



BINDING AND MOBILIZATION OF HEAVY METALS IN CONTAMINATED SEDIMENTS AFFECTED BY pH AND REDOX POTENTIAL

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ABSTRACT

In a contaminated sediment from Hamburg harbour, acid production, mobilization of Cu, Zn, Pb, and Cd at different redox- and pH-conditions, and the transfer and change of those particle bound metals are studied. During oxidation the pH value in the sediment suspension decreases from about 7 to 3.4 because of the low acid neutralization capacity (ANC). This leads to a mobilization of heavy metals whereby Cd and Zn as distinguished from Cu and Pb are strongly released. Also a change in particulate phase specific heavy metal binding forms is found. Generally the easily and moderately reducible fractions increase during oxidation while the sulfidic fraction decreases. Also great changes were found for the dissolved Zn- and Cd-concentrations which increased continuously. The results show that at identical pH values obviously more metals are mobilized in the oxidized sediment than in the reduced state. But although the pH value is the key factor - in particular if it sinks below 4.5 - the redox conditions may also control the mobilization of certain metals. Consequently, also in well buffered sediments a mobilization of metals during oxidation cannot be excluded.

KEYWORDS

Sediments; heavy metal binding forms; periodical redox processes; acid producing capacity; buffer intensity; sediment quality.

INTRODUCTION

Generally, more than 90 % of the heavy metal load in aquatic systems is bound on particulates like suspended matter and sediments. Natural particulates in rivers, lakes and sea consist of clay minerals, iron and manganese oxyhydroxides, carbonates, organic substances (e.g. humic acids), and biological materials (e.g. algae and bacteria). Type and stability of the heavy metal bonding on these solid compounds are decisive factors for potential mobility and bioavailability. The chemical forms of metals greatly differ in their transfer ability and bioavailability in the ecosystem. For example, dissolved or weakly adsorbed metals may be easily available to plants and aquatic organisms, while metals bound in crystalline struc-

tural lattice of primary and secondary minerals are not available to biota, unless the minerals undergo geochemical weathering.

Between the two extremes there exist various amorphous solid compounds which are changed by diagenetic processes. A considerable part of the metals is bound on these reactive sediment compounds and may become potentially mobile and bioavailable because they are dissolved under certain conditions. The physico-chemical and bio-chemical conditions in the aquatic system and sediment, respectively, determine such processes. Considering the mobilization of heavy metals from sediments we have two master variables: pH and redox potential. Processes which control these parameters also control the particulate heavy metal binding forms and their transformation at changing conditions.

The transformation of heavy metal binding forms in sediments include the following main processes:

- sorption and desorption;
- formation and dissolution of carbonate bound metals;
- formation and decomposition of soluble and insoluble metal organic complex compounds;
- formation and dissolution of hydroxides and oxyhydrates;
- sorption and coprecipitation of metals by Fe-/Mn-oxides, particularly in oxidic environments at neutral pH;
- precipitation of metal sulfides in strong reducing environments and dissolution as sulfates under oxic conditions.

River, estuarine, and marsh sediments are more or less submerged and interstitial pore volumes are saturated with water. Oxygen slowly diffuses into pore waters and is consumed by microorganisms within the first few millimetres of the sediment surface. In deeper, anoxic sediment layers microorganisms use oxygen from oxic compounds which are transformed into carbonates and sulfides, thereby decreasing the redox potential of the sediment. Under such anoxic conditions the solid compounds of heavy metals are usually stable, in particular the sulfidic forms.

If anoxic sediments are exposed to atmosphere, redox conditions will change and a new distribution and transformation of heavy metal binding forms in the sediments takes place. In particular such processes occur if the system is subject to periodical changes. Such processes are typical for the sediments of older river- or marine terraces in monsoon regions which have a seasonal changing water level caused by submergence with rain water. Under those conditions hydrology favours either lateral or vertical drainage and leads to the change in redox potential.

In large rivers periodical oxidation and reduction of sediments may also take place, although the intervals are not constant. In the rainy season or during melting of snow, current velocity is faster than in the dry season, and bottom sediments are displaced by turbulent flow conditions. The anoxic sediments are suspended in the oxic river water, where usually the redox potential can reach +500 mV. If current velocity decelerates, the particulate matter will sink to the bottom, e.g. in stagnant water zones of harbour basins and reducing conditions arise again.

Tidal currents daily lead to periodical redox changes in coastal and estuarine sediments. In some coastal plains the sediments and soils are seasonally flooded. By these processes chemical properties of sediment compounds are changed. For example ferrous sulfide (or pyrite) is formed by reduction of sulfate from sea water, while partly dissolved hydrogen carbonate is removed by diffusion or convection. A very important factor is that sulfate from sea water will "split" into mobile alkalinity (HCO_3^-) and immobile potential acidity (FeS_2) that is left behind in the sediments. Over several years or decades appreciable amounts of sulfide can be accumulated in tidal sediments (Kittrick *et al.*, 1982).

Some lakes change their area by seasonal flooding of rivers. For example, the area of Boyang Lake, the largest lake in China, strongly depends on the water-freight of Yangtze River. In the flooding season,

large area is submerged for several months and sediments become anoxic. During the dry season, on the other hand, the water level of Yangtze River declines, the area of Boyang Lake shrinks again, and a large part of the sediments is exposed to atmosphere. Like lakes, some water reservoirs yearly undergo periodical redox processes. In developing countries such reservoirs play an important role in agriculture. In the seasons for seeding and growing - usually in spring and summer - the water is used to irrigate farmland. Particularly in spring, before the rainy season, the water in the reservoir is often exhausted for agricultural use and the sediments become parched and oxidized. Heavy metal binding forms greatly depend on the different developing stages of redox processes and flooding in such reservoirs. Periodical flooding in a reservoir and its effects on the transformation of metal forms in the sediment have been studied by Hong and Wang (1986).

In the last two decades transformation of heavy metal binding forms under changing redox conditions has been given much attention. Some authors studied the transformation of Cd in Mississippi sediments under controlled redox and pH conditions (Khalid *et al.*, 1981), of Hg, Pb, and Zn in estuarine sediments of Mobile Bay (Gambrell *et al.*, 1980), and Fe and Mn in soils (Gotoh & Patrick, 1972, 1974; DeLaune *et al.*, 1981). Dissolution and change of exchangeable Fe and Mn in a reduction/oxidation cycle have been studied by Patrick and Henderson (1980). Chemical extraction experiments for estimating characteristic particulate binding forms of metals in anoxic marine and freshwater sediments were carried out by Kersten and Förstner (1986), both in the presence and absence of atmospheric oxygen during the analytical procedure. By drying the sediments the proportion of sulfidic bound metals decreased distinctly.

Recently we studied the mobilization and transfer of heavy metals to major sediment compounds in a specially developed multichamber device after changing redox-, salinity- and pH-conditions (Calmano *et al.*, 1988a, 1988b, 1992; Förstner *et al.*, 1989). Algae cell walls of *Scenedesmus quadricauda*, bentonite, aluminium oxide, manganese oxide, quartz powder, and goethite were used as model sediment components. Oxidation of anoxic sediments caused remobilization of heavy metals and re-adsorption on the model components, in particular on algae cell walls. The dominant role of organic material in the binding of metals such as Cd and Cu is of particular relevance for the transfer of these elements into the biological system.

Up to now no studies on transformation of heavy metal binding forms in sediments during periodical oxidation and reduction processes have been reported. In this paper we will discuss the following questions.

- How do changes of pH and redox potential affect the mobilization of heavy metals in sediments ?
- How does the pH of a sediment/water system change in course of periodical redox processes ?
- How do the phase specific metal binding forms of Cu, Zn, Cd, and Pb change during a threefold redox cycle ?

ACID PRODUCING CAPACITY AND ACID NEUTRALIZATION CAPACITY

Contaminated dredged sediments are deposited on spoiling areas on land or directly restored in the water. As a result anoxic sediments have contact with air oxygen or oxygenous water, and redox conditions are changing. The change of redox potential entails changes in particulate heavy metal binding forms. In weakly buffered sediments this may lead to a distinct decrease of the pH value which has consequences in increasing mobilities of most heavy metals. An especially evident example is shown in figure 1 which represents pH and redox potential development during the oxidation of a dredged mud suspension from Hamburg harbour.

After exposing the anoxic suspension to atmospheric oxygen, redox potential increased constantly from about -100 mV to +500 mV. At the same time the pH decreased from the neutral region to a value of 4 and later on to nearly 3. This distinct pH decrease is not only due to chemical oxidation processes but is also to a

great extent intensified by the activity of thiobacteria (*T. thiooxidans* and *T. ferrooxidans*) (Calmano and Ahlf, 1988c).

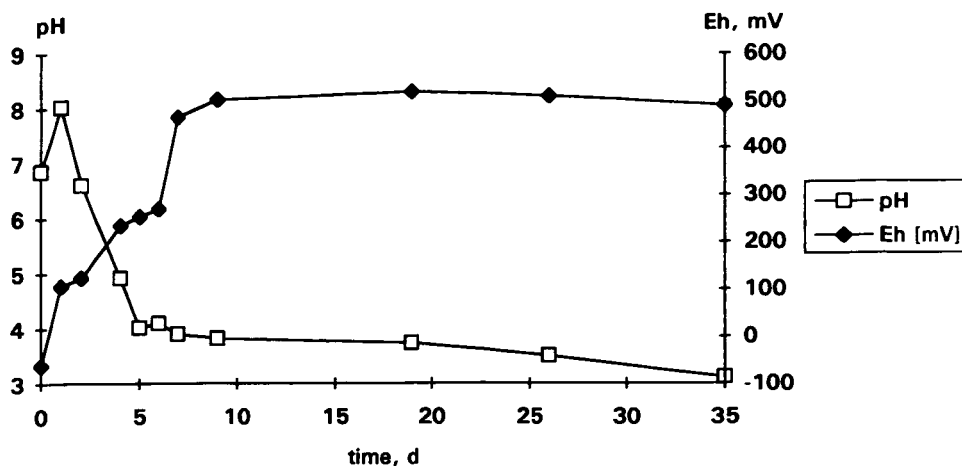


Fig. 1. Development of redox potential and pH during the oxidation of a low buffered dredged mud suspension from Hamburg harbour

The most important oxidation reactions leading to a decrease of pH in low buffered sediments are listed in table 1.

TABLE 1. Important acid producing oxidation reactions in aquatic systems

Elements	Reactions	f
inorganic	S $\text{H}_2\text{S} + 2 \text{O}_2 = \text{SO}_4^{2-} + 2 \text{H}^+$	2
	S $\text{S}^\circ + 3/2 \text{O}_2 + \text{H}_2\text{O} = \text{SO}_4^{2-} + 2 \text{H}^+$	2
	S, Fe $\text{FeS} + 9/4 \text{O}_2 + 3/2 \text{H}_2\text{O} = \text{FeOOH} + \text{SO}_4^{2-} + 2 \text{H}^+$	2
	S, Fe $\text{FeS}_2 + 15/4 \text{O}_2 + 5/2 \text{H}_2\text{O} = \text{FeOOH} + 2 \text{SO}_4^{2-} + 4 \text{H}^+$	4
	Fe $\text{Fe}^{2+} + 1/4 \text{O}_2 + 5/2 \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 2 \text{H}^+$	2
	N $\text{NH}_4^+ + 2 \text{O}_2 = \text{NO}_3^- + \text{H}_2\text{O} + 2 \text{H}^+$	2
N	$\text{NO}_x + 1/4(5-2x)\text{O}_2 + 1/2 \text{H}_2\text{O} = \text{NO}_3^- + \text{H}^+$	1
organic	N $\text{R-NH}_2 + 2 \text{O}_2 = \text{R-OH} + \text{NO}_3^- + \text{H}^+$	1
	S $\text{R-SH} + \text{H}_2\text{O} + 2 \text{O}_2 = \text{R-OH} + \text{SO}_4^{2-} + 2 \text{H}^+$	2

f = acid formation coefficient

In a sediment/water system the most important components producing hydrogen ions at oxidation are above all inorganic and organic sulfur-, nitrogen- and iron-species listed above. They include the acid producing capacity (APC) of the system. Acidification of a sediment leads to mobilization of heavy metals. To what extent such a system is acidified and whether heavy metals are dissolved depends on the acid neutralization capacity (ANC). The acid neutralization capacity of a natural aquatic system is composed of the acid neutralization capacity of the solids ANC_s and that of the dissolved phase ANC_{aq} :

$$ANC = ANC_s + ANC_{aq}$$

The ANC_{aq} of the dissolved phase may be described by the following equation:

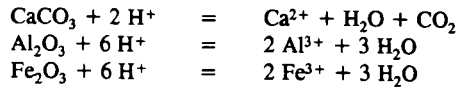
$$ANC_{aq} = [HCO_3^-] + 2 [CO_3^{2-}] + 2 [S^{2-}] + [HS^-] + [NH_3] - [H^+]$$

A similar rule shall apply to the ANC_s of the solids at $pH > 5$:

$$ANC_s = 2 [CaO] + 2 [MgO] + 2 [Na_2O] + 2 [K_2O] + 2 [MnO] + 2 [FeO] - 2 [SO_3] - 2 [P_2O_5] - HCl$$

In aquatic systems ANC_s is always much greater than ANC_{aq} . The most important buffer reactions taking place in sediments are listed in table 2.

TABLE 2. Important buffer reactions in sediments



From the two parameters ANC and APC an effective acid producing capacity APC_{eff} can be calculated which may be helpfully in practice for the specification of sediment quality criteria. The APC_{eff} of a sediment suspension may be defined as:

$$APC_{eff} = V/W \cdot ([H^+]_e - [H^+]_o)$$

- APC_{eff} = effective acid producing capacity
 V = suspension volume
 W = solid mass
 $[H^+]_{o,e}$ = hydrogen ions concentration before and after oxidation of the suspension.

For example, for an anoxic Elbe River sediment with an original $pH_o = 7.03$ and a $pH_e = 3.29$ after an oxidation time of 35 d an $APC_{eff} = 5.12$ mmole/kg could be calculated. Such simple test procedures allow better statements of the sediment quality than simple considerations of limiting values.

In a sediment/water system, which undergoes periodical redox processes, the acid producing capacity may be changed under certain conditions. Considering a closed system we will not find any changes in total acid producing capacity. During oxidation a transfer of hydrogen ions into the water phase takes place. Those hydrogen ions are consumed again by the following reduction processes. Altogether the balance is equalized.

The conditions in an open system, e.g. in a river, are of a different kind. According to the specific properties of the system and to the reaction conditions, acid producing and acid consuming components may be displaced, and thus the total acid producing and neutralization capacity, respectively, can be changed irreversibly.

This will be discussed on two examples without considering the multitude of possible reactions (see figure 2).

<u>oxic conditions</u>		<u>anoxic conditions</u>
$4 \text{ MeSO}_4 + \text{Fe}_2\text{O}_3$ sulfate reduction	$\xrightarrow{\text{"CH}_2\text{O"}}$	$2 \text{ FeS}_2 + 4 \text{ Me}(\text{HCO}_3)_2$
$4 \text{ H}_2\text{SO}_4 + \text{Fe}_2\text{O}_3$	$\xleftarrow{\text{O}_2}$	ANC _{aq} increases
$2 > \text{Me} + \text{Fe}_2\text{O}_3$ iron oxide reduction	$\xrightarrow{\text{"CH}_2\text{O"}}$	$2 > \text{Fe} + 2 \text{ Me}(\text{HCO}_3)_2$
$2 > \text{H}_2 + \text{Fe}_2\text{O}_3$	$\xleftarrow{\text{O}_2}$	ANC _{aq} increases

Me = metal; > = solid bound

Fig. 2. Change of acid producing capacity in periodical redox processes - Example: The formed ANC_{aq} is mobile and removed from the sediment.

The first reaction is characterized by reduction of sulfate. The formed sulfide is fixed in the sediment and leads to an increase of APC_s. At the same time ANC_{aq} increases by formation of HCO₃⁻, and because it is mobile it can be displaced by diffusion or advection into the overflowing water. A separation in mobile ANC_{aq} and immobile APC_s takes place. That immobile APC_s leads at the following oxidation to a further decrease of ANC_{aq} because hydrogen ions are produced which react with HCO₃⁻ to volatile CO₂ and H₂O. In this way a low buffered sediment may become permanently acid.

In the second example, by reduction of iron oxides dissolved Fe²⁺ displaces other cations, like Ca²⁺ or Mg²⁺, from the solid surface. Again dissolved cations and HCO₃⁻ are removed from the sediment by diffusion or advection. In the following oxidation reaction Fe²⁺ is transformed into Fe(OH)₃, and hydrogen ions are produced which can displace other cations and contribute to an acidification of the system.

METHODS AND MATERIALS

The original anoxic sediment sample with a pH = 6.43, no carbonate reaction and a low redox potential of -289 mV was collected from the Hamburg harbour. The water content was calculated by weighing a 5 g aliquot of the sample before and after drying at 105 °C. With 150 g (dry mass) of the original sediment a suspension in distilled water was prepared in a 2 l glass; the solid/liquid ratio was 1:10. During the experiment the suspension was stirred with a magnetic stirrer. Redox potential and pH were recorded continuously. Samples were taken at regular intervals from the suspension and centrifuged for 10 min at 2000 rpm. The supernatant was filtered through a 0.45 µm membrane and acidified with HCl to pH 2 for later analysis by AAS. The solid residue was stored for a sequential extraction procedure to determine the phase specific metal binding forms.

During the oxidation cycles air was pumped into the suspension continuously, based on the method of Charoenchamratchee *et al.* (1987). At the beginning of the reduction cycles the gas pump was switched over to nitrogen. Each redox period took 70 days, 35 days for reduction and oxidation, respectively. The experiment was carried out in the dark.

For determination of heavy metal binding forms a sequential extraction procedure was used in this study (Kersten and Förstner, 1986). By means of that procedure changes of metal portions in exchangeable, carbonatic, easily reducible, moderately reducible, and sulfidic/organic fractions could be determined during the three redox cycles. The reagents and chemical extracts of the first 4 steps of the extraction sequence were carefully kept oxygen-free by handling in a argon glove box, to prevent chemical changes of metal binding forms by atmospheric oxygen. After the extractions the supernatants were centrifuged and filtrated through 0.45 µm membranes. The ammonium- and sodium acetate extracts were stabilized by addition of a chelator (10 mg EDTA), to prevent hydrolyzation and precipitation of metals during storage in the refrigerator. The residual fraction of the solid bound metals was not analyzed because this fraction is usually considered not to participate in transformations caused by redox changes (Hong and Wang, 1984; Kersten and Förstner, 1987). All metals were analyzed with flame- and graphite-tube-AAS. The reagents applied for fractionation and extracted sediment phases are summarized in table 3.

TABLE 3 Sequential extraction scheme for determination of heavy metal binding forms in sediments

Fraction	Extraction Reagent	Extracted Sediment Phase
exchangeable	1 M NH ₄ OAc, pH 7	exchangeable cations
carbonatic	1 M NaOAc, pH 5	carbonates
easily reducible	0.1 M NH ₂ OH·HCl, pH 2	Mn-oxides
moderately reducible	0.1 M oxalate buffer, pH 3	amorphous Fe-oxides
sulfidic/organic	30 % H ₂ O ₂ + 0.1 M HNO ₃ , extracted with 1 M NH ₄ OAc in 6 % HNO ₃	sulfides and organic materials

RESULTS AND DISCUSSION

Mobilization

The first question was, how changes of redox potential affect the mobilization of heavy metals. In low buffered sediments such changes are always accompanied by alterations in pH. Thus, it is of great interest to study both influence of redox potential and of pH. In an anoxic sediment from Hamburg harbour and in the same, but oxidized sample, various pH values were fixed and mobilization of Cd, Cu, Pb, and Zn determined. Figures 3a and 3b show the results for Cd and Cu.

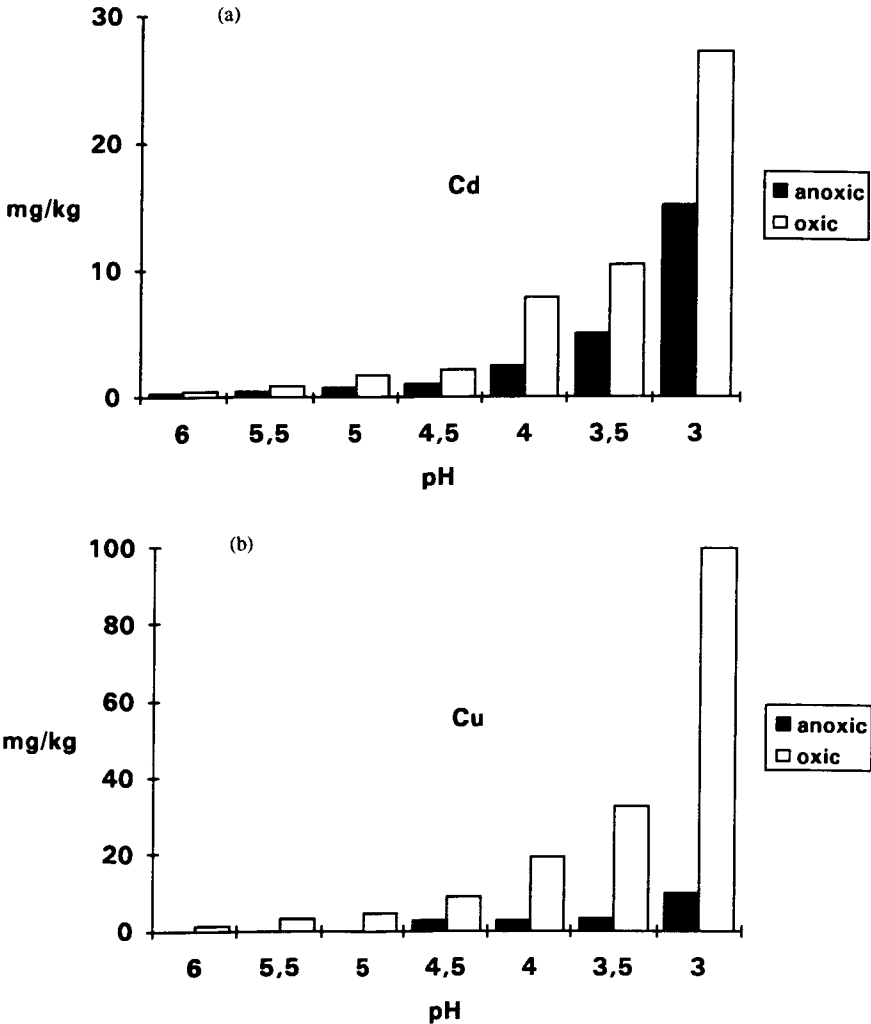


Fig. 3a and 3b. Mobilization of Cd and Cu from an Elbe River sediment at various redox and pH conditions

As expected, pH was the dominating mobilizing factor for both metals. At pH values < 4.5 that effect always comes to the fore, though from the oxic sediment distinctly higher metal portions are mobilized than from the anoxic sample. The reasons for that effect are discussed later. At identical pH values the mobilized portions of Cu (and Pb) from the oxic sediment are tenfold higher. The differences for Cd (and Zn) are not so great (factor 2). The results show that both factors, pH and redox potential, affect the mobilization of heavy metals from sediments.

pH Variations in Periodical Redox Cycles

Figure 4 shows the pH development in a sediment from Hamburg harbour during 3 succeeding redox cycles in 210 days. Generally, it can be stated that pH decreased during oxidation cycles and increased again during reduction cycles.

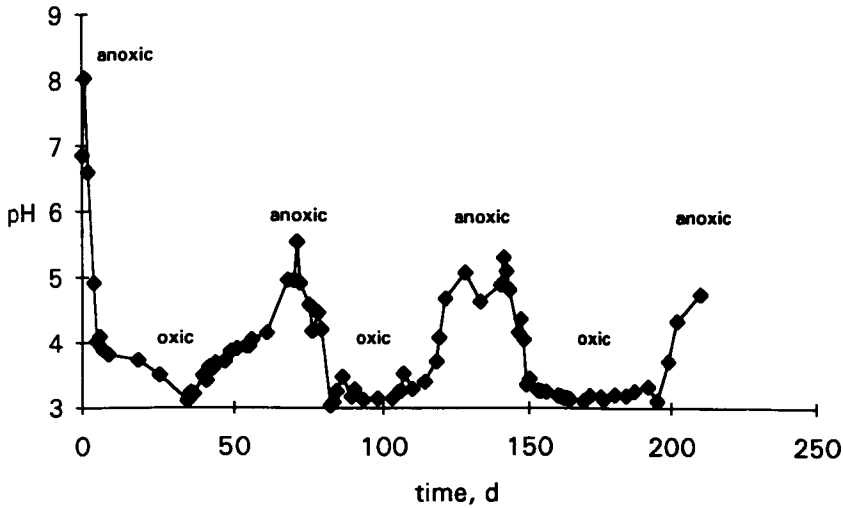


Fig. 4. pH development during succeeding redox cycles in an Elbe River sediment

During the first oxidation step of the anoxic sediment sample pH decrease was relatively quick and reached values of pH 3 - 3.5; the same could be observed in the following oxidation cycles. In contrast, the increase of pH during redox cycles was slower. It was generally noticed that pH never returned to the neutral value of the original sediment, but finds a level between 5.5 and 5 with a distinct decrease from the first to the last cycle. It can be concluded that a major part of the acid neutralization capacity of the sediment is already consumed after the first oxidation and further decreases in the course of the experiment.

Changes in Heavy Metal Binding Forms

During the three cycles of periodical oxidation and reduction heavy metal binding forms in the sediment changed significantly. Figure 5 shows the results for Zn.

In the original sediment about 40 % of Zn has been found in the sulfidic/organic fraction. At the end of the 3 stage redox cycle only 30 % remained in this fraction under reducing conditions. After each oxidation step the percentage in this fraction decreased continuously.

The greatest changes were found for the dissolved Zn concentrations which increased continuously. While after the first reduction cycle no Zn could be found in solution, about 20 % of the initially solid bound Zn was dissolved after the two following cycles. In the course of the experiment the easily reducible portions decreased, but the carbonatic and exchangeable portions increased. Altogether, a transformation in less stable phases took place.

A similar development can be stated for Cd (see figure 6). In the original sediment about 65 % of Cd was bound in the sulfidic/organic fraction. These portions decreased continuously. Simultaneously a distinct Cd-mobilization could be determined, in particular after the oxidation cycles.

Pb-portions in the sulfidic/organic fraction were even higher than for Cd and Zn (see figure 7). As well as for these two metals a transformation from the sulfidic/organic fraction into moderately and easily reducible phases could be shown. After the second and third oxidation cycle a weak mobilization can be stated which, however, is negligible in comparison to Cd and Zn.

As can be seen in figure 8 the Cu-portions in the sulfidic/organic fraction (about 90 %) were the highest in the original sediment in comparison to the other metals. The rest was found in the moderately reducible fraction. During the oxidation cycles the percentage of Cu in the moderately reducible fraction increased, while it decreased in the sulfidic/organic fraction, and minor portions were dissolved. Like for the other metals the portions in the sulfidic/organic fraction decreased continuously in the course of the experiment, but in all the percentage of Cu did not drop under 40 % in this fraction.

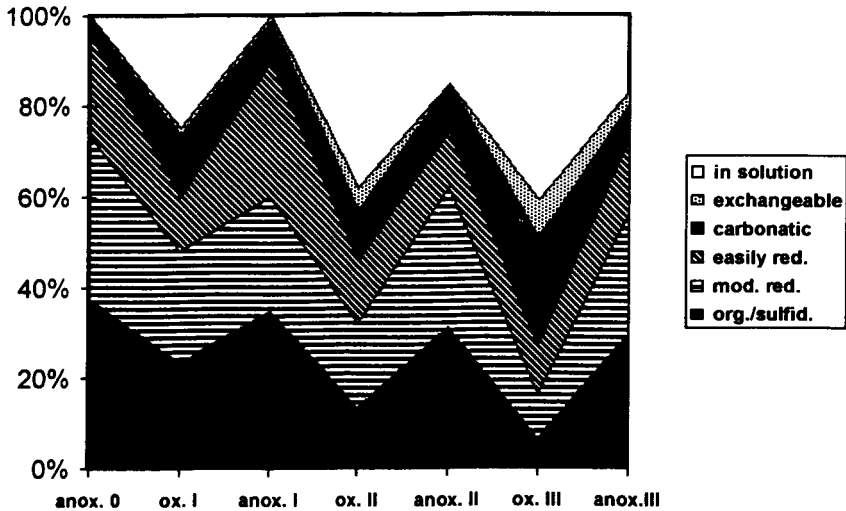


Figure 5. Transformation of Zn binding forms in succeeding redox cycles

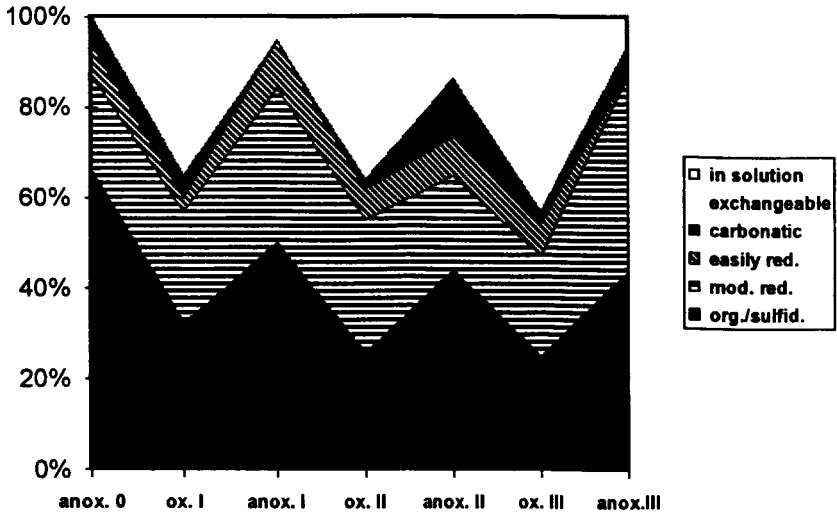


Figure 6. Transformation of Cd binding forms in succeeding redox cycles

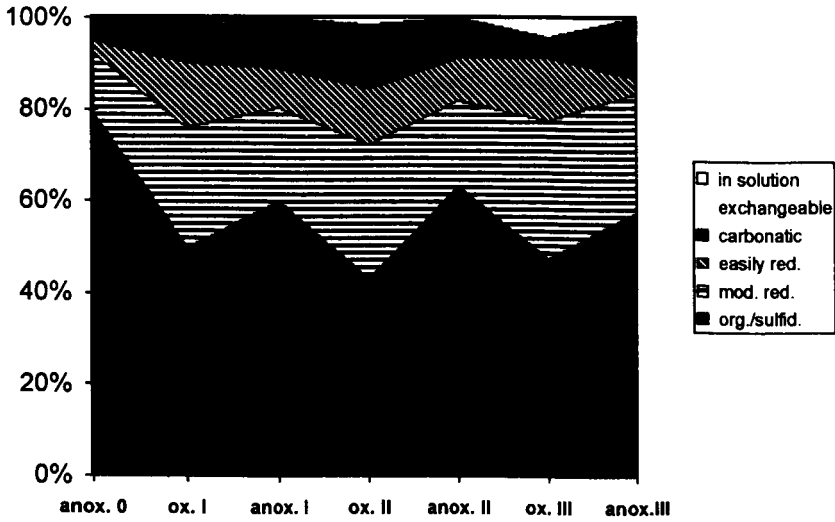


Figure 7. Transformation of Pb binding forms in succeeding redox cycles

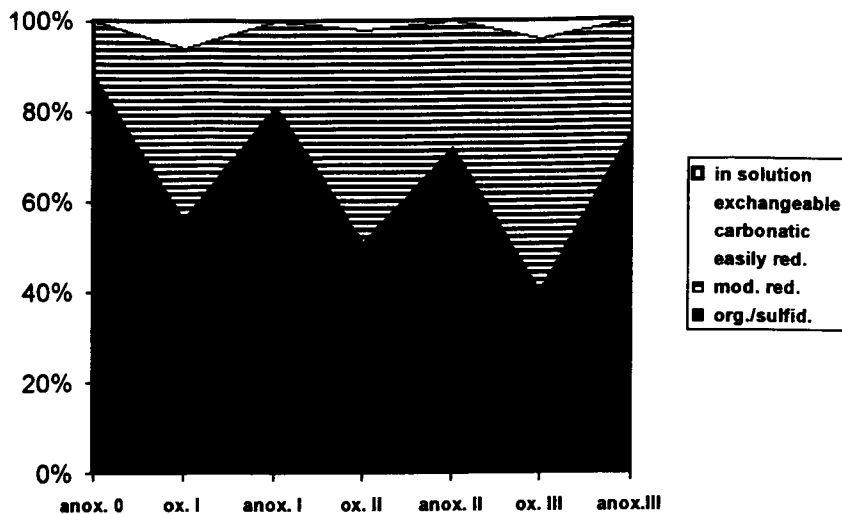


Figure 8. Transformation of Cu binding forms in succeeding redox cycles

Up to now, there does not exist a satisfactory method to separate sulfidic bound metals from organic bound metals. With the applied sequential extraction procedure amorphous sulfides are oxidized under acid conditions and to a large extent dissolved during the oxidation cycles. It may be assumed that the Cu-positions found after oxidation in that fraction mainly exist in organic binding forms.

Generally, in the original harbour sediment very high metal portions were found in the sulfidic/organic fraction. They increase in the order: $Zn < Cd < Pb < Cu$, which may be interpreted by the corresponding stability constants of the metal sulfides. Under sulfidic conditions these metal bondings are relatively stable. At contact with atmospheric or dissolved oxygen, the sediment is oxidized and sulfidic compounds are dissolved. As a result a part of the heavy metals is mobilized. Depending on their chemical attributes, some species remain in solution or are re-adsorbed on freshly precipitated iron hydroxides and oxyhydroxides which are formed during oxidation. In the same way a transfer to other reactive sediment components (e.g. algae) takes place. These mechanisms could be established by the aid of a multichamber system (Calmano *et al.*, 1988b).

By periodical redox changes a low buffered sediment may be strongly changed, because during oxidation buffering substances are consumed and displaced, respectively. As could be shown the form of binding by some metals changed significantly. In particular after oxidation of the sediment a transformation into more labile binding positions takes place. Especially affected by these processes are strongly contaminated sediment depositions as occur in the upper Elbe River. Therefore, such scientific findings should be adopted to dredging or sediment disposal projects.

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