D.H., and Stokes, C.E., Heavy metals in North Carolina soils: occurrence and significance. North Carolina Department of Agriculture and Consumer Services, Raleigh, NC. Available at; (http://www.ncagr.com/agronomi/pdffiles/hflyer.pdf), 2003.
63. Kiesling, T.C., Lauer, Walker, and Henning, Visual, tissue, and soil factors associated with Zn toxicity of peanuts. *Agron. J.*, 69, 765, 1977.
64. Batey, T.E., Berryman, C. and Line, C., The disposal of copper-enriched pig manure on grasslands. *J. Br. Grassland Soc.*, 27, 139, 1972.
65. Wallingford, G.W., Murphy, Powers, and Manges, Effects of beef-feedlot manure and lagoon water on iron, zinc, manganese and copper content in corn and in DTPA soil extracts. *Soil Sci. Soc. Am. Proc.*, 39, 482, 1975.
66. Kornegay, E.T., Hedges, Martens, and Kramer, Effect of soil and plant mineral levels following application of manures of different copper levels. *Plant Soil*, 45, 151, 1976.
67. Payne, G.G., Martens, Kornegay, and Lindemann, Availability and form of copper in three soils following eight annual applications of copper-enriched swine manure. *J. Environ. Qual.,* 17, 740, 1988.

68. Mullins, G.L., Martens, Gettier, and Miller, Form and availability of copper and zinc in a Rhodic Paleudult following long-term $CuSO_4$ and $ZnPO_4$ applications. *J. Environ. Qual.*, 11, 573, 1982.
69. Sutton, A.L., Nelson, Mayrose, and Kelly, Effect of copper levels in swine manure on corn and soil. *J. Environ. Qual.*, 12, 198, 1983.
70. Manahan, S.E., *Environmental Chemistry*, 5th ed., Lewis Publishers, Chelsea, MI, 1991.
71. Edwards, D.R., Moore Jr., Daniels, Srivastava, and Nichols, Vegetative filter strip removal of metals in runoff from poultry litter-amended fescue grass plots. *Trans. Am. Soc. Agric. Eng.*, 40, 121, 1997.
72. National Academy of Sciences, National Academy of Engineering (NAS/NAE), Water quality criteria, Washington, D.C., U.S. Government Printing Office, 1972.
73. U.S. Environmental Protection Agency (USEPA), Water quality criteria. *Fed. Reg*. Washington, D.C., 1980.
74. Kuo, S., Effects of drainage and long-term manure application on nitrogen, copper, zinc, and salt distribution and availability in soils. *J. Environ. Qual.*, 19, 365, 1981.
75. Chang, C., Sommerfeldt, T.G., and Entz, T., Soil chemistry after eleven annual applications of cattle feedlot manure. *J. Environ. Chem.*, 20, 475, 1991.
76. McLaren, R.G. and Crawford, D.V., Studies on soil copper. II. The specific adsorption of copper by soils. *J. Soil Sci.,* 24, 443, 1973.
77. McBride, M., *Environmental Chemistry of Soils*. Oxford University Press, New York, 1994.
78. Mehlich, A., Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.*, 18, 1, 1984.
79. Southern Cooperative Series, Reference soil test methods for southern region of the United States. *Southern Cooperative Service Bulletin 289*. Georgia Agricultural Experimentation Station, Athens, GA, 1983.
80. Oste, L.A., Lexmond, T.M., and Van Riemsdijk, W.H., Metal immobilization in soils using synthetic zeolites. *J. Environ. Qual.*, 31, 813, 2002.
81. Bolan, N., Adriano, Mani, and Khan, Adsorption, complexation, and phytoavailability of copper as influenced by organic manure. *Environ. Toxicol. Chem.,* 22, 450, 2003.
82. Blaylock, M.J., Salt, Dushenkov, Zakharova, Gussman, Kapulnik, Ensley, and Raskin, Enhanced accumulation of Pb in Indian mustard by soil-applied chelating agents. *Environ. Sci. Technol.,* 31, 860, 1997.
83. Baker, A.J., McGrath, Reeves, and Smith, Metal accumulator plants: a review of the ecology and physiology of biological resources for phytoremediation of metal-polluted soils, In: N. Terry (Ed.), *Phytoremediation*. Ann Arbor Press, MI, 1989, 86.
84. Baker, A.J. and Brooks, R.R., Terrestrial higher plants which hyperaccumulate metallic elements — a review of their distribution, ecology and phytochemistry. *Biorecovery*, 1, 81, 1989.
85. Reeves, R.D. and Brooks, R.R., Hyperaccumulation of lead and zinc by two metallophytes from mining areas in Central Europe. *Environ. Pollut.*, 31, 277, 1983.
86. Malaisse, F., Gregoire, Brooks, Morrison, and Reeves, *Aeolanthus biformifolius* De Wild.: a hyperaccumulator of copper from Zaire. *Science,* 199,887, 1978.
87. Banuelos, G.S., Ajwa, Mackey, Wu, Cook, Akohoue, and Zambruzuski, Evaluation of different plant species for phytoremediation of high soil selenium. *J. Environ. Qual.*, 26, 639, 1997.
88. Davis, A., Drexler, Ruby, and Nicholson, Micromineralogy of mine wastes in relation to lead bioavailability, Butte Montana. *Environ. Sci. Technol.*, 27, 1415, 1993.
89. Zhang, M., Alva, Li, and Calvert, Chemical association of Cu, Zn, Mn, and Pb in selected sandy citrus soils. *Soil Sci.*, 162, 181, 1997.
90. Shen, Z.G., Li, Wang, Chen, and Chua, Lead phytoextraction from contaminated soil with high-biomass plant species. *J. Environ. Qual.*, 31, 1893, 2002.
91. Kayser, A., Wenger, Keller, Attinger, Felix, Gupta, and Schulin, Enhancement of phytoextraction of Zn, Cd, and Cu from calcareous soils: the use of NTA and sulfur amendments. *Environ. Sci. Technol.*, 34, 1778, 2000.
92. Knox, A., Seaman, Mench, and Vangronsveld, Remediation of metal- and radionuclide-contaminated soils by *in situ* stabilization techniques, in I.K. Iskander (Ed). *Environmental Restoration of Metal Contaminated Soils*. Ann Arbor Press, Chelsea, MI., 2000, 21.
93. Seaman, J., Meehan, T., and Bertsch, P., Immobilization of ^{137}Cs and U in contaminated sediments using soil amendments. *J. Environ. Qual.,* 30, 1206, 2001.

94. Knox, A., Kaplan, Adriano, Hinton, and Wilson, Apatitie and phillipsite as sequestering agents for metals and radionuclides. *J. Environ. Qual.,* 32, 515, 2003.
95. Seaman, J.C., Hutchinson, Jackson, and Vulava, *In situ* treatment of metals in contaminated soils with phytate. *J. Environ. Qual.*, 32, 153, 2003.
96. Hooda, P.S. and Alloway, B.J., The effects of liming on heavy metal concentrations in wheat, carrots and spinach grown on previously sludge-applied soils. *J. Agric. Sci.*, 127, 289, 1996.
97. Singh, B.R. and Myhr, K., Cadmium uptake by barley as affected by Cd sources and pH levels. *Geoderma*, 84, 185, 1998.
98. Vangronsveld, J., Colpaert, J., and Van Tichelsen, K., Reclamation of a bare industrial area contaminated by nonferrous metals: physicochemical and biological evaluation of the durability of soil treatment and revegetation. *Environ. Pollut.,* 94, 131, 1996.
99. Chlopecka, A. and Adriano, D.C., Mimicked *in situ* stabilization of metals in a cropped soil: bioavailability and chemical form of zinc. *Environ. Sci. Technol.,* 30, 3294, 1996.
100. Boisson, J., Ruttens, Mench, and Vangronsveld, Evaluation of hydroxyapatite as a metal immobilization soil additive for the remediation of polluted soils. Part 1. Influences of hydroxapatite on metal exchangeability in soil, plant growth and plant metal accumulation. *Environ Pollut.,* 104, 225, 1999.
101. Sistani, K.R., Brink, Adeli, Tewolde, and Rowe, Year-round soil nutrient dynamics from broiler litter application to three Bermuda grass cultivars. *Agron. J.,* 96, 525, 2004.
102. Thompson, L.M. and Troeh, F.R., *Soils and Soil Fertility.* 4th ed. McGraw–Hill, New York, 1993.
103. Arora, C.L., Nayyar, and Randhawa, Note on secondary and microelement contents of fertilizers and manures. *Indian J. Agric. Sci.,* 45, 80, 1975.
104. Adriano, D.C. *Trace Elements in the Terrestrial Environment*. Springer–Verlag, Berlin, 1986.