

Mobility of Heavy Metals in Dredged Harbor Sediments

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Solubility, mobility, and bioavailability of sediment-bound metals can be increased by four major factors: (1) Lowering of pH; (2) changing of redox conditions; (3) formation of organic complexes; and (4) increasing salinity. While the first two factors are particularly important for on-land deposition of dredged materials, the effect of salinity is particularly important for resuspended cadmium-rich sediments in estuaries. Chemical extraction studies, which were carried out under carefully controlled conditions on both fresh and freeze-dried samples, indicate that aeration of anoxic sediments (e.g., on-land disposal) may both increase and decrease the mobility of heavy metals. Transformation from sulfidic or carbonatic associations to oxidic phases will reduce mobility of manganese, whereas the respective changes from moderately reducible forms to carbonatic and easily reducible phases will enhance the reactivity of zinc during oxidation of dredged material.

Introduction

Sediments are increasingly recognized as both a carrier and a possible source of contaminants in aquatic systems; furthermore, there are potential biological effects from polluted solid materials disposed on agricultural land. Metals, for example, are not necessarily fixed permanently by sediment, but may be recycled via biological and chemical agents both within the sedimentary compartment and the water column. This is especially true for "dredged materials," which threaten not only organisms, but also the quality of potable water. Human activities promote the accumulation of polluted sediments in many water courses; this has increased the need for maintenance dredging, and has resulted in the problem of disposing large amounts of contaminated solids for which safe disposal sites are difficult to find. We present examples from Hamburg harbor, Rotterdam harbor, and from the middle Neckar River in southern Germany.

Factors Affecting Mobility of Metals

In discussions of environmental problems associated with contaminated sediments, it is now widely accepted that the ecological significance of metal

inputs is determined by the specific form and reactivity of a metal compound, rather than by its rate of accumulation. This effect typically refers to adsorbed metal pollutants, which may become partly mobilized in the aquatic milieu by changes in pH and redox conditions, by increased salinities, or by concentrations of organic chelators. While the first two factors typically relate to on-land disposal of dredged materials, the effects of salinity and organic chelators are most important for sediments in rivers, which may be naturally or artificially resuspended.

Salinity Increase

Riverborne metals entering an estuarine environment can be affected by a change in the pH, chlorinity, turbidity maximum, and formation of new particulate matter (Salomons, 1980). Significant changes occur even in the low-salinity region of an estuary; the removal of riverborne iron and, in some estuaries, of manganese at low salinities is well established (Duinker, 1980). However, apart from the flux of riverine material into an estuarine environment, the deposited particulates may provide a source of dissolved and newly formed particulate components (Duinker et al., 1979; Sundby et al., 1981). As a result of biological or biochemical

pumping, the intertidal flats in many estuaries act as a source of dissolved metals (Morris et al., 1982). Release of trace metals from particulate matter has been reported from several estuaries; for example, the Scheldt estuary (Salomons and Eysink, 1981), Savannah/Ogeechee estuaries (Windom et al., 1983), and Gironde estuary (Jouanneau, 1982). It has been partly related to the intensive breakdown of organic matter. If the released trace metals become complexed in the water column, with chloride and/or ligands from the decomposing organic matter, their uptake or precipitation onto the suspended matter may be inhibited. In addition, it has been suggested by Millward and Moore (1982) that the major cations, magnesium and calcium, are probably coadsorbed; competition from these species for adsorption sites increases with increasing salinity.

Figs. 31.1 to 31.3 indicate the different behaviors of dissolved zinc and cadmium in the salinity gradient of the Elbe River estuary. While the distribution of zinc exhibits the expected "dilution" effect of mixing with relatively clean seawater, the general increase of dissolved cadmium in the fluvial/estuarine transect suggests remobilization of this element from contaminated particulates.

Synthetic Organic Chelators

It seems that naturally dissolved organic matter, such as humic material or amino acids (present in both fresh water and saltwater), has little effect upon the speciation of dissolved Cd, Pb, or Zn (Nürnberg, 1983); only the distribution of Cu species is affected markedly by natural organic chelators (Stumm and Morgan, 1981). However, significant effects from strong synthetic chelators (such as nitrilotriacetic acid [NTA], which is used in some countries as a substitute for detergent polyphosphates) can be expected on most heavy metals in fresh water. In discussions on the introduction of NTA into detergents for the West German market, major emphasis has been given to the possible effects on river sediments that are strongly polluted by heavy metals (Bernhardt, 1984). In the case of Hamburg harbor, significant remobilization of nickel and copper was observed from sediments at NTA concentrations as low as 100 $\mu\text{g/l}$ (Fig. 31.4; Dehnad et al., 1984). It has been argued that this situation might be extreme, because: (1) much of the wastewater effluent in the Hamburg area is still poorly treated; (2) sediments of the harbor area are strongly enriched with heavy

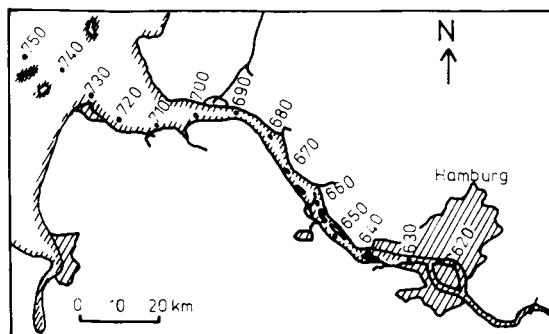


Fig. 31.1. The Elbe estuary between Geesthacht and the North Sea. Sample locations are 670–750 km from the Czechoslovakian border.

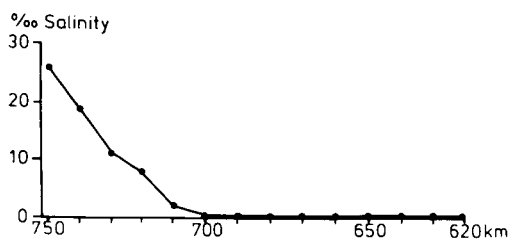


Fig. 31.2. Salinity at sampling sites in the Elbe estuary. Sampling cruise, RV *Victor Hensen*, April 18–19, 1983 (Ahlf, 1983).

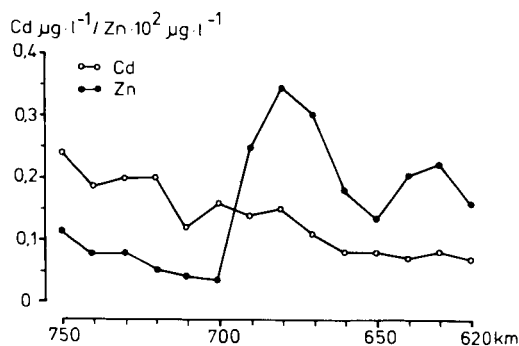


Fig. 31.3. Concentrations of dissolved cadmium (Cd) and zinc (Zn) in the Elbe estuary.

metals from both upstream and local sources; and (3) many polluted sediments are deposited in the tidal section of the Elbe River as the stream is widening (this effect results in large volumes of maintenance dredging, but is beneficial for the water quality in the German Bight of the southeastern North Sea). If a mechanism existed to mobilize metals from the harbor sediments, many metals

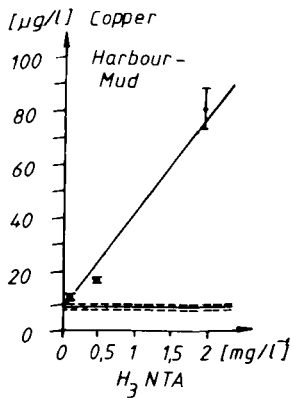


Fig. 31.4. Mobilization of copper from dredged sediment (Hamburg harbor) by different concentrations of nitrilotriacetic acid (NTA) in artificial river water (Dehnad et al., 1984).

could be released into the lower estuary and eventually into the North Sea (Förstner et al., 1984).

Lowering of pH

Acidity of surface waters causes problems in all aspects of soluble metal enrichment ranging from the contamination of drinking water to problems concerning the growth and reproduction of aquatic organisms, the increased leaching of nutrients from soil and ensuing reduction of soil fertility, the increased availability and toxicity of metals, and also to an increased methylation of mercury in sediments (Fagerström and Jernelöv, 1972). On a regional

scale, acid precipitation is probably the most important single factor affecting metal mobility in surface waters, particularly for Al, Cd, Mn, and Zn (Haines, 1981). In mine waters and dredged sediments disposed of on-land, acid solutions can result from the oxidation of sulfide minerals; kinetics of these transformations are typically affected by bacteria (Singer and Stumm, 1970).

Titration experiments, applying different concentrations of sulfuric acid, were performed on suspensions of dredged sediments from Hamburg harbor and the Neckar River (Fig. 31.5). From the good correlations between the titration curves of suspensions containing 1% calcium carbonate and those containing 10% Neckar River sediment, it is evident that the buffering capacity of this material is mainly related to the carbonate content (approximately 15% in the Neckar River mud). In Elbe River sediment, where the carbonate content is low (less than 5%), a continuous decrease of pH values is found upon addition of acid (Fig. 31.5).

Treatment of dredged sludge from Hamburg harbor with 6% sulfurous acid caused a nearly complete removal of Cd, Zn, and Mn within the first 10 min (Calmano et al., 1983). The ability of certain bacteria (*Thiobacillus thiooxidans* and *T. ferrooxidans*) to oxidize sulfur and ferrous iron, while decreasing the pH value from 4.0 to 5.0 to about 2.0 enhanced the process of metal dissolution from dredged sludge. Acidification with sulfurous acid to pH 4.0 and subsequent bacterial leaching solubilized the following metal percentages from the dredged sediments of Hamburg harbor: Cd and Co, 98%; Mn, 91%; Cu, 84%; Ni, 66%; Cr, 45%; Fe, 27%; and Pb.

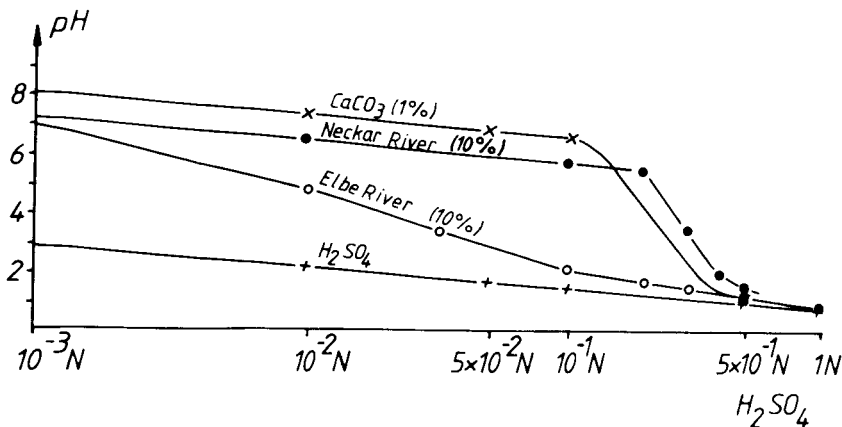


Fig. 31.5. pH changes of suspensions of calcium carbonate (CaCO_3) and river sediments from additions of sulfuric acid (H_2SO_4) in different concentrations.

17%. Despite this, the original objective to "detoxify" the material to the quality standard required for agricultural application (e.g., Müller and Riethmayer, 1982) could not be reached, even by the combined methods of acid/bacterial leaching.

Redox Changes

Much of the dredged material removed during harbor and channel maintenance dredging is high in organic matter and clay, and is both biologically and chemically active. Decomposition of organic matter, which is mediated by microorganisms, generally follows a definite succession in sediments depending upon the nature of the oxidizing agent (Berner, 1981). The successive events are oxygen consumption (respiration), nitrate reduction, sulfate reduction, and methane formation. In the freshwater environment, where sulfate concentrations are relatively low, the methanogenic state is reached relatively fast and available reducible iron is converted to siderite (iron carbonate).

The early diagenetic reactions have been studied experimentally in the field, where large pits (80 × 30 × 6 m) were dug in the Rhine estuary below the water table and filled with dredged sediments. While the SO_4 content in porewater is continuously diminished by the formation of H_2S , the concentration of iron in porewater reaches a maximum, resulting from the reduction from iron (III) to iron (II); subsequently, there is precipitation as iron sulfide (mainly marine environment) or iron carbonate (Fig. 31.6). As a result of siderite formation, the reducible iron acts as a buffer against decreasing pH by increasing the alkalinity (Salomons, 1984).

Estimates from selective extraction procedures (see below) suggest that in sediments from the Rhine River, about 50–70% of the iron is present in a reducible form. After all the reducible iron is converted to siderite, the pH drops as a consequence of the continuing degradation of organic matter. Salomons (1984) has stressed that the anoxic layer in sediments plays a central role, since it determines the stable phases of contaminants and metal concentrations in porewater. Metal concentrations in porewater show a rather narrow range of values, both from highly contaminated and less contaminated environments, indicating that characteristic effects of metal sulfides that dominate the systems.

These sediment conditions favor effective immobilization of many contaminants, provided the

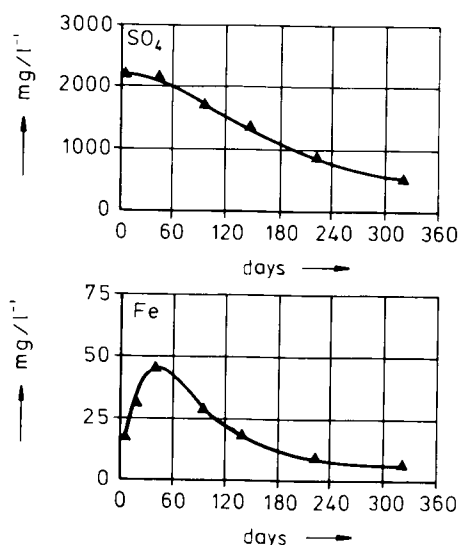


Fig. 31.6. Changes in sulfate and iron porewater concentrations with time during early diagenesis of dredged brackish water sediment disposed in the Rhine River estuary (Kerdijk and Salomons, unpublished data).

dredged materials are not subject to aeration through mixing, resuspension, or drying. In addition to the effects of pH changes, the mobility of most potentially toxic metals is influenced by oxidation-reduction conditions to some extent, and certain of the metals can be strongly affected by Eh conditions. Field evidence for changing cadmium mobilities was reported by Holmes et al. (1974) from Corpus Christi Bay harbor. During the summer, when the harbor water is stagnant, cadmium is precipitated as CdS at the sediment-water interface; in the winter months, however, the increased flow of oxygen-rich water into the bay results in the release of some of the precipitated metal. Gambrell et al. (1977) conducted a laboratory study to determine the effects of pH and redox conditions on the distribution of Hg, Cd, Pb, Zn, Cu, Mn, Fe, P, and $\text{NH}_4\text{-N}$ among selected chemical forms in sediment-water systems from four sites. These studies indicated that considerable proportions of the total cadmium and mercury content could be transformed to soluble and exchangeable forms as a result of comparatively small changes from reduced to oxidized conditions. This effect is accentuated by decreasing pH. The authors suggested that a reducing, near-neutral pH disposal condition favors the long-term stability of sulfide and organic complexes, and will thus minimize mercury and cadmium release. On the

other hand, at high levels of contamination, a moderately acid, oxidized disposal environment may result in substantial release. Thus, the potential for environmental impact from dredged sediments contaminated with the most potentially hazardous toxic metals may be enhanced at many intertidal and upland disposal sites as a consequence of expected pH and oxidation changes, which favor increased leaching and plant uptake (Gambrell et al., 1978).

Interactions of Mobilizing Factors

As shown from our examples, the mobility of elements in sediments is affected by pH, redox potential, and complexing ligands (both organic and inorganic). It has been stressed by Plant and Raiswell (1983) that the predominance of simple mineral solution equilibria explains the concentrations of major elements in the surface environment, but the behavior of many trace elements is more complex and is also determined by coprecipitation, surface effects, and interactions with organic phases. Many interactions, however, can be estimated from the simple scheme in Table 31.1, which includes data from soil studies and dredged material (Gambrell et al., 1977; Mattigod and Page, 1983; Plant and Raiswell, 1983), and from recent studies on the effects of acid precipitation (Campbell et al., 1983).

It can be expected that changes from reducing to oxidizing conditions, which involve transformations of sulfides and a shift to more acid conditions, will increase the mobility of typical "chalcophilic" elements, such as Hg, Zn, Pb, Cu, and Cd. On the other

hand, the mobility is characteristically lowered for Mn and Fe under oxidizing conditions. The antagonistic behavior of Fe and Mn, on the one hand, and of chalcophilic elements, on the other, during changes of pH/Eh conditions has been exemplified by Herms and Brümmer (1978) with Cd and Fe in experiments on municipal solid waste compost.

Geochemical mobility in response to environmental acidification will significantly increase, if the following metals are present in the noncrystalline fraction of the sediment (Campbell et al., 1983): Al, Mn, and Zn, and perhaps Cd, Co, and Ni; on the other hand, the elements exhibiting anionic species, such as S, As, Se, Cr, and Mo are appreciably solubilized—for example, from fly ash sluicing/ponding systems at neutral to alkaline pH conditions (Dreesen et al., 1977; Turner et al., 1982). From experiments described in the literature, Jonasson (1977) established a probable order of binding strength for a number of metal ions onto humic or fulvic acids: $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$. There are few data on the effects of higher concentrations of organic ligands in porewater, but here too the sequence of stability has been established in the order $\text{Cu} > \text{Pb} > \text{Cd}$ (Batley and Giles, 1980). The effect of inorganic ligands on metal mobility is usually predicted from the respective stability constants (e.g., Smith and Martell, 1976). In this respect, the influence of salinity has been estimated from the difference between the hydroxo- and chloro-complex stabilities (Dryssen and Wedborg, 1980). It seems that from the common heavy metals introduced from anthropogenic sources, only Ag and Cd are strongly mobilized at the seawater interface (Lion and Leckie, 1981).

Table 31.1. Relative mobilities of elements in sediments and soils as a function of Eh and pH.

Relative mobility	Electron activity		Proton activity	
	Reducing	Oxidizing	Neutral-alkaline	Acid
Very low mobility	Al, Cr, Mo, V, U, Se, S, B, Hg, Cu, Cd, Pb	Al, Cr, Fe, Mn	Al, Cr, Hg, Cu, Ni, Co	Si
Low mobility	Si, K, P, Ni, Zn, Co, Fe	Si, K, P, Pb	Si, K, P, Pb, Fe, Zn, Cd	K, Fe (III)
Medium mobility	Mn	Co, Ni, Hg, Cu, Zn, Cd	Mn	Al, Pb, Cu, Cr, V
High mobility	Ca, Na, Mg, Sr	Ca, Na, Mg, Sr, Mo, V, U, Se	Ca, Na, Mg, Sr	Ca, Na, Mg, Sr, Zn, Cd, Hg, Ni, Co, (Mn)
Very high mobility	Cl, I, Br	Cl, I, Br, S, B	Cl, I, Br, S, B, Mo, V, U, Se	Cl, I, Br, S, B

Estimation of Mobility From Solid Speciation Data

Since adsorption of pollutants onto particles is a primary factor in determining the transport, deposition, reactivity, and potential toxicity of these materials, analytical methods should be related to the chemistry of a particle surface and/or the metal species that is highly enriched on the surface. Apart from direct analysis at the particle surface (Keyser et al., 1978), solvent-leaching techniques provide the most useful information on the behavior of metal pollutants under typical environmental conditions. Common single reagent leaching tests (e.g., the U.S. EPA, ASTM, IAEA, and ICES, and the German Water Chemistry Group) use either distilled water or dilute acetic acid. Sequential extraction procedures were used to differentiate the relative bonding strength of metals on various groups of solid phases. Sequential leaching techniques, while being problematic for the assessment of bioavailability (Salomons and Förstner, 1984), are useful for estimating potential remobilization of toxic metals from polluted solid material; they have been used to classify dredged substances for ocean dumping, on-land disposal, or storage in confined water bodies (Gambrell et al., 1983).

One of these procedures, which has become most generally accepted in the study of aquatic particulate matter, was originally designed by Tessier and others (1979); it has been modified by us to the following sequence (Calmano and Förstner, 1983):

- Fraction 1: Exchangeable cations. The sediment sample is extracted for 2 h shaking time with 1 M ammonium acetate, pH 7.0, at solid/solution ratio of 1:20.
- Fraction 2: Carbonate fraction. The residue from fraction 1 is leached for 5 h with 1 M sodium acetate adjusted to pH 5.0 with acetic acid.
- Fraction 3: Easily reducible phases (Mn oxide, amorphous Fe oxide). The residue from fraction 2 is leached for 12 h with 0.1 M hydroxylamine hydrochloride + 0.01 M nitric acid; pH 2.0; dilution 1:100.
- Fraction 4: Moderately reducible phases (amorphous + poorly crystallized Fe oxide). The residue from fraction 3 is extracted for 24 h with 0.2 M ammonium oxalate + 0.2 M oxalic acid; pH 3.0; dilution 1:100.

Fraction 5: Metals bound to organic matter and sulfides. The residue from fraction 4 is extracted at 85°C for 5 h with 30% H₂O₂, adjusted to pH 2.0 with HNO₃, and then at room temperature with 3.2 M ammonium acetate in 20% nitric acid.

Fraction 6: Residual metals (e.g., detrital silicates, crystalline Fe oxide). The residue from fraction 5 is digested with a 5:1 mixture of hydrofluoric and perchloric acids or with concentrated nitric acid; 120°C, dilution 1:100.

The data from a large number of leaching experiments on dredged materials (Engler et al., 1974; Gupta and Chen, 1975; Förstner et al., 1981) suggest that the surplus of metal contaminants, introduced into the aquatic system by human activities, usually exists in relatively unstable chemical form. They should, therefore be more accessible for short- and middle-term geochemical processes (including biological uptake) than the detrital, predominantly natural metal compounds (see also Chester et al., 1984, in press).

Our recent investigations on the effect of various drying procedures on metal speciation in anoxic sediments have demonstrated that:

1. Sample preparation affects the distribution of metal phases in an extraction scheme.
2. Stability of metal phases may both increase and decrease during oxidation.

Examples for manganese and zinc illustrate these effects (Fig. 31.7).

The above fractionation scheme was applied to fresh and freeze-dried samples of sulfide-rich, carbonate-rich, and high-organic content sediments. These sediments represent different, early diagenetic environments according to the classification of Berner (1981). The sulfidic sediment (a) with high H₂S concentrations represents anoxic (-sulfidic) conditions and was taken from Athens harbor. The calcareous sample (b) was taken from a highly reducing sediment of Rotterdam harbor, where all sulfate and hydrogen sulfide have been consumed and methane is being produced (methanic environment). The organic-rich samples (c) were collected from an intertidal flat of the Elbe estuary near Hamburg harbor. The organic matter decomposition at this site has not yet proceeded to the sulfate reduction stage; thus, it represents a postoxic sedimentary environment (Kersten and Kerner, 1985).

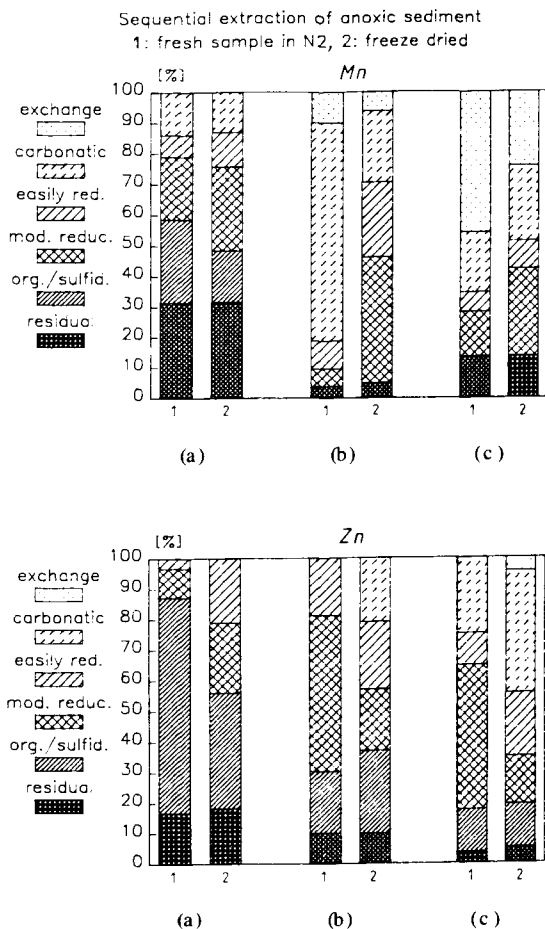


Fig. 31.7. Chemical extraction results on fresh and freeze-dried samples. Examples of manganese (Mn) (above) and zinc (Zn) (below). Early diagenetic environments: (a) sulfidic; (b) methanic (postsulfidic); and (c) postoxic.

Characteristic transformations from carbonatic to oxidic phases, probably implying a stronger association of manganese with the sediment substrate, take place in the calcareous and the organic-rich sample during freeze drying. In the sulfide-rich sample, on the other hand, reducible fractions increase at the expense of the hydrogen peroxide-ammonium acetate extractable fraction during the process of oxidation and drying. From comparison of sulfide-rich and high-organic content samples, which contain no measurable H_2S , it is suggested that fraction 5 represents exclusively sulfidic Mn associations and predominantly sulfidic Zn forms. This fraction is particularly problematic in these schemes, because it comprises both labile and more stable organic sub-fractions in combination with sulfidic phases

(Engler, 1980). The existence of manganese sulfide in highly polluted coastal marine sediments has been postulated from extraction experiments and calculations of saturation indices in interstitial waters (Nembrini et al., 1982). Discrete manganese and zinc sulfide minerals were identified by scanning electron microscopy, with energy-dispersive X-ray analysis, in sediments from Landsort Deep in the central Baltic Sea (Suess, 1979) and Newark Bay, New Jersey (Luther et al., 1980), respectively. The exchangeable portion of manganese is possibly an artifact, as already described by Jenne (1968); neutral NH_4OAc causes dissolution of recently formed hydrous oxides of manganese. This fraction is the predominant form of manganese in the organic-rich sediment, and it dramatically decreases with freeze drying. The manganese that was removed from the exchangeable fraction was generally recovered in the easily reducible fraction, thus indicating aging mechanisms.

The total extractable zinc in all of the three sediment materials selected was generally in the same narrow range (Fig. 31.7). The response of the various zinc forms to freeze drying is variable and depends on the sediment environment. In the reduced sediment-water system, containing considerable sulfide, the formation of zinc sulfide is expected to contribute to the predominant zinc fraction extracted by the hydrogen peroxide digestion. The level of this form decreases to nearly half, with freeze drying, and was recovered in the reducible forms by the sequential fractionation procedure. This suggests a rapid oxidation of the sulfidic zinc species (a), which may be tied up predominantly by poorly crystalline oxides of iron (see below). Little or no difference in zinc recovery with hydrogen peroxide digestion was found in the absence of sulfide in the methanic (b) and high-organic content samples. A possible explanation would be chelation of zinc by naturally occurring insoluble organics, which contribute to this fraction and have been reported to persist in oxidized environments for a sufficient time (Reddy and Patrick, 1975). Transformation of the moderately reducible (oxalate extractable) to carbonatic (sodium acetate, pH 5.0 extractable) fraction in the nonsulfidic sediments clearly involves a weakening of the bonding strength, suggesting an increase in poorly crystallized iron oxides that reacts with Zn. Considerable iron was released by the easily reducing hydroxylamine-hydrochloride extraction in the postoxic (c) sample (Kersten, unpublished data), which could be related to reduction of ferric oxyhydroxides to inter-

mediate ferrous hydroxide gel forms brought about by anaerobic conditions (Patrick and Khalid, 1974). The well-established role of hydrated iron oxide, in at least partially governing trace metal sorption, suggests that this conversion to more soluble and highly dispersed iron forms increases the activity and surface area of the oxide compounds reactive with Zn.

These findings are in agreement with experimental data of Gambrell et al. (1977) on the variations of selected chemical forms of manganese and zinc in response to changes of physicochemical sediment parameters. Both pH and redox potential were found to regulate levels of soluble and exchangeable manganese and zinc in the sediment-water systems. Generally, these forms of manganese decreased with an increase in both pH and redox potential, particularly as the redox potential increased above 250 mV (postoxic environment; Berner, 1981). The result of this study on zinc fractionation suggests that in strongly reduced sediments containing sulfides, an increase in readily available zinc may be expected if the material remains in suspension for considerable periods; also, particularly in dredged material deposited on land where slow drainage and subsequent oxidation of the surface horizon may occur. In strongly reduced sediments with minor sulfide content, there may be considerably less influence of increasing redox potential above the reduced levels, suggesting that only a small release of zinc (e.g., by insoluble organics) would occur from such dredged materials.

Conclusions

Species differentiation can be used in estimates of remobilization of metals under changing environmental conditions.

1. In the estuarine environment, the "exchangeable fraction" will be particularly affected; however, changes of pH and redox potential could also influence other weakly held phases (e.g., carbonate and manganese oxides).

2. Lowering of pH will affect the "exchangeable," then the "easily reducible," and then parts of the "moderately reducible" fractions, with the latter consisting of Fe oxyhydrates in less crystallized forms.

3. Aeration of anoxic sediments may both increase and decrease mobility of metals. In the examples presented, the sequence of relative mobili-

ties, as depicted in Table 31.1, is confirmed; while manganese is transferred from a "medium mobility" state to a "very low mobility" during oxidation, the reactivity of zinc is clearly enhanced under these conditions.

4. These data demonstrate that during analytical fractionation, anoxic sediments must be extracted with great care and under oxygen-free conditions for at least the first three steps (exchangeable, carbonate, and easily reducible fractions). The respective leaching agents must be deaerated prior to contact with the original wet samples.

5. If these prerequisites are respected, the chemical leaching approach may exhibit distinct advantages compared to thermodynamic models, since these data (although still unsatisfactory) incorporate information on diagenetic effects (aging, diffusion) and reaction kinetics, which influence the mobility of contaminants in highly complex matrices.

6. To assess the mobility of heavy metals in sediments under field conditions, particularly during changes of pH/redox values, solid speciation experiments should be complemented by the analysis of respective pore solution chemistry. These investigations must also require precautionary measures, mainly with regard to the exclusion of oxygen, and they are preferably carried out by *in situ* methods.

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