Chapter 21

Mobilization and Scavenging of Heavy Metals Following Resuspension of Anoxic Sediments from the Elbe River

W. Calmano, U. Förstner, and J. Hong[1]

Technical University of Hamburg-Harburg, Eissendorfer Strasse 40, D–2100 Hamburg 90, Germany

Resuspension of sediments from the Elbe River can significantly decrease pH values due to high acid-producing potential and low neutralizing capacity. Metals can be released into the dissolved phase, but may subsequently be readsorbed or precipitated in part to solid phases. To evaluate the potential for metal release and scavenging on a regional and long-term scale, experiments were undertaken at stable neutral-pH values. Rates of total metal release and metal scavenging were extrapolated from time series of net-release values measured over 630 hours. The order of total release from the sediment was Cd (5%) > Zn (1.5%) > Cu (1%) > Pb (0.7%). The scavenging of released metals was in the reverse order: Pb (86%) > Cu (53%) > Zn (34%) > Cd (30%). Dominant processes are adsorption on organic substances, adsorption/coprecipitation by fresh Fe-Mn oxides and precipitation of metal phosphates originating from the decomposition of organic matter. Based on our experimental results and relevant published data, a four-stage interaction model is developed for metals in anoxic sediments. This model describes the behavior of heavy metals in the system subsequent to oxidation.

Many investigations have shown that the sediments of the Elbe River have been severely contaminated by heavy metals and other pollutants during the last decades (1-4). The sediments of the Hamburg harbor, situated at the downstream end of the Elbe River, are dredged to meet the needs of shipping. Dredging produces 2 million m^3 of material per year consisting of about 0.8 million m^3 of sand and approximately 1.2 million m^3 of contaminated harbor mud (5). During dredging,

[1] Current address: Department of Chemical Engineering, Tulane University, New Orleans, LA 70118

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the anoxic bottom sediments are suspended. These sediments are exposed to the overlying water, which is rich in dissolved oxygen. A pollution problem arises when heavy metals bound or adsorbed to solids are released into the aqueous phase or transformed into more bioavailable forms during the suspension of the anoxic sediments. Similar problems occur if the polluted sediments are deposited onto spoil areas and exposed to air. Such effects may also occur at the sediment-water interface under different redox conditions during early diagenesis.

Oxidation of the sediments from the Hamburg-Harburg section of the harbor can decrease the pH due to their high acid-producing potential and low acid-neutralizing capacity (6,7). During suspension, anoxic sediments are oxidized by oxygen in water. A lack in understanding of the opposed and interacting effects of certain of these processes originates from two views of the effects of changing redox potential. One view is that the presence of sulfide under reduced conditions will precipitate toxic metals, resulting in very low metal concentrations; the oxidation of sulfides to sulfates under oxidizing conditions will release these metals into the overlying water (8-12). The opposite view is that Fe and Mn compounds will tend to sorb or coprecipitate heavy metals under oxidized conditions. These hydrous oxides are more soluble under reduced conditions due to the reduction of Fe and Mn hydrous oxides (13-17). The effect of sulfides, oxides and hydroxides of Fe and Mn in controlling the solubility of trace metals in the sediment/water systems (interstitial waters) is greatly modified by the presence of organics (18-22).

A study of the release of Cd and Pb from dredge spoil suspended in estuarine water was carried out by Prause et al. (23). A considerable release of Cd from polluted sediments of the Bremen harbor was observed in long-term experiments. Hirst et al. (24) did not observe similar results for Cu, Zn, Fe, and Mn during experimental resuspension and reoxidation of polluted anoxic sediments collected from the Mersey estuary, northwest England. Hirst et al. concluded that, in the estuarine environment, the resuspension of metal-rich (polluted) anoxic sediments is exceedingly unlikely to result in increased metal concentrations in surface waters. It was stressed that such sediments may in fact act as additional scavengers of trace elements.

Khalid et al. (25) and Wallmann (8) found an increase in dissolved Cu, Cd and Pb concentrations with time during the oxidation of an anoxic estuarine sediment in seawater and fresh water. In their experiments, pH was not controlled and became progressively lower. Although metal mobilization was investigated intensively in controlled pH-Eh systems (26-28), these studies only focused on the transformation (including dissolved phase) of metals in sediment/water systems without consideration of interacting processes.

For polluted sediments, some important questions remain:

- Can heavy metals in the sediments be released into solution during oxidation under stable neutral-pH conditions?
- If so, which metals and what concentrations can enter the aqueous phase?
- Which release process is dominant during suspension/oxidation?

This study was designed to answer these questions. Based on the results, a model is developed to explain the behavior and interacting processes controlling the concentrations of heavy metals in sediment/water systems during suspension of anoxic sediments.

Materials and Methods

Sediment Sampling. A sediment core was collected from the Mühlenberger Loch, which is situated at the downstream Elbe near the Hamburg harbor (Figure 1). The sedimentation rate here is about 8 cm$\cdot$y^{-1} (29). The core was sealed without air space. Care was taken to avoid exposure to atmospheric O_2 during transportation and storage prior to laboratory studies. In an O_2-free glove box, under a nitrogen atmosphere, the sediment core was cut and divided into sections. The sediment at the depth 7-10 cm was used for the suspension experiment. Some of the sediment properties are presented in Table I.

Table I. Characteristics of the Sediment

Parameter	Value		Parameter	Value	
Organic carbon	3.83	mass %	Extractable Fe (1N HCl)	222	μmol$\cdot$g^{-1}
Loss on ignition	10.2	mass %	Extractable Fe^{2+} (1N HCl)	184	μmol$\cdot$g^{-1}
Protein	24.17	mg$\cdot$g^{-1}	Extractable Fe^{3+} (1N HCl)	38	μmol$\cdot$g^{-1}
$CaCO_3$	7	mass %	Total Cu	87	mg$\cdot$kg^{-1}
Water content	65.4	mass %	Total Zn	538	mg$\cdot$kg^{-1}
Acid volatile sulfide	3.8	μmol$\cdot$g^{-1}	Total Pb	64.6	mg$\cdot$kg^{-1}
Pyrite	42.8	μmol$\cdot$g^{-1}	Total Cd	2.59	mg$\cdot$kg^{-1}

Laboratory Simulation Experiment. Wet sediment material was transferred to a 180 ml reaction cell. 135 ml of artificial river water (2 mM $CaCl_2$ and 5 mM NaCl) was added to the reaction cell. Together with the sediment material the total suspension volume in the reaction cell was 140 ml. The solid:liquid ratio was 1:64. The suspension was stirred with a magnetic stirrer. Air was continuously bubbled through the system. pH was automatically adjusted with 0.1 N NaOH or 0.1 N HCl by a control system (30). During the experiment, the pH of the system was maintained at 7.5. The experiments were carried out under exclusion of light. The temperature during the experiments was not controlled, but was recorded. The variation was between 21-23°C.

Analysis. The suspension was sampled at regular intervals. The suspension samples were centrifuged and filtered through a 0.2 μm membrane. The same volume of artificial river water used to wash the centrifugation tube was added into the reaction cell in order to maintain a constant suspension volume. Part of the filtrate was acidified with concentrated nitric acid to pH 1.5 for determination of concentrations of heavy metals by atomic absorption spectroscopy (AAS). Another part of the filtrate was used for nitrate and sulfate determinations by ion chromatography (IC). Sulfide and pyrite were analyzed by polarography. The details can be found elsewhere (31). After digestion of the sediment with concentrated nitric acid at 80°C for 6 hours, the total content of each metal was determined.

Results

Data Treatment. Because the solution was sampled at regular time intervals and artificial river water was added into the suspension to keep the volume constant, part of the dissolved metals were removed from the system and the original suspension was diluted. Release of heavy metals from the sediment phase and scavenging from the aqueous phase are determined by the following equation:

$$\alpha = C_i^m - C_{i-1}^m \left[\frac{V_0 - V_i}{V_0}\right] \tag{1}$$

where C_i^m and $C_{i-1}{}^m$ are measured dissolved metal concentrations at *i*th time and (*i*-1)th time, respectively; V_0 and V_i are total volume and sampled volume, respectively; α is a discriminating factor.

If

$$f = \frac{V_0 - V_i}{V_0} \tag{2}$$

we get

$$\alpha = C_i^m - fC_{i-1}^m \tag{3}$$

where f is the residual coefficient of the solution. If $\alpha < 0$, metals are scavenged from the solution; if $\alpha > 0$ metals are released into the solution. If $\alpha = 0$, the system is stable with constant metal concentrations in solution.

For the whole process the release of metals from the sediment can be calculated as follows:

$$C^{re} = \sum\left[C_i^m - fC_{i-1}^m\right] \tag{4}$$

where C^{re} is the total released concentration.

The scavenging concentration can be calculated by equation 5:

$$C^{sc} = \sum\left[C_{i-1}^{net} - C_i^{net}\right] \tag{5}$$

where C^{sc} is the scavenging concentration, C_i^{net} and $C_{i-1}{}^{net}$ are net-release concentrations at *i*th time and (*i*-1)th time, respectively. The net-release concentration is calculated by equation 6:

$$C_i^{net} = C_{i-1}^{net}\left[\frac{C_i^m}{C_{i-1}^m\left[\frac{V_0 - V_i}{V_0}\right]}\right] \tag{6}$$

where C_i and C_{i-1} are the concentrations at ith time and (i-1)th time. Equation 6 assumes that the metals removed by sampling would participate in interacting processes and would be scavenged proportionally, if they had not been removed from the operational procedure.

If

$$\beta = \frac{C_i^m}{C_{i-1}^m\left[\frac{V_0 - V_i}{V_0}\right]} \tag{7}$$

we get

$$C_i^{net} = \beta C_{i-1}^{net} \tag{8}$$

Combining equations 5 and 8 we can calculate the total scavenged concentration:

$$C^{sc} = \sum\left[(1 - \beta)C_{i-1}^{net}\right] \tag{9}$$

The total concentration changes of net release are:

$$C^{net} = C^{re} - C^{sc} \tag{10}$$

That part of released metal, which was sampled at regular time intervals, is not considered to be scavenged by sediment phase. So:

$$C^{net} = C_i^m + \frac{\sum C_{i-1}^m V_{i-1}}{V_0} \tag{11}$$

If there is only release but no scavenging in the suspension, equation 11 is suitable. If there is both release and scavenging from the aqueous phase, the first method is better to describe the interacting processes. In our experiments we found both release and scavenging. Therefore, we used equations 4, 9, and 10 to calculate release, scavenging and net release during the suspension.

Cadmium Release. Continuous release of Cd in the suspension was observed. As seen in Figure 2, there was a rapid release at the beginning of the experiment, then the release slowed. After about 200 hours the rate of the net release (C^{net}) increased again. The highest release rate occurred after about 300 hours and later.

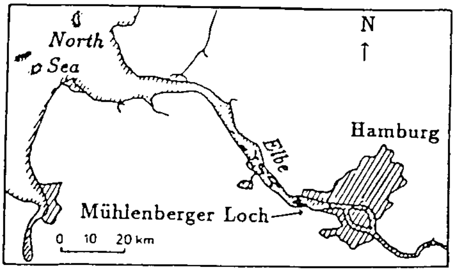

Figure 1. Sampiing site.

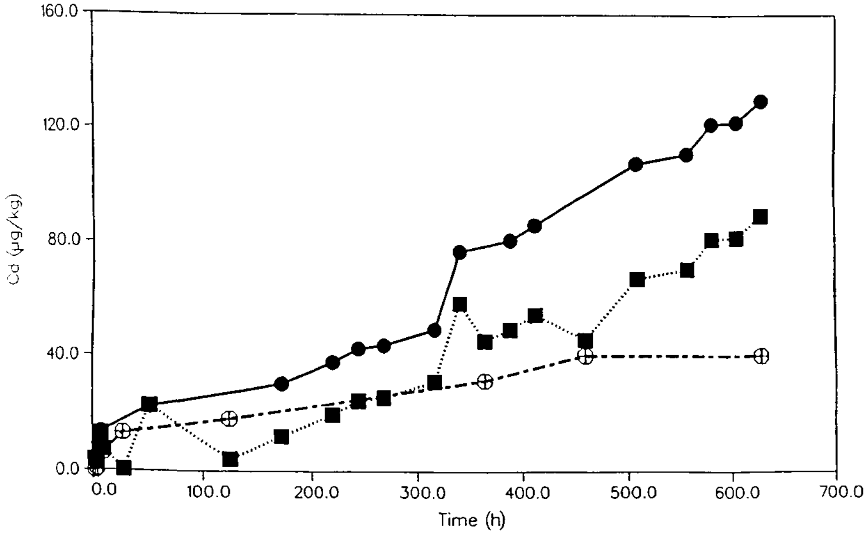

Figure 2. Cadmium release. (•) - total release; (⊕) - scavenging (adsorption/coprecipitation); (■) - net release.

During the entire experiment (over 628 hours) Cd release reached 0.129 mg per kilogram sediment, or 4.99% of the total Cd content in the sediment. A portion of the Cd released was scavenged. Finally only 0.090 mg $Cd \cdot kg^{-1}$ sediment remained in solution, which was about 3.5% of the total Cd content in the sediment (Table II). At the end of the experiment, the concentration of Cd in solution was 1.40 $\mu g \cdot l^{-1}$.

Table II. Release Percentage of Heavy Metals During the Suspension

	Total Content	Total Release		Net Release		Final Conc. in Solution
	($mg \cdot kg^{-1}$)	($mg \cdot kg^{-1}$)	(%)	($mg \cdot kg^{-1}$)	(%)	($\mu g \cdot l^{-1}$)
Cd	2.585	0.129	4.99	0.090	3.5	1.40
Zn	538	8.28	1.54	5.48	1.02	85.6
Cu	87	0.824	0.95	0.388	0.45	6.06
Pb	65	0.441	0.68	0.064	0.10	0.99

This study confirms that Cd in the sediment of the Elbe River can be mobilized during oxidation in early diagenesis, suspension and dredging activities under stable pH conditions. Unfortunately there exist no field data from the Elbe River. More experimental work is needed to explain the unusual release occurring after 300 h. This release is probably due to organic-matter decomposition.

Lead Release. Pb release from the sediment was significantly different from that of Cd and other metals. The dissolved Pb concentration increased at the beginning of the experiment and later decreased continuously (Figure 3). Readsorption during the suspension process is a possible explanation for the concentration decrease. After 10 hours, the highest release concentration reached 0.36 $mg \cdot kg^{-1}$. After about 100 hours, an approximate steady state between release and readsorption processes was attained, and the total concentration of Pb released from the sediment remained relatively constant at a value between 0.15-0.2 $mg \cdot kg^{-1}$. In the whole suspension process, the mass of Pb released from the sediment was 0.441 $mg \cdot kg^{-1}$ (Table II), i.e. 0.68% of the total Pb content of the sediment, however, 85.5% of the Pb released was scavenged by the solids. Net release was only 0.1% of the total Pb content in the sediment.

Copper Release. Cu release is shown in Figure 4. There was a significant increase at the beginning of the experiment. Continuous increase of the dissolved Cu concentration was found until about the 350th hour. Although there was still a slow release, the scavenging rate of Cu was faster than the release rate of Cu at this stage. This process resulted in a decrease of dissolved Cu concentration. As can be seen from Figure 4, the concentration remained relatively constant. At the end of the experiment, 0.824 $mg \cdot kg^{-1}$ of Cu was released into the solution, which

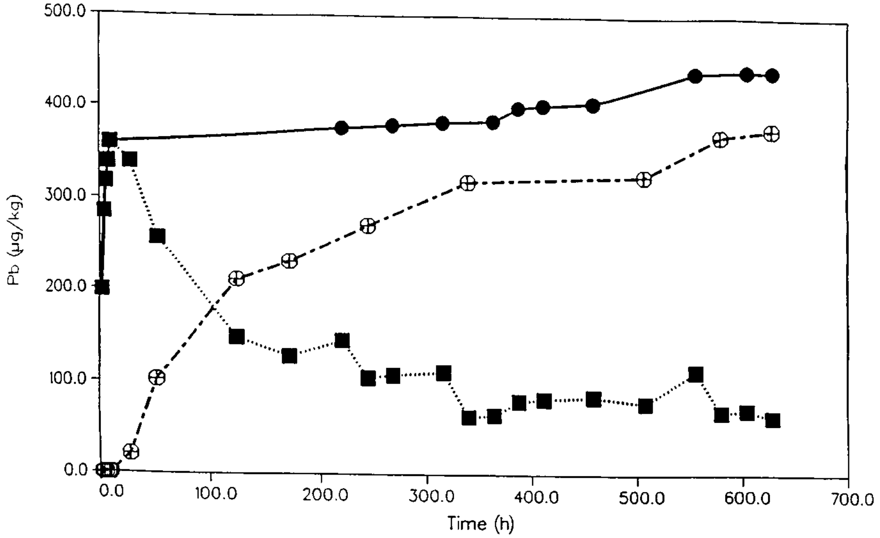

Figure 3. Lead release. (•) - total release; (⊕) - scavenging (adsorption/coprecipitation); (■) - net release.

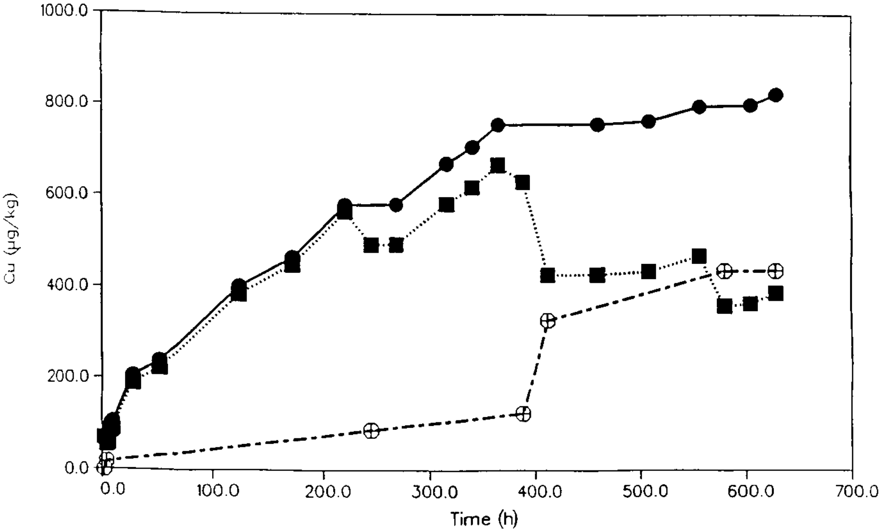

Figure 4. Copper release. (•) - total release; (⊕) - scavenging (adsorption/coprecipitation); (■) - net release.

corresponded to about 0.95% of the total Cu content in the sediment. The net release was only 0.388 mg·kg^{-1}, i.e. 0.45% of the total copper content. At the end of the experiment the Cu concentration in the solution was 6.06 μg·l^{-1}.

Zinc Release. The Zn release was similar to that of Cu at the start of the experiment but Zn was not strongly scavenged at the later stage. Figure 5 shows a continuous increase. The released Zn concentration was relatively high, as a result of the high Zn content in the sediment (538 mg·kg^{-1}). During the experiment, 8.28 mg·kg^{-1} of Zn was released, or 1.54% of the total Zn content. The net-release concentration and net-release percentage were 5.48 mg·kg^{-1} and 1.02%, respectively. A relatively high Zn concentration of 85.6 μg·l^{-1} was found in the solution at the end of the experiment.

Readsorption/Coprecipitation of Metals. The scavenging of different heavy metals during the suspension experiment is listed in Table III. Scavenging is mainly attributed to readsorption and coprecipitation. Approximately one-third of the released Cd (30%) and Zn (33.8%) was scavenged from the solution, mainly by readsorption onto the solid surface. Readsorbed/coprecipitated Cu exceeded half of the released Cu (52.9%). Up to 85.5% of released Pb was scavenged during the suspension. Very little Pb remained in the solution at the end of the experiment. The order of scavenging percentage for metals is: Pb > Cu > Zn > Cd. This order is the inverse of the mobilization percentage for metals (Table II): Cd > Zn > Cu > Pb. However, both orders are different from the total amount of release (mg·kg^{-1}) for the metals: Zn > Cu > Pb > Cd, which is the same order as the original total contents of these metals (Table II).

Table III. Release and Readsorption/Coprecipitation of Heavy Metals During Suspension

	Total Release	Readsorption/coprecipitation		Net Release	
	(mg·kg^{-1})	(mg·kg^{-1})	(% of total)	(mg·kg^{-1})	(% of total)
Cd	0.129	0.039	30	0.090	70
Zn	8.28	2.80	33.8	5.48	66.2
Cu	0.824	0.436	52.9	0.388	47.1
Pb	0.441	0.377	85.5	0.064	14.5

Discussion

Results from Other Studies. Cd release has also been observed in other investigations of polluted harbor sediments. Prause et al. studied the release of Cd from dredged material of the Bremen Europahafen in the harbor environment (23). During a long-term experiment extensive Cd remobilization was recorded. Polluted

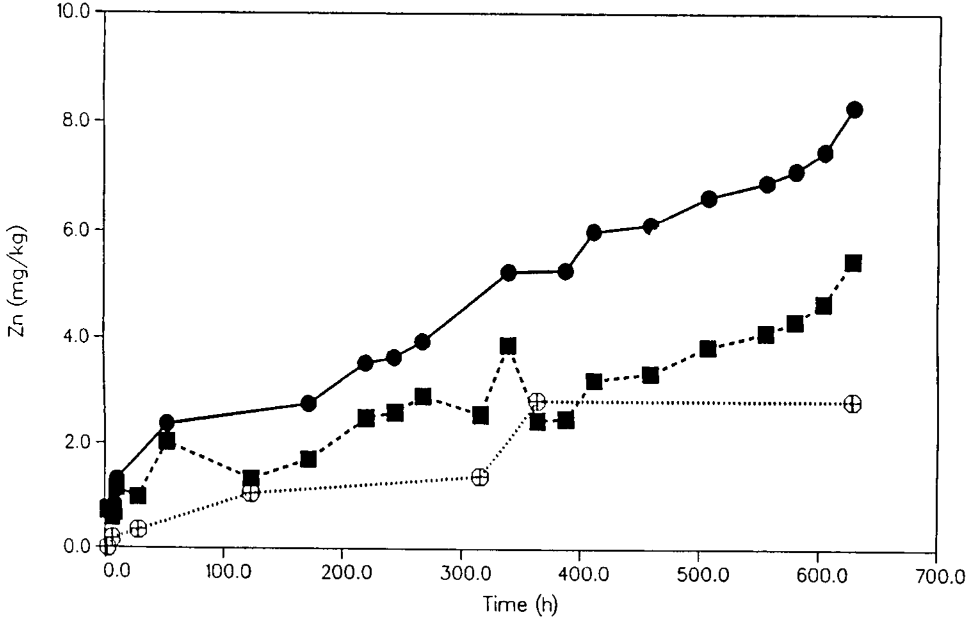

Figure 5. Zinc release. (•) - total release; (⊕) - scavenging (adsorption/coprecipitation); (■) - net release.

fresh-water sediment disposed into seawater at pH 7.9 caused release of 1-2 μg Cd per gram solids (about 25% of total content) in a 50-day experiment.

In a study of periodic oxidation-reduction at pH 6.0, Cd increase in solution during oxidation has also been observed (7). In some investigations, without pH control, oxidation often results in pH decrease and causes Cd release (7,8,25,30,32). Calmano et al. found that in a 3-week suspension experiment using fresh-water sediments treated with seawater, 15.9% of Cd was released (33). In an oxidation experiment without pH control, Cd release can reach 35.6% (pH 3.5) (30).

Gambrell et al. studied Pb mobility in Mobile Bay sediment suspensions (26) spiked with carrier-free ^{210}Pb to determine the dissolved Pb concentration in systems with varying pH and redox potentials. No more than 0.15% of labelled Pb could be found in the solution at a pH range from 5.0 to 8.0. Furthermore, Prause et al. found no release of Pb from the sediments in their long-term and short-term experiment (23). But in an oxidation experiment without pH control (30), 1.6% of the total Pb in the sediment was mobilized when the pH in the system decreased below 3.5. Similar results were found by Khalid et al. (25).

Förstner et al. reported that in a 3-week suspension experiment, 1.3% of the total Cu was released from dredged mud of the Hamburg harbor when treated with seawater, and 0.48% of the total Cu was in solution at the end of the experiment (34). The net-release percentage is very similar to the result of the present study (0.47%). In a 30-day experiment without pH control (30), the Cu mobilization reached 6.8% of the total Cu content at the end of the experiment (pH 3.5).

A different result was observed by Hirst and Aston (24). During resuspension and reoxidation of polluted anoxic sediments, they did not find any release of Cu. After recalculating their results, however, we found that their results and the current study are not contradictory. In their experiment they used a very dilute suspension, where the sediment:water ratio in suspension was 1:2000. If we assume that there was the same net-release proportion as in our experiment (0.45%), the net release of Cu in their experiment would be only 0.2 $\mu g \cdot l^{-1}$. This concentration is insignificant compared with the total-release concentration in our experiment. On the other hand, their experiment was performed only for 72 hours, while the net Cu release of 0.45% in our experiment was determined after 628 hours. In another suspension experiment (34) the redox potential after 100 hours was still below -50 mV. Little or no metal release is expected under these conditions.

Calmano et al. observed that 9.1% of the total Zn in the dredged mud was released during the suspension experiment when river sediments were treated with seawater (35). In a 30-day oxidation experiment without pH control (30), 24.6% of the total Zn was found in the solution at pH 3.5.

Again, Hirst et al. found no release of Zn from anoxic sediment during the suspension in their experiments (24). From the data listed in Tables 3 and 4 of their paper, no Zn was released during suspension at 5°C in all four group experiments. At 20°C, they observed an increased tendency for mobilization during the suspension. These results can be explained by two possibilities. One possibility is that limited microbial activity at relatively low temperatures (5°C).

Prause et al. found strong influence of microbial activity on metal release (23). The second possible explanation is the low sediment:water ratio discussed above.

Sources of the Released Metals. Sulfide oxidation provides the primary source of metal release. The solubility of amorphous sulfide minerals is very low, but they are very unstable in aqueous environments when exposed to oxidants such as dissolved oxygen (DO) or Fe(III). Oxidation will result in remobilization or redistribution of metals. From the data of our experiment Cu release as well as Zn release were correlated with sulfate concentration during the suspension experiment (Figures 6,7), especially at the first stage. Calculations show that there is a marked correlation between sulfate concentration ($[SO_4^{2-}]$) and total metal concentration ([T-Me]) in the solution. The correlation coefficients with $[SO_4^{2-}]$ are 0.98, 0.98, 0.93, and 0.92 for Cu, Zn, Cd, and Pb, respectively. It is not surprising that Cu is more closely correlated to SO_4^{2-}. As can be seen from Table IV, the solubility constant (K_{sp}) of CuS is much lower than that of other metals. In other words, Cu will be the first sulfide precipitated if any sulfide ion (S^{2-}) is present. In a sequential extraction procedure, Cu in the sulfidic/organic fraction can often reach a very high percentage. For example, a sediment sample from the Harburg section of the Hamburg harbor contains more than 80% of total potentially mobile Cu (7).

Table IV. K_{sp} and Metal Sulfide Fraction in Two Hamburg Harbor Sediments

Metal	No. 1*	No. 2**	Sulfide	K_{sp}
Cu	87%	86.9%	Cu_2S	2.5×10^{-48}
			CuS	6.3×10^{-36}
Pb	79%	63%	PbS	8.0×10^{-28}
Cd	66%	58%	CdS	8.0×10^{-27}
Zn	38%	39%	α-ZnS	1.6×10^{-24}
			β-ZnS	2.5×10^{-22}

*No. 1: from Hong et al. (30). In the percentage calculation, the total content does not include the content in the residual fraction treated with concentrated HNO_3.

**No. 2: from Kersten and Förstner (36).

Earlier studies, which are similar to this investigation, have assumed certain mechanisms that result in metal release. Although sulfide oxidation is often discussed, limited evidence has been provided. The increased sulfate concentration with increasing heavy-metal concentration (especially for Cu and Zn) under stable-pH conditions observed in our experiments is probably the first evidence for assessing heavy-metal behavior in anoxic sediment during suspension and oxidation. In addition to metal-sulfide oxidation, pyrite (FeS_2) oxidation is also an important source of metals because pyrite can strongly bind heavy metals during

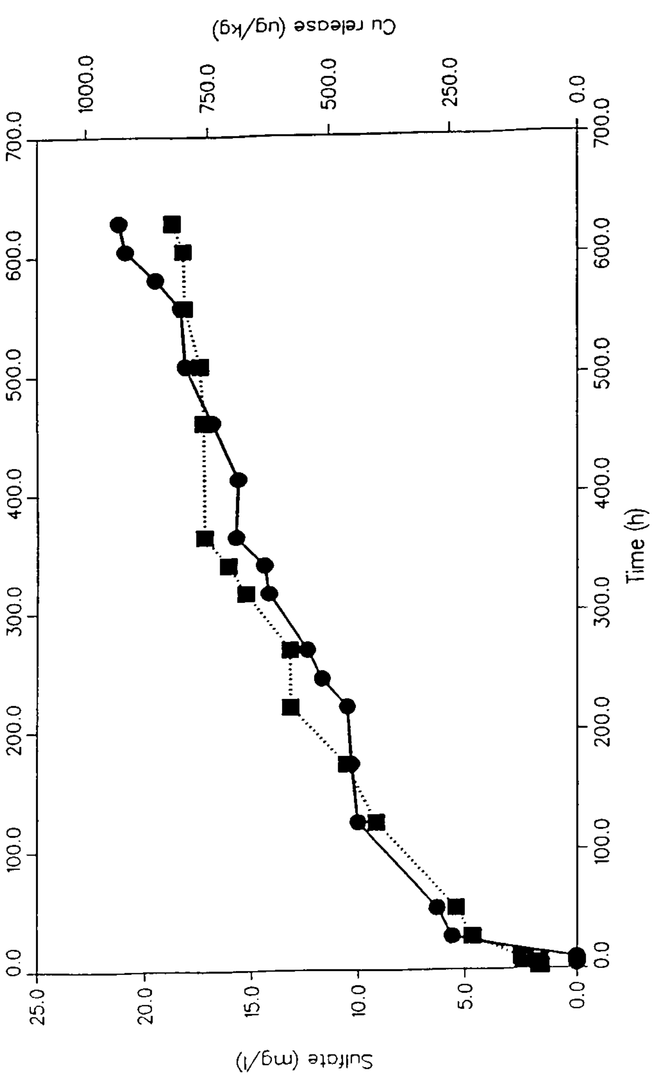

Figure 6. Sulfate concentrations and copper release into the suspension. (•) - sulfate; (■) - copper.

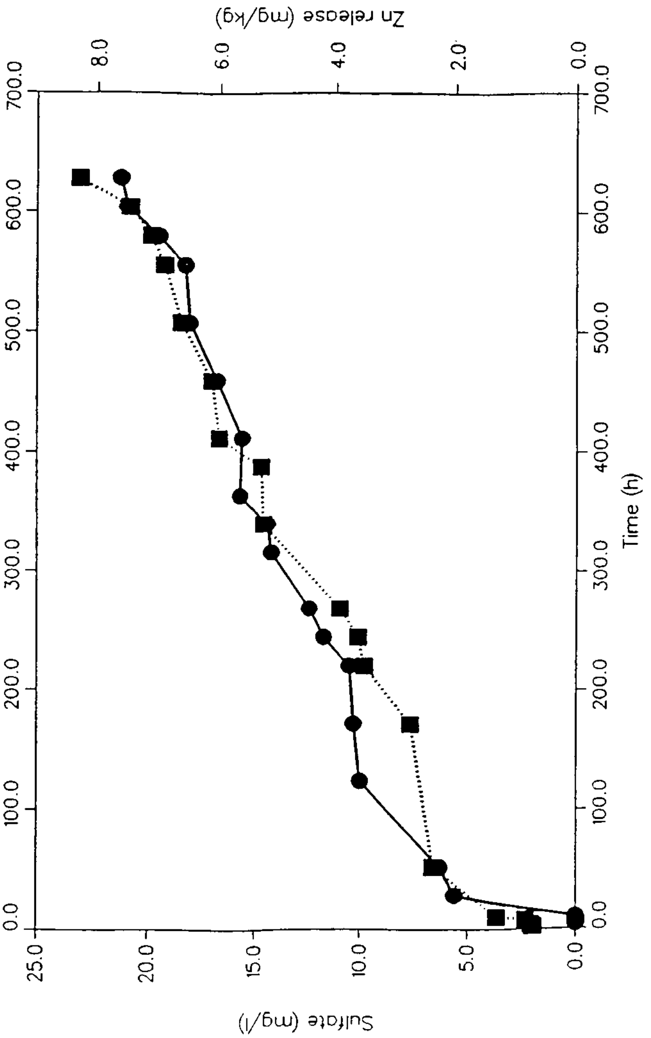

Figure 7. Sulfate concentrations and zinc release into the suspension. (●) - sulfate; (■) - zinc.

formation. A recent study (37) has found that the binding capacity for divalent heavy-metal cations by pyrite increased in the order $Co^{2+} < Cd^{2+} < Mn^{2+} < Ni^{2+} < Zn^{2+}$. When pyrite is oxidized, heavy metals bound by pyrite can be released into the solution. Pyrite oxidation during the suspension experiment is shown in Figure 8.

Displacement by inorganic cations and complexation by Cl^- is known to increase the solubility of trace elements, in particular of Cd, if the concentration of Cl^- ions is high enough to compete with hydroxide formation (38), and complexation with ligands on the organic-solid surface. In our artificial estuarine water, Cl^- was the only complexing anion. Hem (39) suggested the presence of a mixed complex, $Cd(OH)Cl^o$, when the Cl^- concentration exceeds 0.1 M, with a solubility greater than for $Cd(OH)_2^o$. Khalid et al. pointed out that the probable formation of $Cd(OH)Cl^o$ is reasonable in Barataria Bay sediment suspensions containing a 0.3 M sodium-chloride, sodium-sulfate solution.

As can be calculated by the use of stability constants, the most dominant Cd species in waters of low salinity and containing low concentrations of dissolved organic ligands are the positively charged Cd^{2+} and the mono-chloro-Cd-complex (see Table V). With increasing salinity, the positively charged species decrease and the neutral or negatively charged species increase. This changing species distribution has a direct influence on the extent of Cd-sorption on negatively-charged organic surfaces. In addition to competition with positive alkali ions, the decreased Cd sorption at higher salinity may be due to this change in the dissolved Cd speciation.

Table V. Calculated Cd-species Distribution (%) at Different Salinities

	(‰) Salinity			
	5	10	15	20
$[Cd^{2+}]$	19.63	11.43	7.65	5.41
$[CdCl^+]$	65.46	61.97	55.95	49.71
$[CdCl_2^o]$	13.74	22.15	29.40	33.44
$[CdCl_3^-]$	0.72	2.37	4.42	6.56
$[CdCl_4^{2-}]$	0.12	0.84	2.39	4.72
$[Cd(OH)Cl^o]$	0.21	0.19	0.17	0.15
Positively charged species	85.1	73.4	63.6	55.1
Neutral or negatively charged species	14.9	26.6	36.4	44.9

These effects could not be observed in earlier experiments in the multichamber device, where Cd had been mobilized from polluted dredged sediments (35). Cd from dredged mud did not behave like ionic Cd. The reason for this behavior could be that:

- the pore water of the sediment suspension contained high concentrations of dissolved organic ligands which complex Cd;
- the organically-complexed Cd had a high affinity for the organic surfaces of the biological material. Increasing salinity did not prevent sorption on these surfaces.

A number of investigations have focused on studies of organic-bound metals in sediment/water systems. A general assumption is that organic carbon is oxidized continuously by a sequence of energy-yielding reactions with decreasing energy production per mole of organic matter oxidized. The calculated ratios of the metal/C flux support the argument for metal mobilization during organic-carbon oxidation. For example, Wallmann (8) found that a considerable percentage of the total Cu content exists as a labile organic complex during suspension of anoxic sediment.

Interstitial-water studies provide many examples to analyze the relationship between metals and organic ligands in sediment-water systems. The data of Elderfield (40) indicated that approximately 80% of the total Cu was organically bound in the interstitial water of surface sediments. Most of the organically-associated heavy metals are "colloidal" and equivalent in molecular weight to humic substances. Hart and Davies (41) reported that most of the Cd in the interstitial water from a sediment sample of an urban creek at Melbourne, Australia, was associated with colloidal labile species and more strongly bound by organic complexes. Most of the Zn and Pb was associated with the colloidal phase, 20% in labile forms and 10% in more tightly bound (organic) forms. Van den Berg et al. studied the organic complexation capacity of Zn with samples collected from interstitial waters in sediments of the upper Gulf of Thailand and the estuary of the river Mersey in England (42). These authors concluded that between 93 and 98% of the total Zn is complexed by organic material in the interstitial water, as a result of high ligand concentrations. These results indicate that the dissolved Zn concentrations may increase as a result of competition between dissolved ligands and ligands on the particle surface. Ligand production by bacterial or algal decay may, in part, explain increases in dissolved heavy-metal concentrations in solution of sediment-water systems.

Scavenging of Heavy Metals from the Aqueous Phase. In addition to organic and biological material, Fe(III) and Mn(IV) oxide minerals are often considered the most important factors affecting the distribution of heavy metals in sediment-water systems. Freshly precipitated oxyhydroxides are more effective in scavenging trace metals than aged crystalline materials because of greater reactive surface area.

As can be seen from Table VI, at least half of the iron in the sediment exists as ferrous minerals. The oxidation kinetics of some species, such as vivianite, siderite and Fe(II) in clay minerals, are relatively unknown. Oxidation rates of sulfidic-bound Fe(II) have been determined. The change in pyrite content of the sediment during oxidation of the suspension was determined and will be reported in a later paper. Here we give preliminary results in Figure 9.

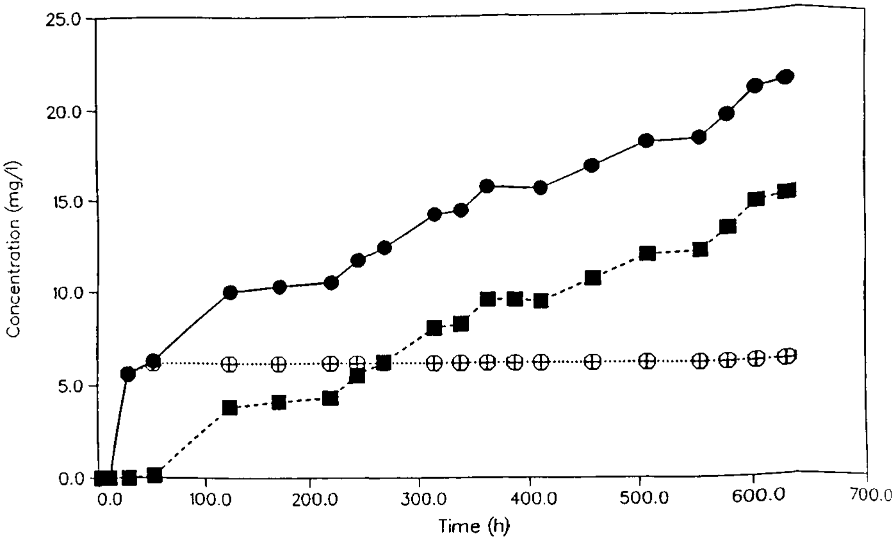

Figure 8. Changes in concentrations of sulfate from different contributing sources. (•) - total sulfate concentration; (⊕) - sulfate from oxidation of acid-volatile sulfide; (■) - sulfate from pyrite oxidation.

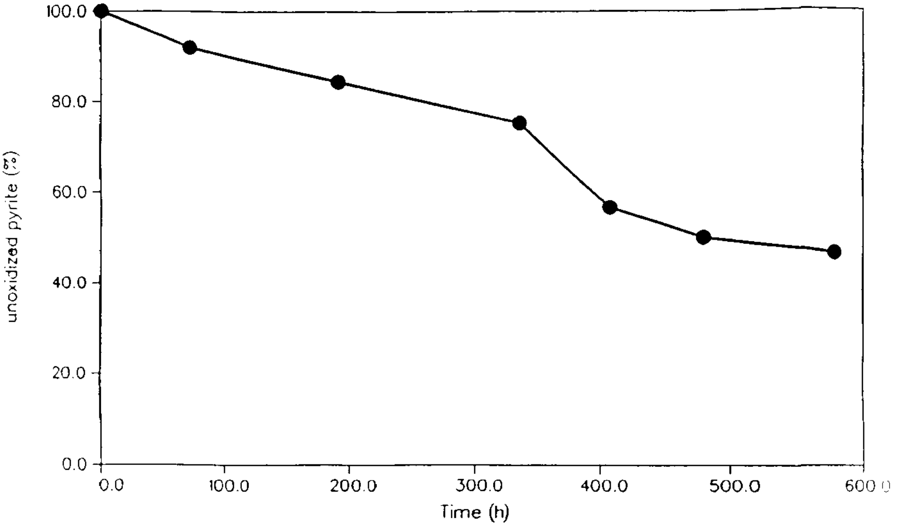

Figure 9. Change in percentage of unoxidized pyrite (FeS_2) in the suspension.

Table VI. Fe Species in Sediments

Iron Species	% of Total Fe
Vivianite ($Fe_3(PO_4)_2$)	20
Siderite ($FeCO_3$)	8
Fe(II) in Ca-Mg carbonate	4
Fe(II) in humic matter	1
Fe(II) in clay minerals	18
Fe(III) and sulfide-bound Fe(II)	49

These results suggest that the suspension system provided ample Fe(II). This Fe(II) was oxidized to Fe(III)-hydroxides. Freshly formed Fe(III)-hydroxides can adsorb and coprecipitate metals released to the solution. Considerable readsorption of Cd, Zn and Cu on Fe-hydroxide, Mn-oxide and algal cell walls has been observed in our experiments with a multi-chamber device, where competition effects of these compounds were studied (35).

Fe(III) and Mn(IV) oxyhydroxides and organic matter, which all are considered heavy-metal adsorbents, tend to form "coatings" and biofilms on mineral surfaces, which show a high affinity to some heavy metals. Studies of adsorption of heavy metals on oxides indicate that Cd, Cu, Pb, Zn, and some other metals are adsorbed more strongly by Mn(IV) oxides than by Fe(III) oxides (43-45). The order of binding stability and affinity of goethite (α-FeOOH) and amorphous Fe(III) oxide for heavy metals is listed as follows (46-50):

$$\mathrm{Pb} \sim \mathrm{Cu} > \mathrm{Zn} > \mathrm{Cd}.$$

The order of adsorption is similar for birnessite (δ-MnO_2) and Mn(IV) oxyhydroxide (46,47,51):

$$\mathrm{Pb} > \mathrm{Cu} > \mathrm{Cd} > \mathrm{Zn}.$$

The affinity of marine oxic sediments with high Mn(IV) contents has been given by Balistrieri and Murray (49):

$$\mathrm{Pb} > \mathrm{Cu} > \mathrm{Zn} > \mathrm{Cd}.$$

The investigations of both Fe-Mn oxide-rich sediments and Fe-Mn oxides as absorbents suggest that the order of affinity of these compounds is the same as the scavenging affinity observed in our experiment (Table III).

The released metals can also be readsorbed by solid organic matter in sediments. Jonasson (52) established a probable order of binding strength for a number of metal ions onto humic or fulvic acids: $Cu^{2+} > Pb^{2+} > Zn^{2+}$. This result has been demonstrated by an investigation on "model" sediment components (34). For example, 1.3% of the total Cu content of the sludge was released during the suspension, but only one third remained in the solution. Two thirds of the released Cu was readsorbed to the various model substrates. Quartz had 3 $mg \cdot kg^{-1}$ of copper, bentonite clay contained about 15 $mg \cdot kg^{-1}$, iron hydroxide retained about 80 $mg \cdot kg^{-1}$, and manganese oxide retained 100 $mg \cdot kg^{-1}$, whereas the cell walls, a minor component of the "model" sediment, accumulated nearly 300 $mg \cdot kg^{-1}$ of the Cu. A similar result for Cd has also been reported (35).

Release and Scavenging Processes: A Four-Stage Interaction Model. Based on this experiment and other supporting materials the behavior of heavy metals during suspension and oxidation of anoxic polluted sediment can be described as four-stage interactions illustrated in Figure 10. These stages are: (I) release stage, (II) transition stage, (III) scavenging stage, and (IV) steady-state stage.

Release Stage. This stage includes amorphous-sulfide oxidation, some pyrite oxidation and some organic-detritus decomposition (Figure 11). At the beginning of the experiment, amorphous-sulfide oxidation is a dominant chemical process. The metals, which are strongly bound with acid-volatile sulfides, will not be released at this stage. This hypothesis is reasonable if we compare the K_{sp} of CuS and Cu_2S as well as other metal sulfides (Table IV). We have found that the oxidation of cadmium sulfide was not significant during stage I compared with the entire release process.

The original sediment samples consisted of very complex compounds with different porosities. During suspension, the degree and rate of sulfide oxidation depend on sediment composition and, to a certain degree, on the stirring speed.

The second contribution is characterized by mineralization of ammonium and pyrite oxidation. In this respect, Prause et al. (23) stressed the effects of microbial activity resulting in decomposition of organic matter. In our experiment Cu showed a relatively high dissolved concentration, perhaps due to organic complexing. An increase in sulfate concentration combined with pyrite decrease, provides an indication of pyrite oxidation in this stage (Figures 6-9). Sulfate is formed from oxidation of both acid-volatile sulfide and pyrite. Assuming acid-volatile sulfide is first oxidized, sulfate formed from pyrite oxidation can be observed in Figure 8. The rate of sulfate accumulation would not necessarily reflect the stoichiometric relationship of pyrite oxidation, however, because of the occurrence of intermediate sulfoxy species such as thiosulfate and polythionates. The relative analysis, based on the sulfate results, is still useful. The release of metals bound with FeS_2, such as Cu, Zn and Cd, is dominant at this stage.

Transition Stage of Release/Scavenging. At this stage, acid-volatile sulfur compounds have been oxidized; pyrite oxidation and organic-detritus decomposition continues. At the same time, metal readsorption becomes stronger. Phosphate, derived from the decomposed organic detritus, accumulates and then

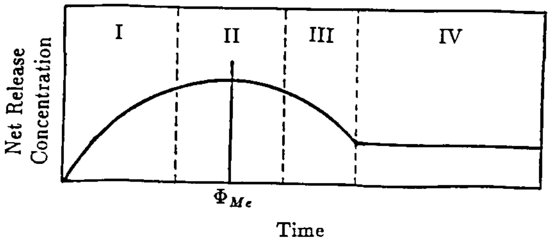

Figure 10. Schematic diagram showing the change in the net metal-release concentration in the four-stage process. I - release stage; II - transition stage; III - scavenging stage; IV - steady-state stage.

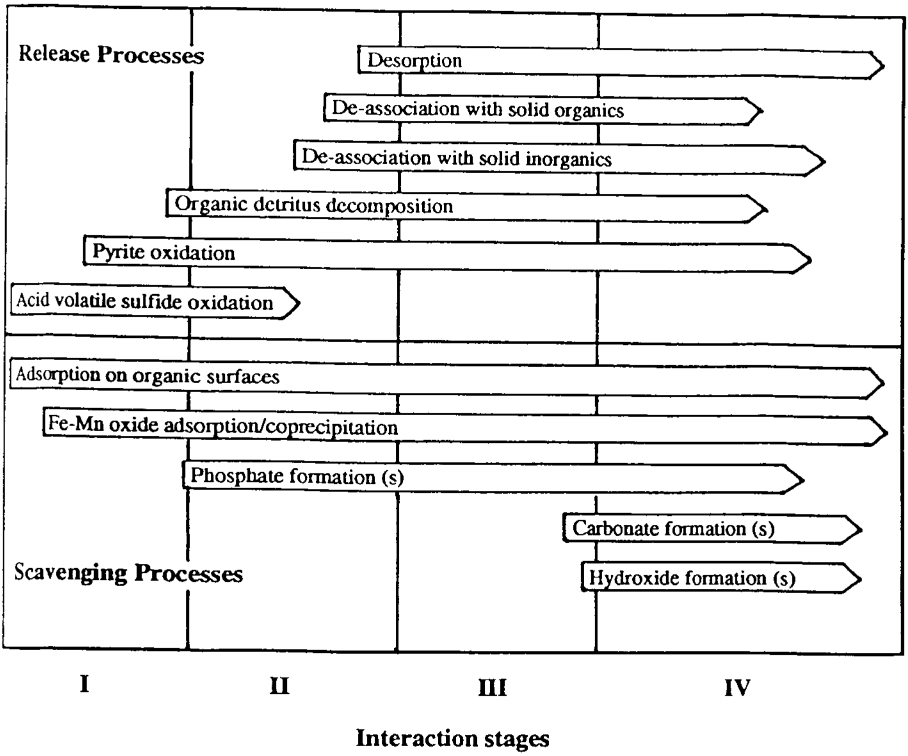

Figure 11. Sequence of chemical and biochemical reactions involved in metal release and scavenging in suspension/oxidation processes. "Acid volatile sulfide oxidation" includes solid monosulfides.

precipitates with some metals. Release and adsorption/precipitation occur together. At this stage neither the release nor the scavenging process is dominant (Figure 10).

Scavenging Stage. At this stage, all release processes decline including pyrite oxidation, organic-detritus decomposition, and metal release from solid organic and inorganic compounds. The formation of Fe-Mn oxide continues and scavenging is a dominant process. This process leads to a decrease in the concentration of metals in the aqueous phase.

Steady-state Stage. Release and scavenging processes have reached a new equilibrium. At this stage, the release rate is equal to the scavenging rate. The metal concentrations in solution will remain constant, however, metal-solid "speciation" and relevant distribution change greatly.

Release and scavenging of Pb, Cu, Zn, and Cd in anoxic sediments during oxidation/suspension can be generalized and are illustrated in Figure 12. For different metals, different stages appear at different times.

Characteristic Value of Net Metal Release, Φ_{Me}, at "the Worst Situation". The time at which the highest value (peak value) of net metal release is found can be designated as the characteristic value of net metal release and is represented by Φ_{Me} in hours. The Φ_{Me} is situated at the peak position of stage II (Figure 10). There are different Φ_{Me} values for different metals, depending on their physicochemical properties and the conditions of suspension. When the oxidation time is $<\Phi_{Me}$, the dominating process is release of metals. When the oxidation time is $>\Phi_{Me}$, the dominating process is scavenging or relative equilibrium. In our experiment, Φ_{Pb} was <10 h, Φ_{Cu} ~ 350 h, both Φ_{Zn} and Φ_{Cd} were >600 h. Φ_{Me} reflects how quickly metals in the system may reach "the worst situation" or the highest concentration in the solution. From Figure 12 we can see that Φ_{Pb} is very small. After a relatively short time of release, rapid scavenging of Pb occurred. Φ_{Zn} and Φ_{Cd} were much higher than Φ_{Pb}.

Conclusions

In this study, the behavior of heavy metals in anoxic sediment during oxidation/suspension has been investigated. Cd, Pb, Cu, and Zn can be released into the aqueous phase during sediment resuspension. The sources of metal release are metal-sulfide oxidation, organic decomposition, and desorption. Different metals showed different release rates. About 5% of the total Cd was mobilized. For Pb, the percentage mobilized was only about 0.7%, and for Cu and Zn, 1 and 1.5%, respectively. The order of net percentage release of total metals from the sediments is Cd > Zn > Cu > Pb. For the total mass released, however, the order is Zn > Cu > Pb > Cd; the same as the order of total concentration in the sediment. At the end of the experiment, the order of net release, and the magnitude of released metals, were similar to that observed in the natural waters of the Elbe River at Hamburg. The released metals are scavenged to a different extent. The order of the scavenging percentage is Pb (86%) > Cu (53%) >

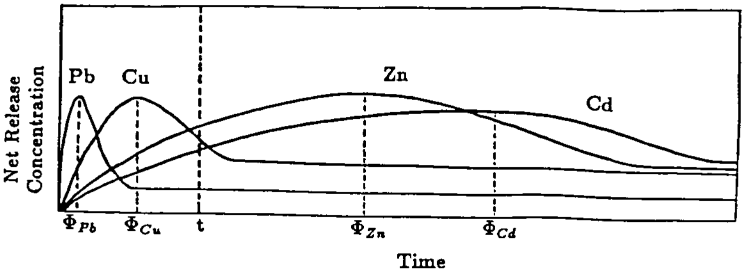

Figure 12. Schematic diagram showing generalized change in relative concentrations for metals during suspension/oxidation. "t" refers to experiment time in this study (628 h).

Zn (34%) > Cd (30%). Dominant processes are sorption by freshly precipitated Fe-Mn oxides and organic matter, and precipitation of some metal phosphates, which result from the decomposition of organic matter.

Based on our experimental results, a four-stage interaction model for metals in anoxic sediment during oxidation has been developed to describe heavy-metal behavior. An index, Φ_{Me}, has been developed to assess the timing of "the worst situation", the maximum net metal release under certain conditions. The results suggest that Pb and Cu can cause only a short-term problem, while Cd and Zn result in a long-term impact on the system if the assessment is based on the metal concentrations in the aqueous phase, which is the most important factor for bioavailability.

The illustration of this study seems to explain some controversial and potentially confusing results of earlier studies. During the first stage, metals can be released to the aqueous phase due to sulfide oxidation and other mobilizing processes; during subsequent stages the metals released will then be readsorbed or precipitate again to different extents for different metals. These metals will reach maximum concentrations at different times, represented by Φ_{Me} values.

Literature Cited

1. Mart, L.; Nürnberg, H.W.; Rützel, H. J. Sci. Total Environ. 1985, 44, 35-49.
2. Förstner, U.; Schoer, J.; Knauth, H.-D. J. Sci. Total Environ. 1990, 97/98, 347-368.
3. Lichtfuss, R.; Brümmer, G. Naturwiss. 1977, 64, 122-125.
4. Knauth, H.-D.; Schroeder, F.; Irmer, U. In Proc. 2nd Int. Conf. Environmental Contamination, Amsterdam; Ernst, W.H.O., Ed.; CEP Consultants: Edinburgh, 1986; pp. 186-188.
5. Tent, L. Hydrobiologia 1987, 149, 189-199.
6. Förstner, U.; Calmano, W.; Hong, J.; Kersten, M. In Proc. 5th Int. Symp.

on River Sedimentation; Larsen, P.; Eisenhauer, N., Eds.; Karlsruhe, 1992; Vol. IV, pp. 1229-1234.

7. Calmano, W.; Hong, J.; Förstner, U. Vom Wasser 1992, 78, 245-257.
8. Wallmann, K. Ph.D. Thesis, Technical University of Hamburg-Harburg, 1990.
9. Engler, R.P.; Patrick, W.H. Jr. J. Soil Sci. 1975, 119, 217-221.
10. Chen, K.Y.; Gupta, S.K.; Sycip, A.Z.; Lu, J.C.S.; Knezevic, M. The effects of dispersion, setting, and resedimentation on migration of chemical constituents during open water disposal of dredged materials, Contract Report U.S. Army Engineer Waterways Experiment Station, Vicksburg, MI, Contract No. DACW39-74-C-0077, 1976, 221 pp.
11. Gobeil, C.; Silverberg, N., Sundby, B.; Cossa, D. Geochim. Cosmochim. Acta 1987, 51, 589-596.
12. Giblin, A.E.; Luther III, G.W.; Valiela, I. Estuarine Coastal Shelf Sci. 1986, 23, 477.
13. Klinkhammer, G. Earth Planet Sci. Lett. 1980, 49, 81-101.
14. Sawlan, J.J.; Murray, J.W. Earth Planet. Sci. Lett. 1983, 64, 213-230.
15. Jenne, E.A. In Trace Inorganics in Water; Gould, R. F., Ed.; ACS Advances in Chemistry Series; American Chemical Society: Washington, DC, 1968; pp. 337-387.
16. Brooks, B.B.; Presley, J.J.; Kaplan, I.R. Geochim. Cosmochim. Acta 1968, 32, 397-414.
17. Palsma, A.J.; Loch, J.P.G. In Heavy Metals in the Environment; Farmer, J.G., Ed.; CEP Consultants: Edinburgh, 1991; Vol. 2, pp 20-23.
18. Morel, F.; McDuff, R.E.; Morgan J.J. In Trace Metals and Metal Organic Interactons in Natural Water; Singer, P.C., Ed.; Ann Arbor Science Publ.: Ann Arbor, MI, 1973; pp. 157-200.
19. Lindberg, S.E.; Harriss, R.C. Environ. Sci. Technol. 1974, 8, 459-462.
20. Nissenbaum, A.; Swaine, D.J. Geochim. Cosmochim. Acta 1976, 40, 809.
21. Piemontesi, D.; Baccini, P. Environ. Technol. Lett., 1986, 7, 577-592.
22. Huynh-Ngoc, L.; Whitehead, N.C.; and Boussemart, M. Mar. Chem. 1989, 26, 119-132.
23. Prause, B.; Rehm, E.; Schulz-Baldes, M. Environ. Technol. Lett. 1985, 6, 261-266.
24. Hirst, J.M.; Aston, S.R. Estuarine Coastal Shelf Sci. 1983, 16, 549-558.
25. Khalid, R.A.; Patrick, W.H. Jr.; Gambrell, R.P. Estuarine Coastal Mar. Sci. 1978, 6, 21-35.
26. Gambrell, R.P.; Khalid, R.A.; Patrick, W.H. Jr. Environ. Sci. Technol. 1980, 14, 431-436.
27. Hong, J.; Wang, T. Environ. Sci. Lett. 1984, 6, 48-56.
28. Brannon, J.M.; Patrick, W.H. Jr. Environ. Sci. Technol. 1987, 21, 450-459.
29. Petersen, W.; Knauth, H.-D.; Pepelnik, R. Sci. Total Environ., 1990 97/98, 531-547.
30. Hong, J.; Calmano, W.; Wallmann, K.; Petersen, W.; Schroeder, F.; Knauth, D.-H.; Förstner, U. In Heavy Metals in the Environment; Farmer, J.G., Ed.; CEP Consultants: Edinburgh, 1991; pp 330-333.
31. Hennies, K. Diplomarbeit, Bayerische Julius-Maximilians-Universität zu Würzburg, 1991.

32. Calmano, W. Schwermetalle in kontaminierten Feststoffen. Verlag: TÜV Rheinland, Köln, 1989; 237 pp.
33. Calmano, W.; Ahlf, W.; Bening, J.-C. Hydrobiologia 1992, 235/236, 605-610.
34. Förstner, U.; Ahlf, W.; Calmano, W. Mar. Chem. 1989, 28, 145-158.
35. Calmano, W.; Ahlf, W.; Förstner, U. Environ. Geol. Water Sci. 1988, 11, 77-84.
36. Kersten, M.; Förstner, U. Mar. Chem. 1987, 22, 299-312.
37. Kornicker, W.K.; Morse, J.W. Geochim. Cosmochim. Acta 1991, 55, 2159-2171.
38. Hahne, H.C.H.; Kroontje, W. J. Environ. Qual. 1972, 2, 444-450.
39. Hem, J.D. Water Resour. Res. 1972, 8, 661-679.
40. Elderfield, H. Am. J. Sci. 1981, 281, 1184-1196.
41. Hart, B.T.; Davies, S.H.R. Aust. J. Mar. Freshwater Res. 1977, 28, 105.
42. Van den Berg, C.M.G.; Dharmvanij, S. J. Limnol. Oceanogr. 1984, 29, 1025-1036.
43. Jenne, E.A. In Molybdenum in the Environment; Chappell, W.R.; Petersen, K.K., Eds.; Dekker: New York NY, 1977; Vol. 2, pp 425-553.
44. Lion, L.W.; Altmann, R.S.; Leckie, J.O. Environ. Sci. Technol. 1982, 16, 660-666.
45. Davies-Colley, R.J.; Nelson, P.O.: Williamson, H.J. Environ. Sci. Technol. 1990, 18, 491-499.
46. McKenzie, R.M. Aust. J. Soil Res. 1980, 18, 61-73.
47. Gerth, J. Ph.D. thesis, Christian-Albrecht-Universität Kiel, 1985.
48. Tessier, A.; Rapin, F.; Carignan, R. Geochim. Cosmochim. Acta 1985, 49, 183-194.
49. Balistrieri, L.S.; Murray, J.W. Geochim. Cosmochim. Acta 1986, 50, 2235-2243.
50. Leckie, J.O. In The Importance of Chemical "Speciation" in Environmental Processes; Dahlem Conference 1986, Bernhard, M.; Brinckman, F.E.; Sadler, P.J., Eds.; Springer Verlag: Berlin - Heidelberg, 1986; 237 pp.
51. Murray, J.W. Geochim. Cosmochim. Acta 1975, 39, 505-519.
52. Jonasson, I.R. In The Fluvial Transport of Sediment-Associated Nutrients and Contaminants; Shear, H.; Watson, A.E.P., Eds.; IJC/PLUARG: Windsor, Ont., 1977, 255 pp.

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