EXCHANGE OF HEAVY METALS BETWEEN SEDIMENT COMPONENTS AND WATER

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I. INTRODUCTION

Sediments are both carriers and potential sources of contaminants in aquatic systems, and these materials may also affect groundwater quality and agricultural products when disposed on land. Such problems have initially been recognized for inorganic chemicals in the early and middle sixties from the studies on artificial radionuclides in the Columbia and Clinch Rivers by Sayre et al. (1963) and on heavy metals in the Rhine River system by De Groot (1966). In the early seventies, following the catastrophic events of cadmium- and mercury-poisoning in Japan, sediment-associated metal contaminants received public attention, for example, with severe effects on aquatic ecosystems in the Wabigoon River, Laurentian Great Lakes, Swedish Lakes, and in many past and present mining areas all over the world (Förstner & Wittmann, 1979).

During the last decade the major objectives of research on metal-polluted waters have changed from the initial surveys of sources and pathways to more detailed investigations of the mechanisms controlling the mobility and bioavailability of different metal species. The general experience that the environmental behavior and toxicity of an element can only be understood in terms of its actual molecular form led to the introduction of the term "speciation", which is used in a vague manner both for the operational procedure for determining typical metal species in environmental samples and for describing the distribution and transformation of such species in various media (Leppard, 1983; Bernhard et al., 1986; Landner, 1987; Patterson & Passino, 1987; Batley, 1989, Allen et al., 1989).

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Problems of "speciation" are particularly complex in heterogenous systems, such as in soils, aerosol particles and sediments; thermodynamic models may give suggestions as to the possible species to expect, but due to the important role of kinetically controlled processes in biogeochemistry, the actual speciation is often different from what can be expected (Andreae et al., 1984).

Conceptually, a sediment can be considered as a heterogeneous mixture of dissimilar particles. Solid phases interacting with dissolved constituents in natural waters consist of a variety of components including clay minerals, carbonates, quartz, feldspar and organic solids. The "matrix vehicle" or residual fraction (Jenne, 1977) is associated with more labile and thermodynamically unstable components such as carbonates, amorphous aluminosilicates, and organic matter (Martin et al., 1987). These fractions are usually coated with Fe- and Mn-oxides and living or non-living organic material. A primary medium for sorption of inorganic components by sediments are metastable iron and manganese oxides and oxyhydrates, which have a high degree of isomorphic substitution (Jenne, 1977).

Organic surfaces for metal sorption could form in three possible ways (Hart, 1982):

(i) from organisms such as bacteria and algae;
(ii) by the breakdown of plant and animal material and by the aggregation of lower-molecular weight organics; and
(iii) by organic matter of lower-molecular weight sorbed onto clay or metal oxide substrates (Davis & Gloor, 1981).

Although the difference between these three surface types is not well understood with respect to metal uptake, there is a general agreement that at least one major binding mechanism involves salicylic entities. Other strong binding entities (such as peptides) may also be present in some systems. At least part of the organic matter adsorbed onto the particulate matter in natural waters has carboxylic and phenolic functional groups available for binding with trace metals. The trace metal adsorption capacity of organic matter is generally between that for metal oxides and clays (Tipping, 1981).

Mineral phases as substrates of pollutants originate from two major sources: Endogenic fractions of particulate matter include minerals that result from processes occurring within the water column (Jones & Bowser, 1978). Enrichment of minerals generated by endogenic processes may be influenced by settling of particulates, filtering organisms, and flocculation. Endogenic processes exhibit a distinct temporal character, often as a result of the variation of the organic productivity. In lakes, the total particulate concentration of trace metals is generally lowest in the hypolimnion due to the decomposition of organic matter. Consequently, net biogenic flux, for example, of metals depends on the lake's capacity to produce organic particulate matter and to decompose it before it is buried definitely in the sediment (Salomons & Baccini, 1986).

Authigenic (or diagenetic) fractions include minerals that result from processes within deposited sediments. Decomposition of organic matter, which is mediated by microorganisms, generally follows a finite succession in sediments depending upon the nature of the oxidizing agent (see Berner, 1981); the successive events are oxygen consumption (respiration), nitrate reduction, sulfate reduction, and methane formation.

The composition of interstitial waters in sediments is perhaps the most sensitive indicator of the types and the extent of reactions that take place between pollutant-loaded sediment particles and the aqueous phase that contacts them. The large surface area of fine-grained sediment in relation to the small volume of its trapped interstitial water ensures that minor reactions with the solid phases will be shown by major changes in the composition of the aqueous phase.

II. MOBILITY, ACID POTENTIAL AND BUFFER CAPACITY

Sediments are an important storage compartment for the metals released into surface waters. Furthermore, because of their ability to accumulate metals, sediments can reflect water quality and record the effects of anthropogenic emissions. Regarding the potential release of contaminants from sediments, changes of pH and redox conditions are of prime importance. In practice, therefore, characterization of sediment substrates with respect to their buffer capacity is a first step for the prognosis of middle- and long-term processes of mobilization, in particular, of toxic chemicals in a certain milieu.

By dredging activities anoxic sediments are suspended, removed from the river bottom, deposited on land or redeposited into the oxic water body. Evaluation of the pH- and redox-changes resulting from the oxidation of anoxic sediment constituents can be performed in the laboratory by ventilation of sediment suspensions with air or oxygen. Another approach for evaluating pH-effects is titration with acids. For quantifying pH-properties and for better comparison of sediment samples it is proposed to use the term "pH_{diff}", which is characterized by the difference of pH-values of 10-percent sludge suspensions in distilled water (pH_o) and in 0.1 N acid (pH_x) after 1 h shaking time (Calmano et al. 1986):

$$pH_{diff} = pH_o - pH_x$$

Three categories of pH_{diff}-values can be established ranging from $pH_{diff} < 2$ (strongly buffered), pH_{diff} 2-4 (intermediate) to $pH_{diff} > 4$ (poorly buffered).

Particularly a short time mobilization of heavy metals takes place, if the buffer capacity of a sediment is low and the acid potential is high. Under "acid potential" we understand the release of hydrogen ions as it can be observed at the oxidation of anoxic sediments e.g. by the following reactions:

$$NH_4^+ + 3/2\ O_2 \longrightarrow NO_2^- + 2\ H^+ + H_2O$$

$$2\ FeS + 7/2\ O_2 + H_2O \longrightarrow 2\ Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$

$$Fe^{2+} + 1/4\ O_2 + H^+ \longrightarrow Fe^{3+} + 1/2\ H_2O$$

$$Fe^{3+} + 3\ H_2O \longrightarrow Fe(OH)_3 + 3\ H^+$$

For a classification of sludges regarding their acid potential which can be produced by oxidation of sulfidic components one can preferentially use the data of calcium and sulfur from the sequential extraction scheme as proposed, for example, by Tessier et al. (1979). In anoxic, sulfide-containing sediments the two elements are selectively released during anaerobic experimental procedures (argon or nitrogen atmosphere in glove box) by the Na-acetate step (Ca from carbonates) and peroxide step (S from oxidizable sulfides, mainly iron sulfide).

Reaction of oxygen with iron sulfide will produce H^+-ions; by reaction with carbonate H^+-ions are buffered. For an initial estimation, one may compare total calcium and sulfur concentrations in the sediment sample to get an index of acidity:

$$I_{Ac} = \frac{[S]}{[Ca]}$$

Experimental approaches for prognosis of acid producing potential of sulfidic mining residues have been summarized by Ferguson and Erickson (1988). A test described by Sobek et al. (1978) involves analysis of total or pyritic sulfur. Neutralization potential is obtained by adding a known amount of HCl and titrating with standardized NaOH to pH 7. Potential acidity is subtracted from neutralization potenital. A value below 5 t $CaCO_3$/1000 t of rock indicates a potential acid producer. Bruynesteyn & Hackl (1984) calculated acid-producing potential from total sulfur analysis. Acid-consuming ability is obtained by titration with standardized sulfuric acid to pH 3.5

(Bruynestein & Duncan,1979). Acid-producing potential is subtracted from acid-consuming ability; a negative value indicates a potential acid producer.

Results from titration experiments using 1 M nitric acid on sediment suspensions of 100 g/l are presented in Figure 1.

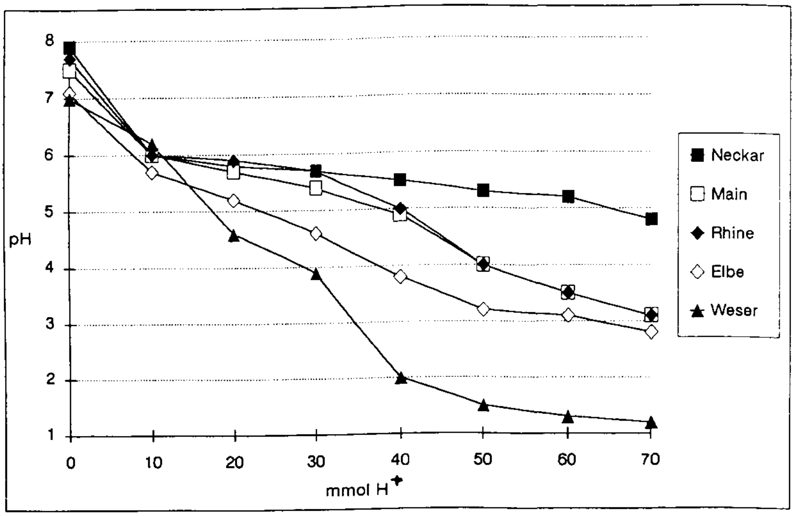

Figure 1. Acid titration curves for 5 German river sediments

The titration curve of the Neckar River sediment exhibits a large plateau in the pH-range of 5 and 6, probable due to the fraction of carbonate which is consumed by the addition of acid. In contrast to this observation the titration curves of both Elbe River and Weser River sediments are continously decreasing because of their small contents of carbonate. The sediments from the Rhine and Main River show small plateaux in the pH-region 5.5-6 which indicate a medium content of buffering substances.

An originally sulfide-rich material from an inland harbor basin of Harburg which had only been stored for 1 year in a closed bottle reached a pH value of 4.3. This was probably due to the consumption of the small residual buffer capacity by oxidation of parts of the sulfide fraction. Similarly, a reduction of the pH has been found at upland disposal sites of dredged sediments from Hamburg harbor (Tent, 1982). Due to the small carbonate content which is consumed during several months or years and subsequent lowering of the pH, metals are easily transferred to agricultural crops, and permissible limits of cadmium have been surpassed in as much as 50% of the wheat crops grown on these materials (Herms & Tent, 1982).

High concentrations of metals have been measured in pore waters from sedimentation polders in the Hamburg harbour area, in the older, oxidized deposits (Maaß et al., 1985; Table 1). Similar effects occured in the aquatic system, particularly on tidal areas affected by periodical drying and wetting (Kersten 1989), and at other sites exhibiting strong resuspension activities. The situation in the Elbe River estuary is particularly critical since small buffering capacities of the sediments coincide with a relative long residence time of suspended particles (Tent, 1987).

Table 1. Composition of anaerobic and oxidized pore waters from sedimentation polders (Maaß et al., 1985)

	"Anaerobic pore water"	"Oxidized pore water"
Nitrate	< 3 mg/l	120 mg/l
Ammonium	125 mg/l	< 3 mg/l
Iron	79 mg/l	< 3 mg/l
Zinc	< 30 µg/l	> 5000 µg/l
Cadmium	< 0.1 µg/l	80 µg/l
Arsenic	150 µg/l	15 µg/l

III. METAL TRANSFER

For a better understanding of the behavior of heavy metals in sediments and pore waters and their potential transfer to biota more experimental speciation studies and identification of solid phases are urgently needed (Hart & Davies, 1977; Batley & Giles, 1980; Elderfield, 1981).

With respect to the modeling of metal partitioning between dissolved and particulate phases in a natural system such as estuarine sediments, the following reqirements have been listed by Luoma & Davis (1983):

- the determination of binding intensities and capacities for important sediment components,
- the determination of relative abundance of these components,
- the assessment of the effect of particle coatings and of multi-component aggregation on binding capacity of each substrate,
- the consideration of the effect of major competitors (Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}),
- the evaluation of kinetics of metal redistribution among sediment components.

It seems that models are still restricted because of various reasons: (i) adsorption characteristics are related not only to the system conditions (i.e., solid types, concentrations, and adsorbing species) but also to changes in the net system surface properties resulting from particle/particle interactions such as coagulation; (ii) influences of organic ligands in the aqueous phase can as yet rarely be predicted; (iii) effects of competition between various sorption sites, and (iv) reaction kinetics of the individual constituents cannot be evaluated in a mixture of sedimentary components. These restrictions have been recently discussed in detail by Honeyman & Santschi (1988), who stated that even for aquatic environments with small concentrations of particles the non-deterministic and interactive effects described above generally influence the estimation of an apparent partitioning coefficient by 1 to 3 orders of magnitude in either direction. With respect to environments of moderate to high particle concentration such as in soils and sediments those authors concluded that theoretical approaches have failed, thus far, to provide a sound basis for the prediction of trace-element behaviour.

At present experimental studies on the solid/solution interactions in such complex systems seem to be strongly needed. One approach is the use of a multi-chamber device, which still permits phase interactions via solute transport of the elements (Calmano et al., 1988). In this way, exchange reactions and biological uptake can be studied for individual phases under the influence of e.g. pH, redox, ionic strength, or solid and solute concentration.

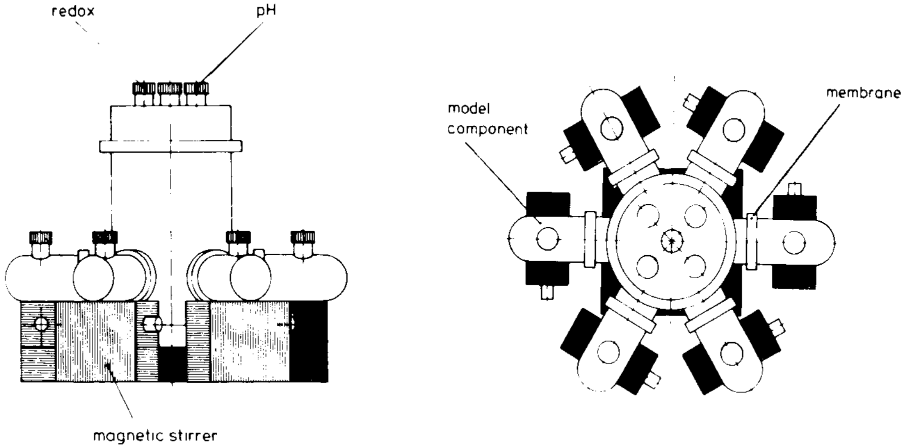

Figure 2. Schematic view of the multi-chamber device

The laboratory system used in these studies was developed from the experience on sediment/algae interactions with a modified two-chambered device (Ahlf et al., 1986). The system is made of a central chamber connected with 6 external chambers and separated by membranes of 0.45 um pore diameter (Figure 2).

The volume of the central chamber is 6 litres and each of the external chambers contains 250 ml. Either solution or suspension can be placed into the central chamber. The external chambers are filled with suspensions of model sediment components like clay, iron- and aluminium oxide, quartz, and algal cell walls. The solid components in each chamber are kept in suspension by magnetic stirring. Redox potential, pH values, and other parameters may be controlled and adjusted in each chamber.

In an experimental series on the effect of salinity on the metal transfer of anoxic dredged mud which has to be disposed into sea water, quantities of model components were chosen in analogy to an average sediment composition. In the central chamber a mud suspension from Hamburg harbour was placed and salts were added to form artificial sea water. After 3 weeks solid samples and filtered water were collected from each chamber.

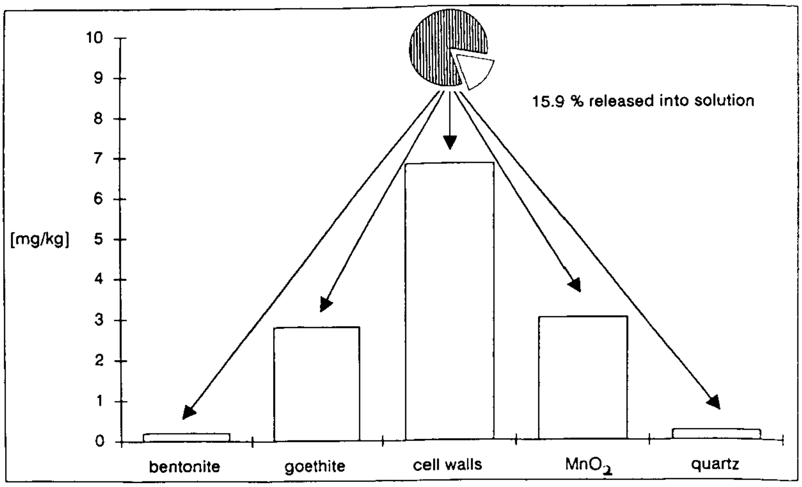

Figure 3. Mobilization of Cd from dredged mud and readsorption on different model sediment components in artificial seawater

The effect of salinity on metal remobilization from contaminated sediments was different for each of the elements studied. While approximately 16% of cadmium in the dredged mud from Hamburg harbour was released (see fig. 3), for metals such as copper the effect of salinity increase seems to have been less important in the transfer both among sediment substrates and to aquatic biota. This is, however, not true as can be demonstrated with a mass balance for the element copper in Figure 4.

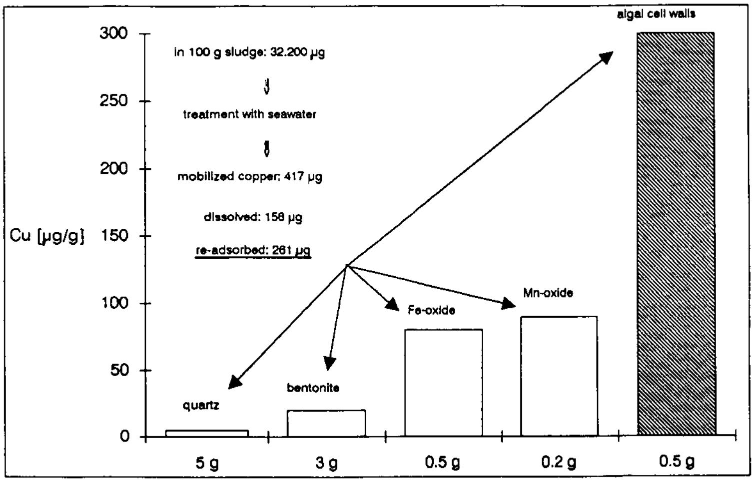

Figure 4. Mass balance for Cu: Distribution between model components and solution

It was found that only 1.3 % of the copper in the sludge sample was released when treated with seawater. Only one third remained in solution, which was equivalent to approximately 40 µg/l, and there was no significant difference to the conditions before salt addition. Two thirds of the released copper was readsorbed but with different affinities to the various model substrates. Copper concentrations in quartz and bentonite clay were not significantly different from their natural contents. Slight enrichment of copper occurred in the hydrous iron oxide and manganese oxide, whereas the cell walls - a minor component in the model sediment - accumulated nearly 300 mg/kg of copper.

The dominant role of organic substrates in the binding of metals such as Cd and Cu is of particular relevance to the transfer of these elements into biological systems. It can be expected that even at relatively small percentages of organic substrates these materials are primarily involved in metabolic processes and thus may constitute the major carriers by which metals are transferred within the food chain.

Metal mobility and transfer from solid matter is strongly affected by redox processes. To simulate such effects, when low buffered anoxic sediments are resuspended in an oxic river water which e.g. happens during dredging activities, the multichamber was filled with an anoxic sludge suspension from Hamburg harbour and model sediment components were added into the external chambers. The suspension was bubbled through with nitrogen to keep the system anoxic. Redox potential and pH values were measured permanently. After 100 hours solid samples and filtered water samples were taken from each chamber and analyzed by atomic absorption spectroscopy. Then the sludge suspension in the central chamber was aerated, and after 240 hours the dissolved and particulate metal concentrations were determined again.

Figure 5 shows the pH and redox development during the experiment. There exists a clear interdependence between these two parameters. During the anoxic run the pH value in the sludge suspension remains at about 8 and redox potential at about -200 mV. After aeration the redox potential increases from -230 mV to about +600 mV and the pH decreases from 8 to 4.2.

Metal concentrations in solution and in solids of the multichamber device are given in figure 6. The bars represent the concentrations of copper, zinc, and cadmium in the anoxic and the oxic system. Under anoxic conditions metal concentrations are generally low. In solution only copper is found in significant amounts, and the transfer to the single model

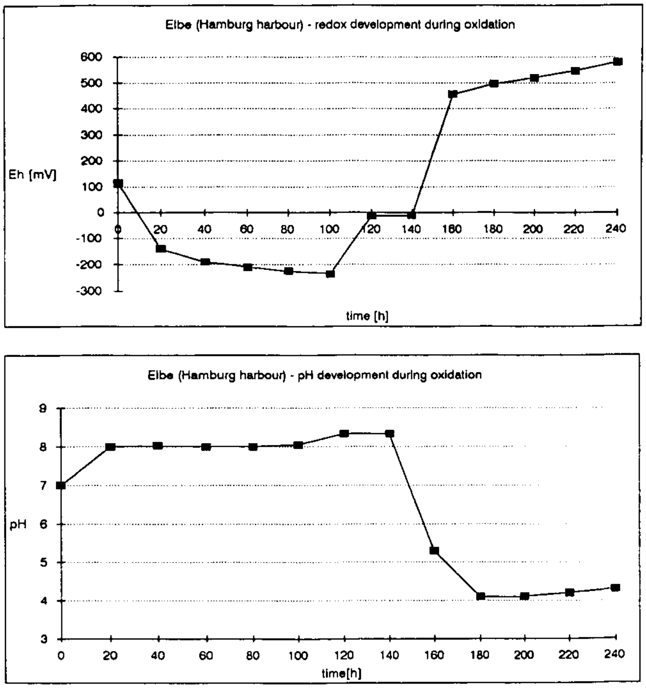

Figure 5. Redox and pH development during the experiment

sediment components is limited. After oxidation of the sediment suspension all dissolved metal concentrations are distinctly higher, and the same can be observed for the solids. The distribution of copper is dominated by the transfer and sorption on the the algal cell walls.

Cadmium and zinc are mainly sorbed on bentonite, but the highest contents for these metals are found in the control chamber, which is due to the precipitation of iron hydroxide after oxidation and sorption on these highly active surfaces. It can be concluded that at least part of the metal concentrations on the other substrates are affected as well by this mechanism. The binding intensities of the metals, in particular on bentonite and iron oxihydrates and additionally for copper on algal cell walls must be relatively strong because of the distinct sorption at these low pH values.

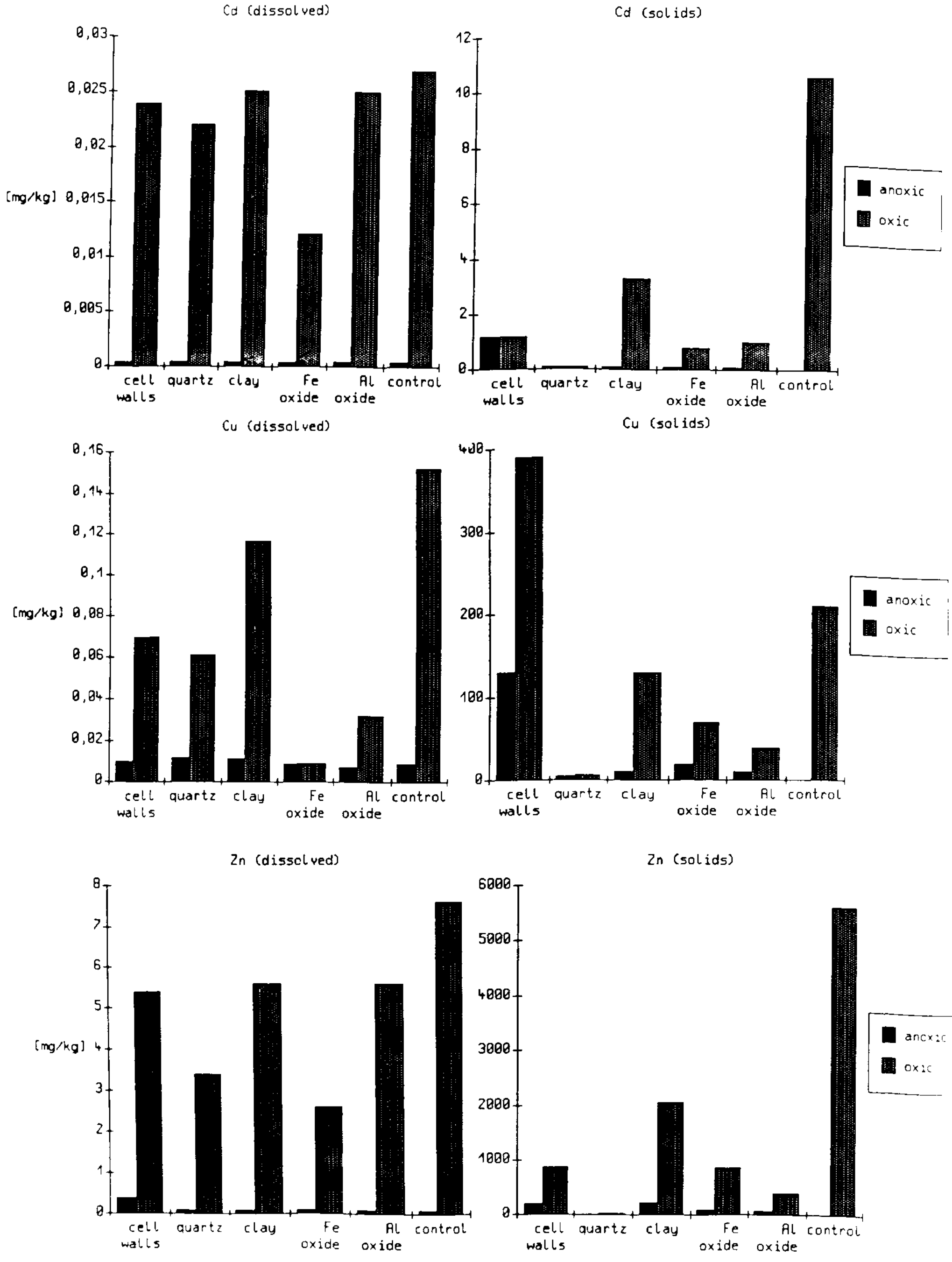

Figure 6. Dissolved and solid concentration of Cd, Cu, and Zn under anoxic and oxic conditions

To study the separate influence of redox potential on metal transfer and redistribution among sediment components a further experiment was carried out, in which pH values were kept constant at 7.5. Apart from this the experimental conditions were the same. Results for copper, cadmium, and zinc showed that metal concentrations in solution, under both anoxic and oxic conditions, were low and no significant transfer to the model sediment components could be observed, with the exception of copper and cadmium for algal cell walls, where an increased content was found under oxic conditions.

Chemical extraction procedures provide a convenient means to determine the major accumulative phases for metals in sediments and mechanisms of their diagenetic transformation. We applied a sequential method (Tessier et al., 1979) to 5 river sediments before and after oxidation. For anoxic sediments the maintenance of oxygene-free conditions during sampling and extractions is of critical importance.

Figure 7 shows the results by example of an Elbe River sediment. Cadmium, e.g., is under anoxic conditions nearly quantitatively found in the organic/sulfidic (H_2O_2-oxidizable) fraction, supporting the hypothesis that it is predominantly bound to sulfides in anoxic sediments. Exposure of the sample to oxic conditions caused the cadmium to be shifted in the extraction scheme to easily reducible and carbonatic fractions, respectively. From these fractions cadmium may be easily mobilized by acid conditions.

The element cadmium showed a similar behaviour in all studied sediment samples (see fig. 8). In anoxic sediments only very small portions were found in the first two steps of the sequential extraction procedure. After oxidation of the sediment samples the portions in both the ammonium- and sodiumacetate fractions were distinctly higher. The somewhat lower contents in these fractions of the Elbe and Weser sediments are related to their low buffer capacities which resulted in pH decrease of the suspension by oxidation and higher cadmium concentrations in solution.

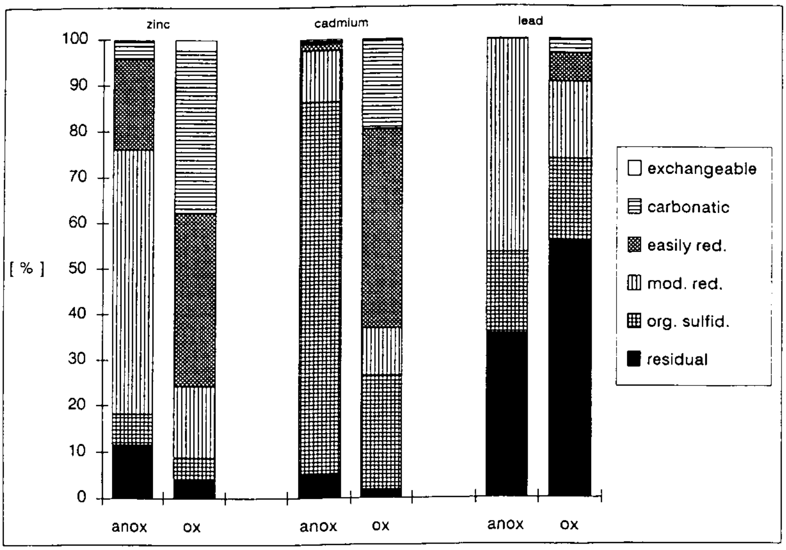

Figure 7. Sequential chemical extraction of an Elbe sediment under anoxic and oxic conditions

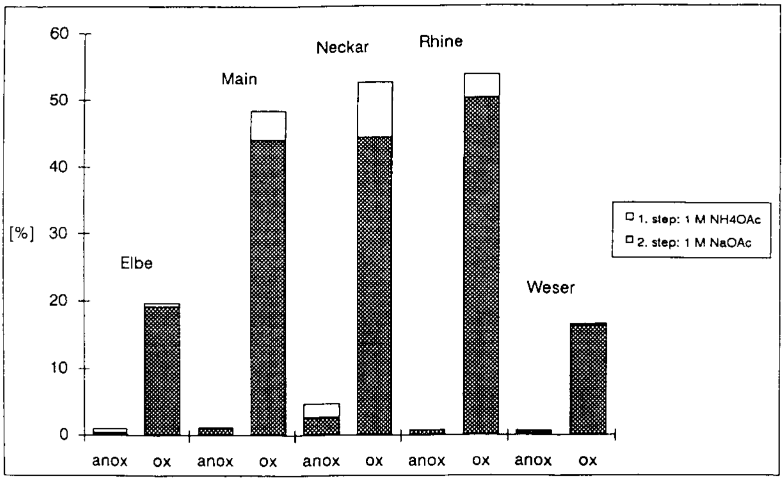

Figure 8. Extractable Cd-portions in the first two steps of the sequential extraction procedure under anoxic and oxic conditions

IV. CONCLUSIONS

The multichamber device allows the investigation of heavy metal sorption/desorption processes on typical sediment components with different surface binding intensities, which are in competition for the metals. It is possible to study the influence of single components on the metal transfer from contaminated material via aqueous phase to solids under changing environmental conditions. The investigations reported here related to the effects of salinity, redox, and pH changes in a low buffered sediment. By oxidation of anoxic sediments hydrogen ions are formed, as a result of e.g. sulfide and ammonium oxidation. The oxidation is catalyzed by microorganisms and the pH value decreases. In systems with higher buffer capacities these pH changes may not be measureable, but there is the possibility of the existence of low pH microenvironments. Metals, e.g. bound as sulfides under anoxic conditions, are mobilized, dissolved within a short time as ions or complexed by dissolved organic acids, and then transported and re-adsorbed on more reactive solid surface sites, like freshly precipitated iron hydroxides or biotic material.

These processes lead to changes of heavy metal binding forms on solids and to a translocation of distinct metals into more reactive sedimentary phases. The present state of knowledge of solid matter speciation of heavy metals is still somewhat unsatisfactory because the appropriate techniques are only operational tools with associated conceptual and practical problems (Kersten & Förstner, 1989). Most instrumental techniques available to date are too sophisticated to be routinely included in trace element speciation studies. The method of sequential chemical extraction is the least sophisticated but most convenient technique available for a speciation assessment. The usefulness of a differentiated approach to the interactive processes between water and operationally defined solid phases has been clearly evidenced. Possible environmental implications, e.g. during dredging operations, after land disposal of sediments, and other processes which lead to changes in the physico-chemical conditions of the interacting environmental milieu, can be qualitatively estimated. A combination of the different methods reported here should therefore help to explain mechanims which determine the interactions of metals between aquatic solids and solution.

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