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Mobilization and transfer processes of heavy metals in dredged mud from Hamburg harbour

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ABSTRACT

The mobilization and transfer of heavy metals to important sediment components after change of the physico-chemical conditions (redox potential, pH-value) in aquatic systems have been studied by using a multi-chamber device. Significant metal enrichments were found on algal cell walls, particularly for Cu and Cd, and on freshly precipitated iron hydroxide. Oxidation of anoxic mud from Hamburg harbour leads to lowering of pH and remobilization of Cd and Zn.

INTRODUCTION

Many problems exist with polluted sediments in rivers, harbours, estuaries, and coastal marine areas. Particular difficulties are connected with the dredged materials which have to be removed from shipping channels and harbours. In the river mouths to the southern coast of the North Sea anually about 20 million m^3 have to be dredged from the Rhine/ Meuse (Rotterdam harbour) and approximately 10 million m^3 from the rivers Scheld (Antwerpen), Weser (Bremen), and Elbe (Hamburg). Problems not only arise from those masses which are removed from the rivers and which have to be deposited on land. Also by those polluted materials, which are redeposited into the water body or which are resuspended by natural processes, adverse effects on biota can be expected.

It is a general experience that most water quality data for heavy metals, routinely measured by the water survey authorities, rarely reflect the possible adverse influences on aquatic biota. There are various explanations for this experience. One is the lack of knowledge of the critical metal species, combined with difficulties in speciation analysis. Another reason is that there are some mechanisms of interactions between organisms and their environment which are not necessarily restricted to the direct uptake of metals from the water phase. There are many indications that — for understanding of these mechanisms — it is important to include the solid phases (sediments, suspended matter) in such systems and to study the transfer reactions between sediments and water, particularly under changing environmental conditions.

Heavy metal associations on sediment particles are the product of interactive processes which have been affected not only by the physico-chemical form of the input metals and the conditions of the aqueous phase, but also by the composition, concentration and conditions of the particulate phase.

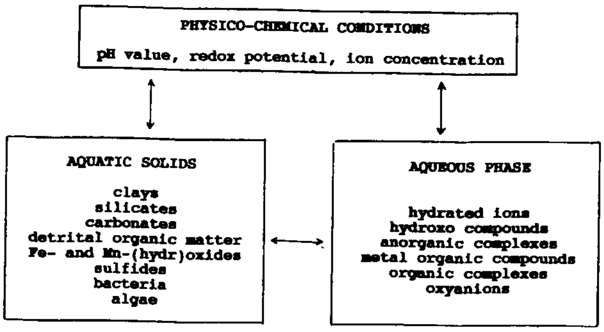

Figure 1: Physico-chemical interactions in aquatic systems

Metals may be sorbed by various sediment fractions like clays, detrital organic matter, iron and manganese (hydr)oxides, carbonates, sulfides and algae or other living cells. Desorption or remobilization of heavy metals from these sedimentary phases is strongly dependent on the type of chemical bonding and on environmental conditions like redox potential, pH-value and ionic strength. The aspect of solid concentration deserves particular attention, since experimental observations of the sorption/complexation characteristics of metals with e.g. humic type substances (1), algal cell walls (2), and hydrous metal oxides (3, 4) have revealed variations in binding intensity as a function of the degree of site occupancy.

Most laboratory experiments on sorption/desorption reactions of heavy metals were performed with single sediment components like iron-, manganese- or aluminiumoxides and quartz. The influence of particle coatings and multicomponent aggregation, major competitors (5) and, in particular, of dissolved organic ligands can rarely be predicted from such experiments. In addition, effects of competition between various sorption sites and reaction kinetics of the individual constituents cannot be evaluated in a mixture of sedimentary components.

In the experimental study of these factors, as well as for predicting predominant source constituents, fluxes or mobilities, transfer mechanisms, and potential sinks of toxic metals in different sedimentary systems, it seems sensible that the individual components be separated, but in a way which still permits phase interactions via solute transport of the elements. In this way, exchange reactions, sorption/ desorption processes, and biological uptake can be studied for individual phases under the influence of pH, redox, ionic strength, solid and solute concentration, and other parameters. In a previous paper (6) we described an apparatus that permits the simultaneous study of six major sedimentary constituents and gave initial data on the effect of seawater on dredged material from the Elbe River and on the interactions between these model components. Such information is needed in practice to predict the possible implications of dredging processes in estuaries, and of dumping dredged material from freshwater into coastal waters. The present article deals with the effects of redox potential changes of transfer processes of heavy metals and re-adsorption on different sedimentary phases, when anoxic sediments are resuspended or redeposited in oxic river water.

METHODS AND MATERIALS

The laboratory system used in these studies is made of a central chamber connected with six external chambers and separated by membranes of 0.45 m pore diameter. The use of other membranes is possible. The volume of the central chamber is about 4 litres and each of the external chambers has a volume of 300 ml. Figure 2 gives a schematic view of the multichamber device.

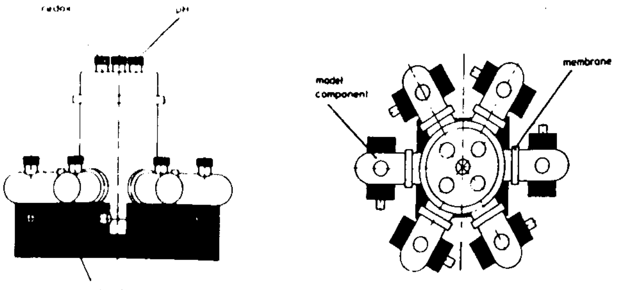

Figure 2: Schematic view of the multichamber device

The central chamber contains the contaminated dredged mud. The external chambers are filled with suspensions of model sediment components like clay, iron- and aluminiumoxide, quartz and algal cell walls. The solid components in each chamber are kept in suspension by magnetic stirring. Redox potential, pH value, and other parameters may be controlled and adjusted in each chamber.

EXPERIMENTS AND RESULTS

In the freshwater section of the Elbe River metal mobility and transfer from solid matter is affected by redox processes to a large extent. The sediments of the Elbe exhibit very low buffer capacities. This fact has been recognized when dredged mud has formerly been used for "melioration" of agricultural land. Shortly after deposition the pH of the soil dropped, and strong accumulations of cadmium and other metals were found in the crops growing in these areas. Figure 3 shows the titration curves of 5 sediment suspensions (100 gl^{-1}) from the Hamburg harbour with 0.1 N nitric acid.

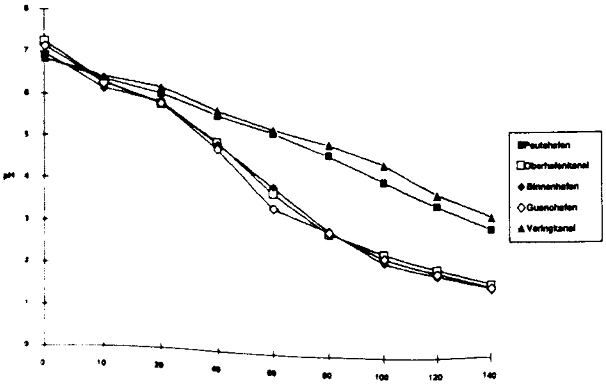

Figure 3: Acid titration curves of Hamburg harbour sediments

To simulate such effects, when low buffered anoxic sediments are resuspended in an oxic river water, the multichamber device was filled with distilled water. In the central chamber a 3 % anoxic harbour sludge suspension was prepared and certain amounts of algal cell walls (Scenedesmus quadricauda), bentonite, aluminium oxide (neutral, 400 mesh ASTM), goethite (synthetically made using the method of Alkinson et al. (7)), and quartz powder were added to the external chambers; the sixth chamber served as control. The concentration of each solid was chosen so that previously determined cation exchange capacities were uniform for all components.

The following quantities were used: 0.278 g algal cell walls, 1.28 g aluminium oxide, 1.19 g goethite, 0.14 g bentonite, and 10 g quartz powder. These quantities were each equivalent to a total cation exchange capacity of 127 mol/100 g. 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 4 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 -50 mV. After aeration the redox potential increases from -75 mV to about +650 mV and the pH decreases from 8 to 4.2.

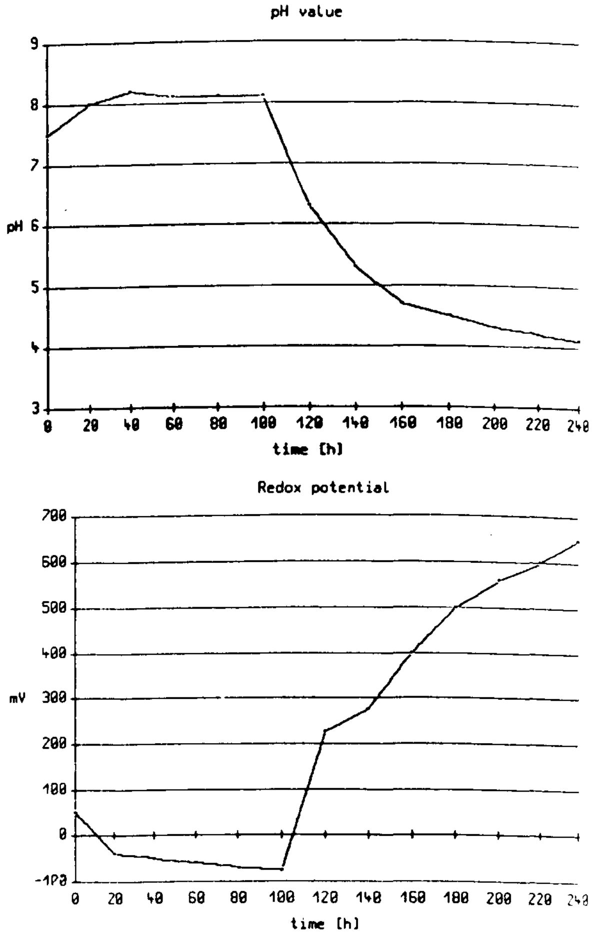

Figure 4: pH and redox development during the experiment

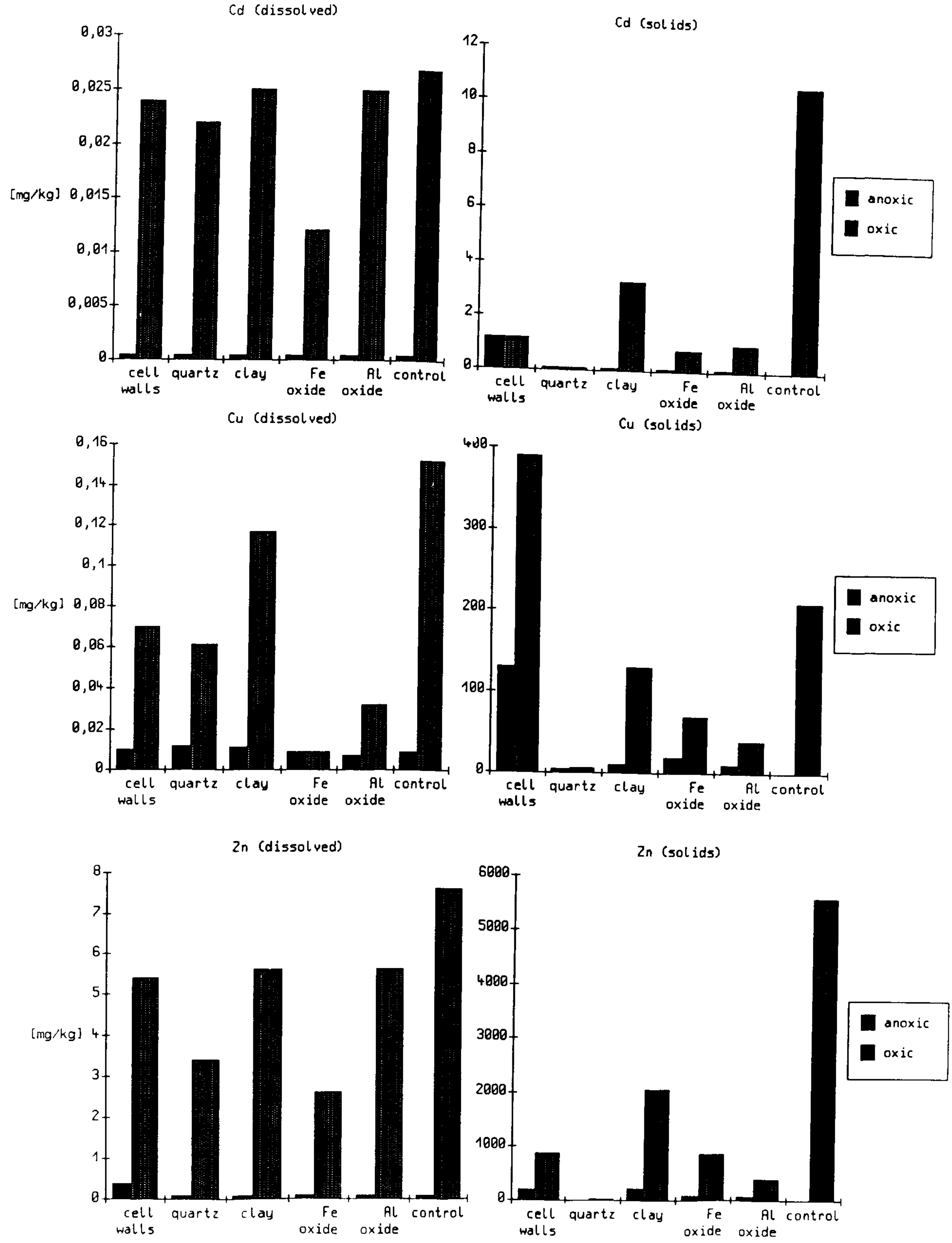

Figure 5: Dissolved and solid concentration of Cd, Cu, and Zn under anoxic and oxic conditions

Metal concentrations in solution and in solids of the multichamber device are given in figures 5a - 5c. 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 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 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 precipitations 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.

To study the separate influence of redox potential on metal transfer and redistribution among sediment components a second experiment was carried out, in which pH values were kept constant at 7.5. Apart from this the experimental conditions were the same. First results for copper, cadmium, and zinc show that metal concentrations in solution, under both anoxic and oxic conditions, are very 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.

CONCLUSIONS

The multichamber devise 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 effect of 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 transfer of distinct metals into biological systems. Even at relative small percentages of organic substrates these materials may be involved in metabolic processes and thus may constitute the major carriers by which metals are transferred within the food chain.

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The Numerical Simulation of Current and Sediment Transport in Harbours and Tidal Estuaries

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Abstract

A three-dimensional finite difference numerical model of hydrodynamics and suspended sediment transport has been applied to different situations to demonstrate the applicability of the model. The following applications are presented in this paper: deposition of suspended sediment in an excavated channel; flow field in a harbour entrance; erosion and deposition in a harbour basin; suspended sediment dynamics in the region of the turbidity maximum of the Weser Estuary.

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