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Metal Associations in Anoxic Sediments and Changes Following Upland Disposal†

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The ecological effects of heavy metals in contaminated sediments are more determined by the chemical form and reactivity than by the level of accumulation. Dredging of anoxic sediments and disposal on land is attended by changes of redox conditions. Under oxidizing conditions some controlling solid compounds may change gradually thus changing the solubility of certain metals.

Chemical extraction experiments for estimating characteristic association forms of heavy metals in anoxic sediments were carried out, both under presence and absence of air during the analytical procedure. Drying of the sediment decreases the proportion of the sulfidic metal fractions to a stronger degree, and oxidized Cd and Zn are found in the most available, exchangeable fraction.

With respect to long-term effects acidification of poorly buffered sludges after disposal on land is probably the most important factor affecting metal associations and mobility. For many metal examples a linear relationship has been found between decreasing pH values and increasing dissolved metal concentrations. To quantify these relationships and for better comparison of samples a simple test procedure is proposed which is based on pH differences before and after addition of acid.

KEY WORDS: Sediment, sludges, speciation, transformation, chemical characterization, pH effects, redox effects, copper, zinc, cadmium, sulfides.

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INTRODUCTION

In the discussion of environmental problems related to contaminated sediments it is now accepted that the ecological effect of pollutants is determined by the specific form and reactivity of the compound rather than by its level of accumulation. Pollutant transfer to organisms predominantly takes place via dissolved species. However, with regard to the selection of disposal options for dredged materials, the study of only the water phase would not be fully satisfying. While most of the actual situation would be reflected in these data, the future potential adverse effects as well as the possible results cannot be predicted.

Two major concepts of assessing the environmental implications of pollutants for different disposal alternatives are:

1. Chemical characterization of critical phases in sediments including elutriate test methods and sequential leaching techniques; and
2. Bioassays, in which organisms are used to measure the presence or effect of one or more substances or conditions.

Elutriate tests were designed to evaluate the interrelations between solid phases and water.[1] The advantage of such experiments is that especially important parameters can be directly observed and particularly unfavourable conditions simulated.

Solubility, mobility, and bioavailability of sediment-bound metals can be influenced by five major factors:

— change of pH
— change of redox conditions
— formation of organic complexes
— microbial interactions
— increase of salinity.

The first four factors mainly concern land deposition of dredged materials.

pH EFFECTS

On a regional scale acid precipitation probably is the most important single factor affecting metal mobility in surface waters, particularly for Al, Cd, Mn and Zn. During land deposition of anoxic dredged sludges, acid solutions can result from the oxidation of sulfidic components. Kinetics of these transformations are typically affected by bacteria (approx. 10^6-fold compared to purely inorganic conditions). In an earlier study we have demonstrated that the capability of certain bacteria (*Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans*) to oxidize sulfides and ferrous iron, while decreasing the pH values from 5–4 to approximately 2, can be utilized for enhanced dissolution of metals from dredged materials.[2]

For many metal examples, a clear relationship has been found between pH values and dissolved metal concentrations. With decreasing pH, metal concentration in solution increases. Therefore, with regard to the mobility of metals, the concentration of dissolved organic matter, but above all the buffer capacity of the sediment, is of prime importance.

Figure 1 shows the titration curves for suspensions of dredged materials from Neckar river and Hamburg harbour. It is obvious that the content of calcium carbonate is the predominant factor affecting buffer capacity. The Neckar sediment contains about 15% carbonate, the Hamburg harbour sludge only 1–2%.

To quantify these properties and for better comparison of samples, we propose a simple test procedure, which is characterized by the

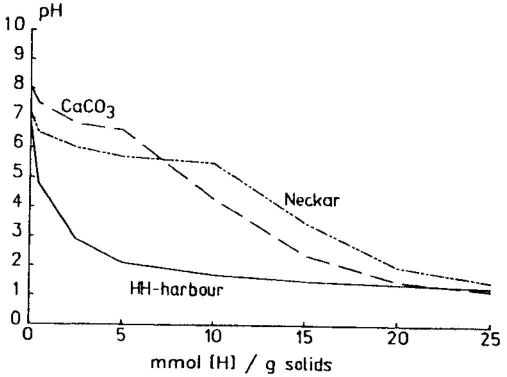

FIGURE 1 pH changes in suspensions of calcium carbonate and river sediments after addition of acid.

difference of pH values (ΔpH) of 10% sediment suspensions in distilled water (pH_0) and in 0.1 N acid (pH_x) after 1 hr shaking time.

Three categories of ΔpH values can be distinguished, ranging from ΔpH less than 2 (strongly buffered), 2–4 (intermediate) to ΔpH more than 4 (poorly buffered).

While the Neckar sediment belongs to the first category, the dredged sludge from Hamburg harbour exhibits very low buffer capacity as evidenced by the immediate lowering of pH values upon addition of acid.

For these poorly buffered sludges, additives can be used for both chemical and mechanical stabilization during land disposal.

Figure 2 shows acid titration curves for dredged sludge from Hamburg harbour without and after addition of cement/fly ash and limestone stabilizers. Best chemical results are attained with calcium carbonate, because pH conditions did not change very much over a wide range. On the other hand, it can also be expected that high pH values will have unfavourable effects on the mobility of certain metals and for the release of ammonia and organic substances.

REDOX EFFECTS

Dredging of anoxic sediments and disposal on land is also attended by changes of redox conditions. Generally the solubility of metal

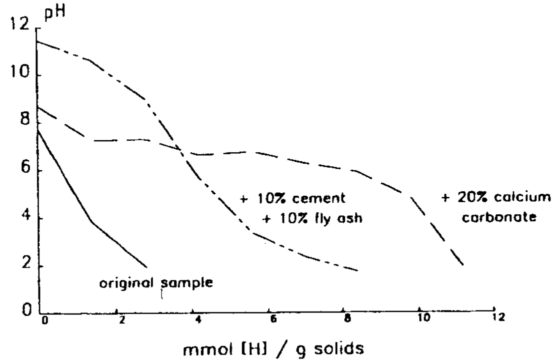

FIGURE 2 Effect of calcium carbonate and cement/fly ash additives on chemical stabilization of fine grained sediment from Hamburg harbour.

sulfides is very low. Under oxidizing conditions some controlling solid compounds may change gradually, for example metal sulfides to carbonates, oxyhydrates or oxides, thus changing the solubility of certain metals.

Such effects can be shown by chemical extraction experiments. Although these techniques are not as selective as sometimes stated, certainly limited and still problematic for determination of metals' bioavailability, they are useful for the estimation of potential remobilization effects.

Based on a procedure, originally designed by Tessier *et al.*,[3] and on our experience,[4] we propose the following sequential extraction scheme:

Exchangeable cations: 1 M ammonium acetate, pH 7, solid/solution ratio 1:20, 2 hr shaking;

Carbonates: 1 M sodium acetate, pH 5, solid/solution ratio 1:20, 5 hr shaking;

Easily reducible phases: 0.1 M hydroxylamine hydrochloride, pH 2 solid/solution ratio 1:100, 12 hr shaking;

Moderately reducible phases: 0.2 M ammonium oxalate + 0.2 M oxalic acid, pH 3, solid/solution ratio 1:100, 24 hr shaking;

Sulfidic and organic fraction: 30% H_2O_2, pH 2, 85°C, extracted with 1 M ammonium acetate in 6% HNO_3, solid solution ratio 1:100, 12 hr shaking;

Residual fraction: concentrated HNO_3, 120°C, solid/solution ratio 1:100.

Problems of sample handling prior to extraction have rarely been recognized as yet. In recent investigations[5] we determined the effects of different drying methods on anaerobic sediment samples. These studies have demonstrated that:

1. the sample preparation is distinctly affecting the distribution of the single particle phases in the extraction scheme, and
2. the stability of metal phases may both increase and decrease during oxidation, for example after land disposal of anoxic sludges.

Anoxic sediment samples were placed in polyethylene bottles, which were completely filled without any trapping of air bubbles. At the laboratory sediments were inserted into a glove box prepared with an inert argon atmosphere.

Subsamples were used to examine the effect of various sample pretreatments including oxygen contact and different drying methods. In the glove box each sediment sample was split into four series of two subsamples to be submitted to the sequential extraction procedure.

Manipulations of the first series were all done under the argon atmosphere to serve as control.

The second series was treated by an elutriate test modified for air bubbling. A subsample of the sediment was mixed with water from the sampling area and the suspension agitated for 1 hr with clean air.

The third series was freeze dried, and the fourth was dried under air in a convection oven at 60°C prior to leaching.

For the anoxic samples, the first four steps of the extraction sequence (exchangeable, carbonate, easily and moderately reducible fraction) were carried out under argon in the glove box. The respective leaching agents have been de-oxygenated prior to contact with the samples.

Figure 3 shows the effects of aeration and drying on the distribution of metal associations in comparison to the original anoxic samples. The residual fractions are omitted.

For *copper* there is a significant shift from the sulfidic/organic fraction to reducible forms. The difference can be explained by the contact of the sediment with air and formation of new compounds by condensation reactions when the sample is dried.

Inhomogeneities of the samples or experimental variations can be excluded, because the sum of metal concentrations in the individual fractions of all four series and of each sample agreed within 10%.

Especially for copper the differentiation in the organic and sulfidic fraction is particularly problematic because both labile and stabile organic subfractions are covered in combination with sulfidic phases.

In the original sample, about 50% of *zinc* phases are found in the organic/sulfidic and the other part in the reducible fraction. Aeration and drying decrease the portion in these fractions and less stable carbonatic and exchangeable phases are formed.

A still more significant shift has been found for *cadmium*. Changes from nearly completely sulfidic associations in the original, anoxic sample to reducible, carbonatic and exchangeable phases would

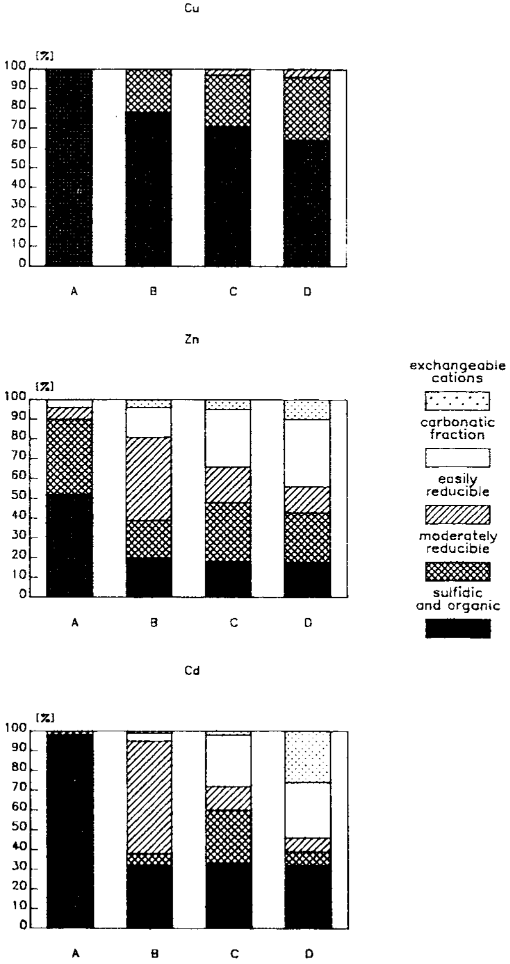

FIGURE 3 Fractionation patterns of Cu, Zn and Cd in relation to the pretreatment procedures: (A) extracted under oxygen free conditions, (B) after 1 hr elutriate test with air bubbling, (C) freeze dried, (D) oven dried (60°C).

TABLE I

Cadmium forms in solids from confined land disposal areas.[6]

	Percent of total cadmium content	
Chemical fraction	Influent	Effluent
Exchangeable	21.0	18.0
Carbonatic	21.4	56.7
Easily reducible	9.2	11.8
Remaining phases	49.3	13.5

clearly involve a weakening of bonding strength of this metal during oxidation and drying of the sludge material, for example at land disposal.

Similar changes in cadmium forms have been observed by Hoeppel *et al.*[6] at dredged material land containment areas. Comparison of four influent and effluent samples (see Table I) indicates that Cd portions increased significantly in the carbonate phases, as a direct result of transformations from sulfidic phases present in the influent slurries.

Apart from typical effects during land disposal, it has been shown from chemical extraction experiments, that biological aeration can mobilize critical metals in deeper parts of anoxic marsh sediments. Aquatic macrophytes can provide oxygen for their soil rhizosphere, thus maintaining oxic to post-oxic environments up to several tens of centimeters deep in the sediment.

Investigations on the effects of redox changes from alternating flooding/draining of inertidal sediments were performed on a freshwater tidal flat near Hamburg harbour.[7] The higher percentage of labile Cd associations in the oxic layers is accompanied by a marked depletion in the total content of the metal. We assume that about 30–50% of the original cadmium content is extracted by a process of "oxidative pumping" through tidal action, and temporarily can be expected in dissolved form.

CONCLUSIONS

The *in situ* characteristics of metal associations in anoxic sediments are received only, if the samples are stored and extracted by appropriate leaching agents under oxygen-free conditions. Neither oven drying nor freeze-drying are adequate pretreatment methods.

The rapid transformations of Zn and especially Cd from sulfidic to easily reducible, carbonatic as far as exchangeable forms after oxidation of anoxic sediments will provide weakly bound metal associations.

Cadmium release, for example, may occur as Cd-contaminated sediment is transported from a near neutral pH, reducing environment to a moderately acid, oxic environment. Under these conditions, cadmium levels of subsurface drainage water from upland disposal areas of dredged material may be increased, and cadmium availability to plants growing on the material enhanced.

An assessment of environmental hazard of particulate metals must concentrate on the mobile fractions. Further studies of these sediment substrates are warranted in order to determine the interrelationships between these metal binding sites and metal remobilization.

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