Published September, 1994

Trace and Toxic Metals in Wetlands—A Review

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ABSTRACT

The mobility and plant availability of many trace and toxic metals in wetland soils is often substantially different from upland soils. Oxidation-reduction (redox) and associated pH changes that occur in soils as a result of flooding or drainage can affect the retention and release of metals by clay minerals, organic matter, iron oxides, and, for coastal wetlands, sulfides. Except where a flooded soil or sediment becomes strongly acid upon drainage and oxidation, as sometimes occurs, the processes immobilizing metals tend to be complimentary such that large-scale metal releases from contaminated soils and sediments do not occur with changing redox conditions. Metals tend to be retained more strongly in wetland soils compared with upland soils.

This is a review paper on processes affecting the mobility and plant availability of trace and toxic metals in wetlands.

In metal-contaminated wetland soils, the chief processes of concern are: (i) release of metals to surface water from sediments and flooded soils, (ii) metal uptake by wetland plants, (iii) metal accumulation by benthic and wetland animals, (iv) runoff losses, and (v) leaching losses.

There are a number of physical and chemical properties of soils affecting metal mobilization–immobilization processes. Physical properties include texture (proportion of sand, silt, and clay), and to some extent the type of clay minerals. Chemical properties include oxidation-reduction status (redox potential), pH, organic matter content, salinity, and the presence of some inorganic chemical components such as carbonates and sulfides.

It is infrequent that predominantly coarse-textured soils and sediments become contaminated with problem levels of trace and toxic metals because such materials have a low affinity for these elements. Exceptions exist such as where high concentrations of metals are released directly to a coarse-textured soil resulting in metals contamination of shallow groundwater in coarse-textured subsurface soils (Kotuby-Amacher et al., 1992). Thus, it is the fine-textured soils and sediment containing an appreciable organic matter content that tend to accumulate contaminants in wetlands and surface water bodies.

In studying wetland soil processes, it is useful to compare wetland and upland soils to appreciate the differences in wetlands. This will be the approach taken in this review of trace and toxic metals in wetlands.

IMPORTANCE OF SOIL OXIDATION-REDUCTION STATUS

Wetlands are characterized by soil conditions that include water saturation to near or above the soil surface for a substantial part of the year, which limits gaseous oxygen diffusion deep into the soil as occurs for drained, upland soils. As a result, available dissolved oxygen is consumed as a terminal electron acceptor by microbial respiration and the microbial population turns to alternate electron acceptors such as nitrate, ferric iron, manganic manganese, sulfate sulfur, and other oxidized materials. Consequently, different chemical and microbial processes occur than would be normal for upland, well-drained soils. However, the situation for wetland soils is somewhat more complex since for dryer periods during the year, the chemical and microbial processes in the surface soil may be similar to upland soils. Soil chemical and microbial processes affecting nutrient transformations, trace and toxic metal mobility and bioavailability, and the degradation of pesticides, petroleum hydrocarbons, and industrial organics are very different in wetland soils compared with upland soils (DeLaune et al., 1990; Gambrell et al., 1991a,b; Gambrell and Patrick, 1988). When changes occur in the oxidation status of soils and sediments, transformations of metals between chemical forms may occur affecting the mobility and plant availability of metals. Soil oxidation conditions also influence soil pH, a major factor influencing metal chemistry.

IMPORTANCE OF SOIL pH FOR METALS

As oxidized soils are flooded and become anaerobic or reducing, the pH tends to converge toward 7 (neutrality), regardless of whether the soil was acid or alkaline initially (Patrick and Mikkelsen, 1971; Ponnamperuma, 1972). Thus, the range of pH in typical wetland soils is much smaller than found for upland soils. The pH of natural wetland soils generally ranges from around 6.5 to 7.5 with a few exceptions. The near neutral pH conditions of wetland soils favors metal immobilization.

As an example not too unusual for sediments, Gambrell et al. (1991b) continuously stirred a New Jersey marsh sediment slurry for a period of 8 d under an air atmosphere. The pH of the wet sediment and initial pH of the slurry was 7.0. After 8 d, the pH had decreased to 3.0 as a result of oxidation and the chemical properties of the sediment. More recently, work done in this institute with a coastal Louisiana salt marsh sediment subjected to the same treatment had an initial pH of about 7.3 after 2 wk of stirring under an argon atmosphere, but the pH of an identical suspension stirred under air had a pH of 3.5 (Prasana, 1994). These stirred suspension studies reflect the potential acidity that can develop as, under natural conditions, some of the acidity produced would be subject to leaching with rainfall events. However, these data do reveal the importance of redox conditions on pH of some coastal marsh soils and sediments.

As another example, Gambrell et al. (1980) grew three species of wetland plants in a Mississippi River floodplain

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Published in J. Environ. Qual. 23:883-891 (1994).

Abbreviations: redox, oxidation-reduction potential measurements.

silt loam soil material under conditions of continuous flooding (reduced), intermediate redox conditions, and typical upland conditions. At the conclusion of the experiment, the pH of the soils under continuous flooding ranged from 6.9 to 7.0; under intermediate oxidation conditions the pH ranged from 5.8 to 6.2; the pH of the soil under oxidized conditions ranged from 5.1 to 6.2.

Mitsch and Gosselink (1986) reported the water pH of many alluvial swamps in the southeastern part of the USA ranges from 6 to 7, although the water pH of cypress domes fed primarily by rainwater have a pH of 3.5 to 5.0 where naturally produced humic acids within this ecosystem type produce the low pH. It should be noted that the *soil* material within cypress domes is primarily a peat with relatively little mineral matter. Mitsch and Gosselink (1986) present data on a number of other peatland chemical conditions where pH levels from moderately to strongly acid are common. Flooded predominantly mineral marsh soils and sediments tend to have a higher pH.

In a study of S forms in a brackish Louisiana coastal marsh, Krairapanond et al. (1992) reported seasonal changes in S forms and pH. The report indicates the marsh soil was not allowed to substantially oxidize prior to measuring pH. The range of pH measured in the spring, summer, and fall of 1987 and the winter and summer of 1988, respectively, were: 6.9 to 7.1, 7.4 to 7.8, 6.6 to 7.5, 6.9 to 7.2, and 6.4 to 7.2.

Wilsey et al. (1992) reported pH and other data on smooth cordgrass (*Spartina alterniflora* Loisel) (a salt marsh grass) dominated marsh near Caminada Bay, Louisiana. The pH in eight plots representing different elevation and nutrient treatments (including controls) ranged from 7.30 to 7.52.

Several activities in water bodies and wetlands provide the opportunity for normally anaerobic, near-neutral pH wetland soils and sediments to undergo substantial oxidation and possible accompanying large changes in pH. One of these is the activity of dredging channels and harbors and placing the dredged material upland where gradual drainage and oxidation will occur. Another is where access channels or canals are constructed through wetlands and the removed material is placed to the side of the constructed channel as a *spoil bank*. Though major, permanent drainage of wetlands is not as common now as it once was, this too offered the potential for wetland soils to become permanently oxidized with possible pH changes, depending on the chemical properties of the original wetland soil. These activities have resulted in large areas of wetland soils subject to drainage and oxidation. Where metals-contaminated wetland soils or dredged materials might be involved, possible changes in pH and the implications of this on local environmental chemistry should certainly be examined.

In summary, flooded, predominantly mineral wetland soils and sediments are going to be near neutral in pH and favor metal immobilization, though some predominantly organic wetland soils may be moderately to strongly acid. Upon long-term oxidation, many wetland soils with a near neutral indigenous pH may become sufficiently acid to increase metals release.

GENERAL CHEMICAL FORMS AND TRANSFORMATIONS OF METALS IN SOILS AND SEDIMENTS

All soils and sediments contain some concentration (usually low) of trace and toxic metals from natural sources. These background levels can vary widely depending on a number of factors such as parent material, sedimentation processes in water bodies, and other things. Usually it is a result of human activities that cause levels of metals to increase in soils and sediments to the point that they present potential health or ecological risks. However, elevated total concentrations of metals do not necessarily result in problem releases to water or excessive plant uptake. In addition to the particular metals present and the amount of these metals, the chemical forms of metals present and processes affecting transformations between these forms are important to assessing risk.

There are a number of general chemical forms of metals in soils and sediments that differ in their mobility and plant availability. These include:

1. Water-soluble metals
   a. Soluble as free ions, e.g., Zn^{2+}
   b. Soluble as inorganic complexes
   c. Soluble as organic complexes
2. Exchangeable metals
3. Metals precipitated as inorganic compounds
4. Metals complexed with large molecular-weight humic materials
5. Metals adsorbed or occluded to precipitated hydrous oxides
6. Metals precipitated as insoluble sulfide
7. Metals bound within the crystalline lattice structure of primary minerals

Water-soluble metals are of course the most mobile and plant available. Exchangeable metals are those bound to soil surfaces by cation exchange processes. Metals in this form are considered weakly bound and may be displaced relatively easily to the water-soluble form.

Together, metals in the soluble and exchangeable form are considered readily mobilized and available.

On the other extreme are metals bound within the crystalline lattice structure of clay minerals by isomorphous substitution for some of the common primary cations making up these minerals. Most of these metals are essentially unavailable and would become available only as a consequence of mineral weathering, typically over very long periods of time.

Between these two availability extremes are a number of general chemical forms listed above (numbers 3–6) that may be considered potentially mobile and available. These potentially available forms will be briefly discussed below.

Metals precipitated as inorganic compounds generally include metal oxides, hydroxides, and carbonates. The stability of these inorganic metal compounds is controlled primarily by the system pH. At near-neutral to somewhat alkaline pH levels, metals tend to be effectively immobilized. If, however, pH becomes moderately to strongly acid, as can sometimes occur when reduced soils or sediments become oxidized, these metals may be released to more mobile forms.

Metals complexed with large molecular weight organics tend to be effectively immobilized. There is some evidence that at least some metals are more tightly bound by organics under anoxic or reducing conditions compared with upland conditions. Gambrell and Patrick (1978) have suggested that the amount of organics in a dredged sediment material tends to decrease and the humic materials may become structurally less complex if dredged material is placed upland for disposal purposes. With some loss of total organic matter and chemical changes to the organic matter, metals that were tightly bound in a sediment tend to become less tightly bound upon long-term, upland placement conditions (Gambrell and Patrick, 1988). The organic matter in upland soils is also effective in immobilizing metals; thus, this is not to say temporary or long-term oxidation of wetland soils or sediments will result in major release of metals from humic materials. However, the release can be significant as has been shown for Cd and Zn in particular (Gambrell and Patrick, 1988; Gambrell et al., 1991b).

It is well established that oxides of Fe and perhaps Mn and Al effectively adsorb or occlude most trace and toxic metals cations (Jenne, 1968; Lee, 1975). These hydrous oxides of Fe are common in upland soils and upland-applied dredged materials. Depending perhaps on age and degree of crystallinity, they tend to become unstable under typically reducing, flooded soil conditions. In wetland transition zones and/or where seasonal changes occur in soil flooding, these hydrous iron oxides may form and dissolve as a function of changing hydrology, consequently holding and releasing metals within the soil. For surface soils and sediment materials (top few millimeters or so), iron oxyhydroxides may be effective in controlling metal retention during flooding and drainage cycles. Giblin et al. (1986) has shown iron oxyhydroxides were important in retaining metals in a surface sediment of a salt marsh receiving trace and toxic metals in sewage sludge applications used as a fertilizer.

In fine-textured, organic coastal marsh soils and sediments, the sulfate in seawater becomes reduced to sulfide as it diffuses into strongly reducing interior pore spaces. Though the soluble and volatile gas, hydrogen sulfide, is first formed, this sulfide will quickly react with most trace and toxic divalent metals forming highly insoluble metal sulfide precipitates. As long as these coastal marsh soils stay strongly reducing, metals are effectively immobilized. Unlike for metal–humic material associations where the change in metal immobilization may be modest, for a transition from strongly reduced to oxidizing conditions, oxidizing sulfide-containing soils and sediments for extended periods will result in loss of all sulfide and subsequent release of metals. These released metals may then be mostly immobilized by other processes, but perhaps immobilized a little less effectively. Kerner and Wallman (1992) conducted a laboratory study simulating alternate periods of anaerobic and aerobic conditions of an intertidal mud and sand flat sediment and followed the mobilization of Zn and Cd. Both elements were believed to be removed from pore water by sulfide precipitation during anaerobic cycles, and released from the sediment solid phase during aerobic cycles. Release under aerobic conditions was attributed to mineralization of organic matter and sulfide oxidation.

In all soils, there is some background level of all trace and toxic metals in all of these forms. Fortunately, in metal-contaminated soils, excess metals become primarily associated with these potentially available forms rather than the readily available soluble and exchangeable forms (Feijtel et al., 1988).

The oxidation conditions associated with upland or wetland soils affect the stability of metals in these potentially available forms. When changes occur in the oxidation status of soils and sediments, transformations of metals between the potentially available forms occurs as well as changes between the potentially and readily available forms.

Of the potentially available forms discussed above, the metal retention capacity for some were noted to be more stable (better immobilized) under oxidizing conditions typical of upland soils, and others were noted to be more stable under reducing conditions typical of sediments or saturated wetland soils. These immobilization processes tend to be complimentary in that a change from oxidized to reducing, or reducing to oxidizing soil or sediment conditions, does not usually result in a large release of metals from potentially available forms to the readily available forms so long as pH does not change substantially. However, changes in mobility and plant availability are often significant. As discussed elsewhere in this review, pH and pH changes in dredged materials and wetland soils does sometimes change greatly as a consequence of flooding–drying cycles.

PLANT AVAILABILITY OF METALS

Early Studies

Rice Culture and Other Work with Wetland Soils and Plants

Much of the early work on metal chemistry and plant availability in submerged soils focused on rice. The first metals of interest included Fe and Mn. These metals are subject to valence changes as a function of changing soil oxidation-reduction conditions that greatly affect their solubility and plant availability. In upland soils, Fe exists as ferric iron (Fe^{3+}) and Mn in the manganic (Mn^{4+}) form. These forms are generally found as very sparingly soluble compounds. If an upland soil becomes flooded where microbial respiration utilizes available oxygen, microbial populations adapt to utilize other terminal electron acceptors for respiration. Nitrate is the first soil component to be utilized as a terminal electron acceptor by facultative and obligate anaerobes after oxygen is depleted (Turner and Patrick, 1968). Then, microbes turn to oxidized forms of Fe and Mn for terminal electron acceptors, reducing them to ferrous iron (Fe^{2+}) and manganous manganese (Mn^{2+}), which are more soluble and available to plants. As a result of reducing conditions in some soils, Fe and Mn were found to accumulate, sometimes to toxic levels in rice (*Oryza sativa* L.) and other wetland plants (Jones and Etherington, 1970; Mandal, 1962; Weeraratna, 1969).

Many of the other trace and toxic metals such as Mg, Cu, Zn, Cd, Pb, and Ni are not subject to changes in oxidation state as a consequence of soil oxidation-reduction conditions. These are divalent metals under the entire redox potential range encountered in upland and wetland soils. Partly for this reason, less attention was given to how soil redox conditions might affect the mobility and plant availability of these metals for a number of years. Some of the earliest information on the availability of these metals in wetland soils came from plant nutrition work, where it was noted that certain metals, such as Cu, were less available to crop plants grown in highly organic soils. These findings pertain to wetland soil chemistry, because most highly organic soils tend to be wetter than typical upland agricultural soils.

Other early work in this area included Kothny (1973), who noted the plant availability of Hg was decreased in reducing soils. Mikkelsen and Brandon (1975) reported Zn deficiency in rice was observed to be more severe in submerged soils, especially when crop residues were undergoing active decomposition, when flooded soils would be expected to be strongly reducing. Jugsujinda and Patrick (1977) reported Zn uptake was greater by rice from aerobic soils than from anaerobic soils. Ito and Iimura (1975) and Reddy and Patrick (1977) also noted the same effect of submerged soil or reducing soil conditions on Cd uptake by rice.

Soil Oxidation Effects on Metal Uptake by Plants from Sludge-Amended Soils

Trace and toxic metal chemistry in sludge-amended soils was a major research topic in the 1970s. Most of this work focused on sludge-amended upland soils, but there were some interesting findings that suggested metal availability in wetland systems would be different from what was observed in typical upland systems. Kirkham (1975) noted Cd uptake from a sludge-amended soil was affected by sludge application frequency, which in turn influenced wetting and drying cycles. Cadmium uptake was greater under dryer conditions. Bingham et al. (1976) noted grain yield in rice grown under flooded and nonflooded conditions. Yield was reduced in sludge-amended soils containing 17 mg Cd/kg under nonflooded conditions, while 320 mg Cd/kg did not affect grain yield under flooded conditions. Gambrell and Patrick (1989) found Cd and Zn uptake by rice and corn (*Zea mays* L.) decreased as sludge-amended soil became more reducing. Giblin et al. (1986) found a number of trace and toxic metals more soluble in a salt marsh soil pore water where fertilization with sewage sludge stimulated plant growth, which subsequently contributed to better oxidation of the sediments.

Oxidation Effects on Metal Uptake by Plants from Dredged Material

Also in the 1970s, there was considerable research interest in the fate of metal contaminants in sediments and dredged materials under different disposal environments that ranged from underwater disposal to marsh creation and upland placement. Underwater placement, the most common disposal method for all dredged material until this time, maintains the original reducing and near-neutral pH conditions of the original sediment material. Marsh creation, and other upland placement results in plant establishment, varying degrees of drainage and oxidation, and sometimes large changes in pH, all of which may affect the mobility and biological availability of metals.

Originally, this work focused on chemical mobilization and immobilization processes of metals as a function of the pH or oxidation-reduction status of contaminated dredged material under one of the disposal or placement methods. This research showed that the chemical mobility of a number of trace and toxic metals that are not subject to valence state changes is nevertheless substantially affected by changes in pH and redox potential in sediments and dredged materials. For example, Cd and Zn are frequently found to be released from tightly bound forms to the more mobile water-soluble and exchangeable forms under oxidizing conditions compared with reducing conditions, especially as the pH drops to moderately acid levels (Gambrell et al., 1980, 1991b; Khalid et al., 1981) as shown in Table 1.

The processes responsible for the observed redox effects were the formation and stability of metal sulfides in typical coastal sediments under strongly reducing conditions, whereas metal sulfides are not stable under oxidizing conditions. Also, the data indicated insoluble humic material associated with reduced sediments more tightly bound trace and toxic metals than did humic materials under oxidized or simulated upland conditions. In strongly reduced sediments from six Chesapeake Bay marshes influenced by tidal action, Griffin et al. (1989) reported Fe was retained as oxides (in surface sediments) and sulfides (in reduced sediments) whereas Cu, Cd, and to a lesser degree Ni and Zn, were controlled by sulfide precipitation. In their study, Pb solubility may have been enhanced by complexation with soluble organics and, as a consequence, perhaps more plant-available.

The above work and related work by other investigators on the effects of soil and sediment redox conditions on the chemical availability of metals raised the question of metal availability from dredged materials to plants under upland vs. wetland conditions. Cadmium and Zn were shown to be much more available to plants under upland conditions compared with wetland conditions in an early laboratory study of the environmental implications of upland placement of contaminated dredged material for disposal or for beneficial use purposes such as marsh development, soils amendment, or upland habitat development. This was especially noted where pH levels decreased from near neutral to moderately acid conditions, as is often the case when sediments and dredged materials are placed upland and become oxidized (Table 2).

In this study, a number of experiments were conducted with different plant species, looking at Cd availability under different salinity conditions, and looking at radio-tracer-labeled Cd uptake as well as total uptake by atomic

Table 1. The effect of pH and redox potential on the chemical form and distribution of selected metals in Mobile Bay (AL) and Mississippi River (LA) sediment materials (adapted from Gambrell et al., 1980; Khalid et al., 1981).

		Redox potential, mV				Redox potential, mV			
		−150	50	250	500	−150	50	250	500
Sediment	Form	pH 5.0				pH 6.5			
		mg/kg on a dry wt. solids basis							
Cadmium[†]									
Miss. River	Soluble	1.1	3.4	27.3	33.7	2.1	1.5	1.0	1.9
	Exchange.	2.0	31.4	39.1	57.1	1.3	1.2	11.4	20.6
Mercury									
Mobile Bay	Soluble	0.43	ND[‡]	ND	0.01	0.12	0.02	0.07	0.03
	Exchange.	0.22	0.03	0.05	0.08	0.09	0.02	0.05	0.07
Lead									
Mobile Bay	Soluble	ND	0.02	0.01	0.02	0.02	ND	0.02	ND
	Exchange.	5.33	4.81	4.01	3.14	0.11	0.28	0.12	0.11
Zinc									
Mobile Bay	Soluble	0.1	8.8	12.3	11.7	1.3	1.0	0.6	1.0
	Exchange.	1.2	18.4	25.2	24.8	0.7	3.0	4.6	7.9

[†] Radiolabeled Cd, Hg, and Pb were added and the concentration based on recovery of the label. For Zn, atomic absorption was used to measure indigenous levels.

[‡] Not detected.

absorption methods. These studies showed the trend of increase Cd content under moderately acid, oxidizing conditions, but often relatively little effect of redox potential at a near-neutral pH level. One exception was spike grass [*Distichlis spicata* (L.) Greene], which, under a variety of experimental variables, showed greater Cd content at the higher pH level, but always more under oxidizing conditions.

This work was done in the laboratory with stirred soil and sediment suspensions where pH and redox potential could be accurately controlled, and it demonstrated the potential for greater Cd uptake under oxidized soil conditions. However, uptake studies where plant roots are suspended in stirred sediment slurries is not a natural rooting environment. This work advanced into the greenhouse where plants were grown in unstirred soil and sediment material maintained under upland and wetland conditions, which more realistically reflects the plant's growing environment. Plants were grown in metal-amended soil in pots under continuously flooded, field moisture capacity, and intermediate soil moisture conditions, allowing pH to change as affected by redox potential. This work confirmed the early laboratory stirred suspension studies, indicating the plant availability of at least some metals was different in upland vs. wetland environments (Table 3).

Table 2. Cadmium content in wetland plants grown in sediment suspensions under controlled pH and redox conditions (adapted from Gambrell et al., 1977).

pH 4.5		pH 7.5	
Reduced	Oxidized	Reduced	Oxidized
Cd content, mg/kg			
Smooth cordgrass, med. salinity, added Cd^{109}			
0.002	0.240	0.001	0.002
Smooth cordgrass, med. salinity, soil Cd			
0.27	1.68	0.39	0.32
Big cordgrass[†], med. salinity, added Cd^{109}			
0.009	0.398	0.001	0.071
Spike grass[‡], high salinity, added Cd^{109}			
0.006	0.145	0.001	0.416

[†] *Spartina cynosuroides.*

[‡] *Distichlis spicata* (L.) Greene.

Simmers et al. (1981) conducted a larger-scale greenhouse study in which a marsh plant species was grown in sediment material from 15 sites from around the country. Two treatments were imposed. In one, the sediment material was continuously flooded, and in the other, upland conditions were simulated in the greenhouse (Table 4). From every sediment but one, Cd uptake was greater by the marsh plant species under upland conditions compared with wetland conditions.

More Recent Research

Much of the more recent research pertaining to trace and toxic metals in wetlands continues to be done in association with placement alternatives for dredged materials, some of which are contaminated. Regulations for placement of contaminated dredged materials are such that restrictions apply when it is known that migration pathways will result in loss of contaminants from the

Table 3. The effect of oxidation-reduction conditions on soil pH and the plant content of selected metals from metals-amended soil in greenhouse studies (adapted from Gambrell et al., 1977).

	Oxidation-reduction Conditions		
Parameter	Reduced	Intermediate	Oxidized
Smooth cordgrass			
pH	6.9	6.2	6.0
Cu, mg/kg	8.0	9.0	11.0
Zn, mg/kg	52.0	79.0	126.0
Cd, mg/kg	8.0	16.8	33.4
Pb, mg/kg	1.0	1.6	2.4
Johnson grass[†]			
pH	7.0	5.9	5.1
Cu, mg/kg	5.0	6.0	4.0
Zn, mg/kg	59.0	93.0	79.0
Cd, mg/kg	8.1	12.9	18.2
Pb, mg/kg	0.5	0.4	1.0

[†] *Sorghum halepense* (L.) Pers.

Table 4. Uptake of Cd by harvested aboveground tissue of yellow nutsedge (*Cyperus esculentus* L.) in a greenhouse study (adapted from Simmers et al., 1981).

Site identification code	Upland	Flooded
	total uptake, mg/m^2	
DE1	1.16	0.24
DE2	15.36	8.26
DE3	0.49	0.06
IN1	0.70	0.34
IN2	4.40	1.90
IN3	1.43	1.22
MC1	49.52	6.26
MC2	98.65	22.34
MC3	28.55	11.88
ME1	2.47	1.41
ME2	0.56	1.53
ME3	16.28	0.05
MW1	53.22	7.39
MW2	3.21	0.94
MW3	1.92	0.70

placement site. The following paragraphs will discuss recent work with selected metals.

A substantial body of research data continues to show that changes in soil pH and redox potential are going to increase the mobility and plant availability of Cd, a toxic metal that should receive priority consideration when found in elevated levels in the environment. Folsom et al. (1988) found excessive Cd was taken up by plants in laboratory and field sites from a contaminated dredged material tested under upland disposal conditions. Kay et al. (1988) reported Cd uptake by plants was enhanced in drained dredged material planted to trees in a study in the Netherlands, and that there was an accumulation of Cd in the litter layer. In another field study, Stafford et al. (1991) worked with a confined dredged material disposal site designed with upland, wetland, and aquatic components. In the upland site, Cd was taken up by cottonwood (*Populus* sp.) trees and subsequently accumulated in the leaf litter layer and in earthworms.

Working with metal accumulation by aquatic birds, White and Cromartie (1985) found Cd did not accumulate in the birds from a confined dredged material disposal site during periods when the facility contained ponded water. Presumably, this was due to much more effective immobilization of Cd in soils and sediments during periods of reduction.

Lead is a toxic metal that has much less propensity for being translocated to the aboveground parts of plants than many other trace and toxic metals such as Cd and Zn (Broyer et al., 1972; Reddy and Patrick, 1977). However, exceptions to this general finding have been noted (Banus et al., 1975); some of these exceptions have been found for marsh plants (Folsom et al., 1988). Simmers et al. (1989) reported where contaminated dredged materials were used to construct wetlands at one experimental site, the plants did not accumulate more Pb than plants growing in nearby natural marshes. However, their predictive plant bioassay test, which had been found to correlate well with field results, indicated greater Pb uptake by plants would have occurred if grown on highly contaminated sediments under upland conditions.

Zinc and Ni (and Cd, as discussed previously) are known to readily accumulate in plants under some conditions (CAST, 1976). In work with Zn, Ni, and Cu in a study of placement options for a highly contaminated harbor sediment being evaluated for dredging, Simmers et al. (1989) reported that under simulated wetland conditions, marsh plants did not accumulate more of these metals than plants in a nearby natural marsh. However, their bioassay tests indicated uptake would be much greater if the material were placed in an upland environment where plants would become established on oxidized material.

Surface Runoff

Surface runoff of metals is a potential process by which metals may be removed from contaminated wetland and upland soils. In wetlands where the soil remains flooded for most of the rhizosphere, Cd should be more effectively immobilized from leaching and surface runoff losses in terms of soluble Cd. Research has shown that if upland areas are constructed with contaminated sediment, runoff losses are enhanced (Palermo et al., 1989; Skogerboe et al., 1987). Under conditions of upland placement of dredged material, initial losses were primarily associated with suspended particulates. However, after drainage and oxidation occurred, soluble levels of Cd became elevated, especially in materials that tended to become acid upon oxidation, as is typical of many dredged materials. For one of these sites, concentrations of filtered metals (soluble) equaled unfiltered metals, and it was reported that the levels of Cd exceeded the Protection of Aquatic Life EPA Maximum Criteria.

In surface runoff tests for several trace and toxic metals for a dredged material being evaluated for upland placement, the following was determined: if contaminated dredged materials are allowed to be placed in environments where drainage and subsequent oxidation will occur, then elevated runoff losses of Cu, Ni, Zn, and Mn would occur, but Cr losses would not follow this trend. As reported for Cd, Cu, and Zn losses by surface runoff occurred at levels that exceeded the USEPA's Maximum Criteria for Protection of Aquatic Life (Palermo et al., 1989).

Losses of Pb by surface runoff were found to be similar for Cd, as reported above. Soluble levels would be substantially increased in runoff from contaminated sites under oxidized conditions, especially where acid conditions developed as a dredged material placed upland became oxidized. Where fine-textured soils containing appreciable organic matter are flooded and likely reduced, metals will tend to be retained upon entering wetlands. Turner et al. (1985), in a study of Pb in a New Jersey pine barrens watershed, reported 98% of incoming Pb was retained by vegetation and muck soil such that very little exported from the wetland with stream flow.

Leaching Losses

The hydrology of many wetlands is such that water permeability is very slow, and leaching of metals would be a minor problem, especially since the strongly reducing conditions of wetland soils favors immobilization of metals with the solid phase. Thus, leaching of trace and toxic metals should not be a problem. Comparing reports of leaching of metals in contaminated dredged materials experimentally used to construct uplands and wetlands will provide relative information on how tightly metals are held in wetland soils vs. upland soils.

Cadmium offers a very high potential for leaching under upland conditions compared with wetland conditions based on laboratory and field data (Palermo et al., 1989). Again, while this loss is accelerated in soil or dredged materials that are moderately to strongly acid under oxidizing conditions, this redox-mediated change in pH occurs often enough in soils and sediments to warrant consideration of maintaining metal-contaminated dredged materials under anaerobic or flooded conditions. For example, Gambrell et al. (1991b) took a contaminated sediment material from the northeastern USA that was initially at a pH of just over 7.0 in its original, anaerobic state. Stirring this material as an aqueous slurry for 8 d under air resulted in the pH dropping to very near 3.0. In a test of the upland disposal alternative for a heavily contaminated sediment, Folsom et al. (1988) reported Cd was the only metal found in this study that leached to groundwater. In wetland soils that are reducing, Cd leaching would be negligible. The behavior of Zn should be similar to Cd.

Lead leaching would be expected under upland, oxidized conditions, especially where a dredged material becomes acid (Brannon et al., 1977; Palermo et al., 1989). In the Palermo et al. study, there was some movement of Pb even through anaerobic sediment material, but much greater leaching levels would be expected in leachate from an upland facility where the sediment material would oxidize. Chromium responded much like Pb.

Some field and lab studies have shown that Cu and Ni would be more susceptible to leaching under aerobic sediment conditions compared with anaerobic conditions, which indicate wetlands more effectively immobilize metal contaminants than upland soils (Hoeppel, 1980; Myers and Brannon, 1988).

FUTURE RESEARCH NEEDS

Because of the seasonal nature of reducing soil conditions in many wetlands, and in wetland–upland transition zones in particular, additional research should be done on factors affecting metal uptake under conditions where wetlands undergo seasonal changes from extended periods of flooding to periods when the water table may fall beneath the rhizosphere and upland soil conditions prevail for extended periods. Under these conditions, several characteristics of the system affecting metal immobilization may be substantially different from permanent upland or permanent wetland conditions. Some of these include the predominant plant species present and soil organic matter contents that may be intermediate between levels found in permanent upland and wetland soils of the area. Gambrell et al. (1980) and many others have shown plant species differences in metal uptake. More recently, Alberts et al. (1990), working with two salt marsh sites with elevated levels of several trace and toxic metals and one unimpacted site, noted relatively little differences in metal uptake by one marsh grass from the three sites. But, large variations in tissue concentration of another marsh grass species was noted, suggesting this species either takes up metals differently, or more variable conditions existed in the rhizosphere environment of the second species.

The association of metals with hydrous oxides of Fe may be different in seasonal wetlands as the freshly formed iron oxides present during dry periods may have a different capacity to retain trace and toxic metals compared with iron oxides in permanent upland environments. The likely seasonal immobilization and release of metals from alternately forming and dissolving iron oxides may affect plant availability in ways that should be better understood to predict the fate of trace and toxic metals in some wetland environments.

Another aspect that should receive more research attention is how the interaction between soil redox conditions and soil pH affect metal chemistry. Lab and some field studies have shown that when some wetland soils and dredged materials are dug out and placed in upland environments where drainage and oxidation will occur, the pH may become strongly acid. Considering the importance of soil pH to metal mobility and plant availability, more attention should be given to: (i) seasonal changes in pH due to changing redox conditions in wetland transition zones, (ii) long-term monitoring of pH in marsh soils and dredged materials subject to upland placement as a result of canal construction and dredging activities, and (iii) the range of pH encountered in wetland environments. For example, it is well known that most fine-textured soils and sediments containing appreciable amounts of organic matter tend to become near neutral in pH upon the development of reducing conditions. These conditions have been shown to contribute to effective metal immobilization. However, some forested wetland soils of somewhat coarser texture have been found to be moderately acid (pH 5 or below) under oxidized conditions, but to increase in pH relatively little upon development of moderately to strongly reducing conditions.

Also, more work should be done on rhizosphere effects on metal mobility and availability in wetlands. Although there is reasonably good understanding of the processes affecting metal mobility and retention in upland vs. wetland soils, many wetland plant species (that are capable of transporting oxygen from aboveground plant tissue and releasing oxygen from roots) generate an oxidizing soil environment immediately around the root that may be in close proximity to strongly reduced conditions in the bulk soil. Giblin et al. (1986) have shown where fertilizer applied as sewage sludge to a smooth cordgrass marsh stimulated the growth of the marsh grass, and marsh soil oxidation was increased, resulting in soluble sulfide levels being substantially lower than in surrounding areas. This increased soluble metal levels (metal sulfide precipitation was reduced) in pore water where the growth of marsh grass was enhanced by fertilization.

SUMMARY

Laboratory, greenhouse, and field studies have shown that trace and toxic metals are more strongly immobilized under wetland compared to upland soil conditions. Though precipitation as insoluble metal sulfides is a major process contributing to this finding in coastal sediments, a strong association of metals with insoluble humic materials and the usual near neutral pH associated with flooded soils and sediments are also factors. At equivalent substrate contamination levels, plant uptake, leaching losses, and surface runoff losses have all been shown to be a significant migration pathway for metals under upland conditions compared to wetland conditions.

The processes contributing to metals immobilization in wetland soils should also contribute to retention of metals released into wetlands from point and nonpoint sources, assuming favorable hydrology and reasonable loading rates. The rhizosphere would be reducing, minimizing metals transport from the soil surface to plant roots and thus minimizing uptake. At relatively slow flow rates, adsorptive surfaces of clays and humic materials should effectively scavenge and retain trace and toxic metals. If sedimentation is occurring in the wetland, the gradual burying of bound metals is going to place them in an environment where immobilizing processes become more effective.

There are several research needs in the area of metal chemistry in wetlands. Because of the seasonal nature of reducing soil conditions in many wetlands, and in wetland-upland transition zones in particular, additional research should be done on factors affecting metal uptake under these conditions. Another aspect that should receive more research attention is how the interaction between soil redox conditions and soil pH affect metal chemistry. Considering the importance of soil pH to metal mobility and plant availability, more attention should be given to: (i) seasonal changes in pH due to changing redox conditions in wetland transition zones, (ii) long-term monitoring of pH in marsh soils and dredged materials subject to upland placement as a result of canal construction and dredging activities, and (iii) the range of pH encountered in wetland environments. Also, more work should be done on rhizosphere effects on metal mobility and availability in wetlands where an oxidizing soil environment immediately around the root can be in close proximity to strongly reduced conditions in the bulk soil influencing metal chemistry and availability.

REFERENCES

Alberts, J.J., M.T. Price, and M. Kania. 1990. Metal concentrations in tissues of *Spartina alterniflora* (Loisel.) and sediments of Georgia salt marshes. Estuar. Coast. Shelf Sci. 30:47–58.

Banus, M.D., I. Valiela, and J.M. Teal. 1975. Lead, zinc, and cadmium budgets in experimentally enriched salt marsh ecosystems. Estuar. Coast. Mar. Sci. 3:421–430.

Bingham, F.T., A.L. Page, R.J. Mahler, and T.J. Ganje. 1976. Cadmium availability to rice in sludge-amended soil under 'flood' and 'nonflood' cultures. Soil Sci. Soc. Am. J. 40:715–719.

Brannon, J.M., R.H. Plumb, Jr., and I. Smith. 1977. Long-term release of contaminants from dredged material. Tech. Rep. D-77-5. U.S. Army Corps of Eng. Waterways Exp. Stn., Vicksburg, MS.

Broyer, T.C., C.M. Johnson, and R.E. Paull. 1972. Some aspects of lead in plant nutrition. Plant Soil 36:301–313.

Council for Agricultural Science and Technology. 1976. Application of sewage sludge to cropland: Appraisal of potential hazards of the heavy metals to plants and animals. USEPA Rep. 430/9-76-013. USEPA, Washington, DC.

DeLaune, R.D., R.P. Gambrell, J.H. Pardue, and W.H. Patrick, Jr. 1990. Fate of petroleum hydrocarbons and toxic organics in Louisiana coastal environments. Estuaries 13:72–80.

Feijtel, T.C., R.D. DeLaune, and W.H. Patrick, Jr. 1988. Biogeochemical control on metal distribution and accumulation in Louisiana sediments. J. Environ. Qual. 17:88–94.

Folsom, B.L., Jr., J.G. Skogerboe, M.R. Palermo, J.W. Simmers, S.A. Pranger, and R.A. Shafer. 1988. Synthesis of the results of the field verification program upland disposal alternative. Tech. Rep. D-88-7. U.S. Army Corps of Eng. Waterways Exp. Stn., Vicksburg, MS.

Gambrell, R.P., V. Collard, and W.H. Patrick, Jr. 1980. Cadmium uptake by marsh plants as affected by sediment physicochemical conditions. p. 425–444. *In* R.A. Baker (ed.) Contaminants and sediments. Vol. 2. Ann Arbor Science, Ann Arbor, MI.

Gambrell, R.P., V.R. Collard, C.N. Reddy, and W.H. Patrick, Jr. 1977. Trace and toxic metal uptake by marsh plants as affected by Eh, pH, and salinity. Tech. Rep. D-77-40. Dredged Material Res. Program, U.S. Army Corps of Eng. Waterway Exp. Stn., Vicksburg, MS.

Gambrell, R.P., R.D. DeLaune, and W.H. Patrick, Jr. 1991a. Redox processes in soils following oxygen depletion. p. 101–117. *In* M.B. Jackson et al. (ed.) Plant life under oxygen deprivation. SPB Academic Publishing, The Hague, the Netherlands.

Gambrell, R.P., R.A. Khalid, and W.H. Patrick, Jr. 1980. Chemical availability of mercury, lead, and zinc in Mobile Bay sediment suspension as affected by pH and oxidation-reduction conditions. Environ. Sci. Technol. 14:431–436.

Gambrell, R.P., and W.H. Patrick, Jr. 1978. Chemical and microbiological properties of anaerobic soils and sediments. p. 375–423. *In* D.D. Hook and R.M.M. Crawford (ed.) Plant Life in Anaerobic Environments. Ann Arbor Science, Ann Arbor, MI.

Gambrell, R.P., and W.H. Patrick, Jr. 1988. The influence of redox potential on the environmental chemistry of contaminants in soils and sediments. p. 319–333. *In* D.D. Hook (ed.) The ecology and management of wetlands. Vol. 1. Timber Press, Portland, OR.

Gambrell, R.P., and W.H. Patrick, Jr. 1989. Cu, Zn, and Cd availability in a sludge-amended soil under controlled pH and redox potential conditions. p. 89–106. *In* B. Bar-Yosef et al. (ed.) Inorganic contaminants in the vadose zone. Springer-Verlag, Berlin.

Gambrell, R.P., J.B. Wiesepape, W.H. Patrick, Jr., and M.C. Duff. 1991b. The effects of pH, redox, and salinity on metal release from a contaminated sediment. Water Air Soil Pollut. 57-58:359–367.

Giblin, A.E., G.W. Luther III, and I. Valiela. 1986. Trace metal solubility in salt marsh sediments contaminated with sewage sludge. Estuar. Coast. Shelf Sci. 23:477–498.

Griffin, T.M., M.C. Rabenhorst, and D.S. Fanning. 1989. Iron and trace metals in some tidal marsh soils of the Chesapeake Bay. Soil Sci. Soc. Am. J. 53:1010–1019.

Hoeppel, R.E. 1980. Contaminant mobility in diked containment areas. *In* Management of bottom sediments containing toxic substances: Proc. of the 5th U.S.-Japan Experts Meeting. USEPA Rep. 600/9-80-044. USEPA, Washington, DC.

Ito, H., and K. Iimura. 1975. Absorption of cadmium by rice plants in response to change of oxidation-reduction conditions of soils. Abst. of Nippon Rozyohiryogaku Zasshi. J. Sci. Soil Manure 46: 82–88.

Jenne, E.A. 1968. Controls of Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides. *In* R.A. Baker (ed.) Trace inorganics in water. ACS Adv. in Chem. Ser. 73:337–387

Jones, R.L., and J.R. Etherington. 1970. Comparative studies of plant growth and distribution in relation to waterlogging: I. The survival of *Erica cinera* L. and *E. Tetralix* L. and its apparent relationship to iron and manganese uptake in waterlogged soil. J. Ecol. 58:487–496.

Jugsujinda, A., and W.H. Patrick, Jr. 1977. Growth and nutrient uptake by rice in a flooded soil under controlled aerobic-anaerobic and pH conditions. Agron. J. 69:705–710.

Kay, S.H., M.C.Th. Scholten, and C.T. Bowmer. 1988. Mobility of soil contaminants in an ecosystem of trees growing on dredged material – the Broekpolder (Rotterdam, the Netherlands). TNO Rep. R 88/488. TNO, Delft, the Netherlands.

Kerner, M., and K. Wallman. 1992. Remobilization events involving Cd and Zn from intertidal flat sediments in the Elbe Estuary during the tidal cycle. Estuar. Coast. Self Sci. 35:371–393.

Khalid, R.A., R.P. Gambrell, and W.H. Patrick, Jr. 1981. Chemical availability of cadmium in Mississippi River sediment. J. Environ. Qual. 10:523–529.

Kirkham, M.B. 1975. Trace elements in corn grown on long-term sludge disposal site. Environ. Sci. Technol. 9:765–768.

Kothny, E.L. 1973. The three-phase equilibrium of mercury in nature. *In* E.L. Kothny (ed.) Trace elements in the environment. ACS Adv. in Chem. Ser. 123:48–80.

Kotuby-Amacher, J., R.P. Gambrell, and M. Amacher. 1992. Distribution and environmental chemistry of lead in soils at an abandoned battery reclammation site. p. 1–24. *In* I.K. Iskandar and H.M. Selim (ed.) Engineering aspects of metal-waste management. Lewis Publishers, Chelsea, MI.

Krairapanond, N., R.D. DeLaune, and W.H. Patrick, Jr. 1992. Distribution of organic and reduced sulfur forms in marsh soils of coastal Louisiana. Org. Geochem. 18:489–500.

Lee, G.F. 1975. Role of hydrous metal oxides in the transport of heavy metals in the environment. Prog. Water Technol. 17:137–143.

Mandal, L.N. 1962. Levels of iron and manganese in soil solution and the growth of rice in waterlogged soils in relation to the oxygen status of soil solution. Soil Sci. 94:387–391.

Mikkelsen, D.S., and D.M. Brandon. 1975. Zinc deficiency in California rice. California Agric., p. 8–9.

Mitsch, W.J., and J.G. Gosselink. 1986. Wetlands. Van Nostrand Reinhold Company, New York.

Myers, T., and J.M. Brannon. 1988. New Bedford Harbor superfund project, Acushnet River estuary engineering feasibility study of dredging and dredged material disposal alternatives. Rep. 5. Tech. Rep. EL-88-15. U.S. Army Corps of Eng. Waterways Exp. Stn., Vicksburg, MS.

Palermo, M.R., R.A. Shafer, J.M. Brannon, T.E. Myers, C.L. Truitt, M.E. Zappi, et al. 1989. Evaluation of dredged material disposal alternatives for US Navy homeport at Everett, Washington. Tech. Rep. EL-89-1. U.S. Army Corps of Eng. Waterways Exp. Stn., Vicksburg, MS.

Patrick, W.H., Jr., and D.S. Mikkelsen. 1971. Plant nutrient behavior in flooded soil. p. 187–215. *In* R.A. Olson et al. (ed.) Fertilizer technology and use. 2nd ed. SSSA, Madison, WI.

Ponnamperuma, F.N. 1972. The chemistry of submerged soils. Adv. Agron. 24:29.

Prasana, M. 1994. Trace and toxic metal chemistry of redmud being considered for wetland restoration. M.S. thesis. Louisiana State Univ., Baton Rouge, LA.

Reddy, C.N., and W.H. Patrick, Jr. 1977. Effect of redox potential and pH on the uptake of Cd and Pb by rice plants. J. Environ. Qual. 6:259-262.

Simmers, J.W., B.L. Folsom, Jr., C.R. Lee, and D. Bates. 1981. Field survey of heavy metal uptake by naturally occurring saltwater and freshwater marsh plants. Tech. Rep. EL-81-5. U.S. Army Corps of Eng. Waterways Exp. Stn., Vicksburg, MS.

Simmers, J.W., R.G. Rhett, S.H. Kay, and B.L. Folsom, Jr. 1989. Synthesis of the results of the field verification program wetland disposal alternative. Tech. Rep. D-89-2. U.S. Army Corps of Eng. Waterways Exp. Stn., Vicksburg, MS.

Skogerboe, J.G., C.R. Lee, R.A. Price, D. Brandon, and G. Hollins. 1987. Prediction of surface runoff water quality from Black Rock Harbor dredged material placed in an upland disposal site. Misc. Pap. D-87-1. U.S. Army Corps of Eng. Waterways Exp. Stn., Vicksburg, MS.

Strafford, E.A., J.W. Simmers, R.G. Rhett, and C.P. Brown. 1991. Interim report: Collation and interpretation of data for Times Beach confined disposal facility, Buffalo, New York. Misc. Pap. D-91-17. U.S. Army Corps of Eng. Waterways Exp. Stn., Vicksburg, MS.

Turner, F.T., and W.H. Patrick, Jr. 1968. Chemical changes in waterlogged soils as a result of oxygen depletion. Trans. 9th Int. Congr. of Soil Sci. 4:53–56.

Turner, R.S., A.H. Johnson, and D. Wang. 1985. Biogeochemistry of lead in McDonalds Branch Watershed, New Jersey pine barrens. J. Environ. Qual. 14:305–314.

Weeraratna, C.S. 1969. Adsorption of manganese by rice under flooded and unflooded conditions. Plant Soil 30:121–125.

White, D.H., and E. Cromartie. 1985. Bird use and heavy metal accumulation in waterbirds at dredged disposal impoundments, Corpus Christi, Texas. Bull. Environ. Contam. Toxicol. 34:295–300.

Wilsey, B.J., K.L. McKee, and I.A. Mendelssohn. 1992. Effects of increased elevation and macro- and micronutrient additions on *Spartina alterniflora* transplant success in salt-marsh dieback areas in Louisiana. Environ. Manage. 16:505-511.