5th International Symposium on River Sedimentation
Karlsruhe 1992

Sediment Quality Criteria - Role of Redox-Sensitive Components

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ABSTRACT: Regarding the potential release of contaminants from sediments changing 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.

Introduction

New objectives regarding the improvement of water quality as well as problems with the resuspension and land deposition of dredged materials require a standardized assessment of sediment quality. Biological criteria integrate sediment characteristics and pollutant loads, while generally not indicating the cause of effects. With respect to chemical-numerical criteria immediate indications on biological effects are lacking; major advantages lie in their easy application and amendment to modeling approaches. Numerical approaches, on the one hand, are based on (1) accumulation, (2) pore water concentrations, (3) solid/liquid equilibrium partition (sediment/water and organism/water) and (4) elution properties of contaminants; the second component in an assessment scheme would include characteristics of the solid substrate, in particular, buffer capacity against pH-depression.

Both pH and redox potential in a sediment/water system are significant parameters in the mobilization and transformation of metals (Stumm & Morgan, 1981; Hong & Wang, 1984). Many investigations have shown that the pH value declines during the oxidation of sediments (e.g., Calmano, 1989). 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.

Evaluation of pH-Changes

The acidification problem of a sediment/water system arises after hydrogen ions are generated during the oxidation, e.g., during dredging or resuspension mainly of fine grained material containing less carbonate than needed for long-term neutralization (Drever, 1982; Breemen et al., 1984). The concept of acid-producing potential (APP) was initially developed in the prediction and calculation of acid mine drainage and waste tailings management (Anonymous, 1979; a summary is given by Ferguson & Erickson, 1988). Our findings on the effects of perrodical redox processes on both APP and metal mobility in estuarine sediments (Kersten et al., 1985 Kersten & Förstner, 1991) have further enhanced research interest in this field. Because of the manifold implications with dredging activities and other sectors of river quality management a number of typical effects will be described here.

Direct assessment of the pH-changes resulting from the oxidation of anoxic sediment constituents can be performed by ventilation of sediment suspensions with air or oxygen and subsequent determination of the pH-difference between the original sample and oxidized material. As greater is this difference, as higher is the short-term mobilization potential of metals, e.g. during dredging, resuspension and other processes, by which anoxic sediments get into contact with oxygenated water or - following land deposition of dredged material - with atmospheric oxygen. A typical example demonstrating the temporal development of redox and pH-values in a sludge suspension from Hamburg harbour is presented in Figure 1 (Calmano et al., 1992).

Results from titration experiments using 1 molar nitric acid on sediment suspensions of 100 g/l are presented in Figure 2. The titration curve of the Rhine River sediment exhibits a small plateau in the pH-range of 5.5 and 6, probably due to a certain fraction of carbonate, which is consumed by addition of 80 mmol of acidity. On contrary, the titration curves of both Elbe River sediments are continously decreasing as a result of the low contents of carbonate in these samples. The sediment from the inland harbor basin of Harburg, originally sulfide-rich material which has been stored for 1 year in a closed bottle, has already reached an initial-pH of 4.3; this is probably due to the consumption of the low residual buffer capacity by oxidation of parts of the sulfide fraction. Respective lowering of pH has been found from upland disposal sites of dredged sediments from Hamburg harbor (Tent 1982).

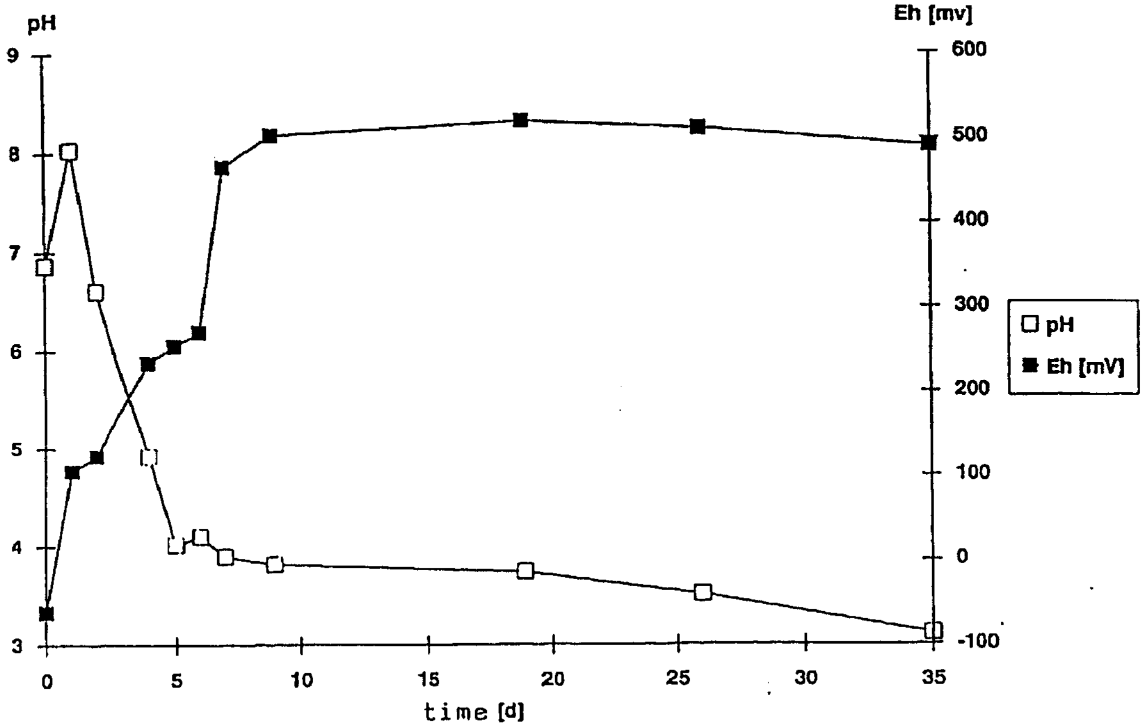

Figure 1. Influence of redox potential on the pH-value during oxidation of a sludge suspension from Hamburg harbour (Calmano et al., 1992)

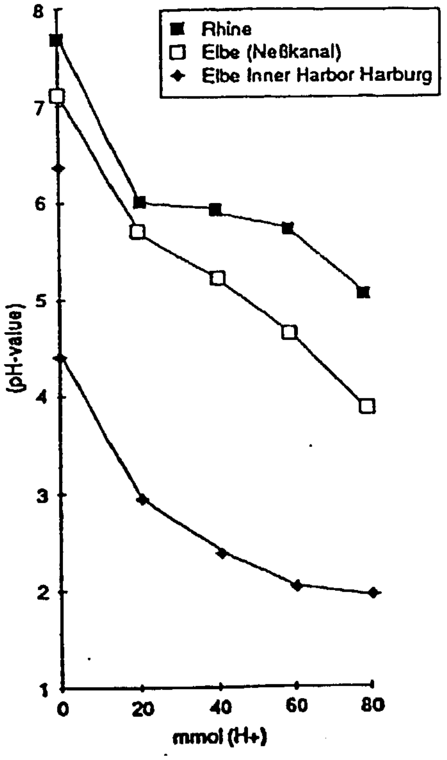

Figure 2. Variation of pH-values (titration curves) of suspensions (100 g/L) of sediment samples from the Rhine and Elbe Rivers after addition of 1 M nitric acid (Förstner et al., 1989)

Effects on Metal Mobility

In connection with the problems arising from the disposal of solid wastes, particularly of dredged materials, extraction sequences have been applied which are designed to differentiate between the exchangeable, carbonatic, reducible (hydrous Fe/Mn oxides), oxidizable (sulfides and organic phases) and residual fractions. With sequential extraction procedures rearrangements of specific solid "phases" can be evaluated prior to its actual remobilisation. One of the more widely applied extraction sequences of Tessier and co-workers (1979) has been modified by various authors (Kersten & Förstner, 1987)

Partition of metals was determined in a sample of sediment from Hamburg Harborg, which was pretreated in different ways, including: (1) The EPA Standard Elutriate Test, 1:4 sediment/site water for 30 min.; (2) Freeze-dried sample; (3) Oven-drying at 60°C. It was observed that oxidation had a great effect on regulating the chemical form of Cd and other trace metals (Fig. 3, Kersten et al. 1985). Compared to the original sample (A), which was extracted under an argon atmosphere, there was a typical change from oxidizable phases, which were mainly Cd-sulfide, to easily reducible forms upon application of the shaking/bubbling test (B). During freeze-drying - which is commonly assumed to present a relative smooth mode of sample pretreatment, transformation to carbonatic and exchangeable forms takes place (C). This effect is further enhanced during oven-drying at 60°C (D).

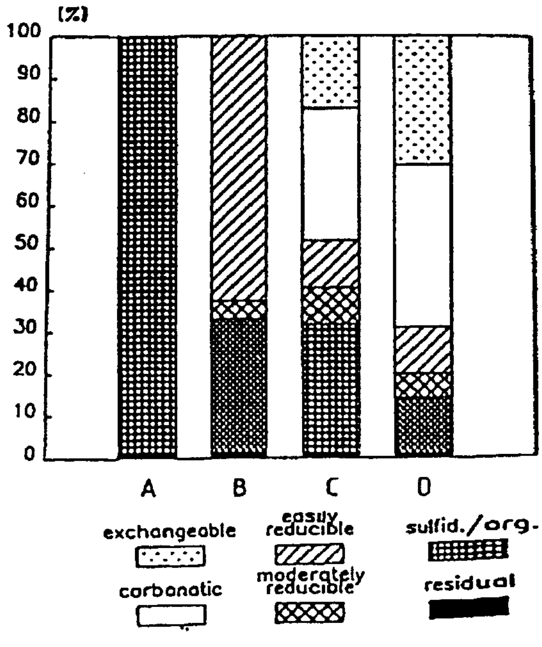

Figure 3. Partitioning of cadmium in anoxic mud from Hamburg harbour in relation to the pretreatment procedures (Kersten et al., 1985)

Applying the before-mentioned extraction scheme, a more reliable prognosis can be made regarding the acid potential of a sediment sample, which can be produced by oxidation of sulfidic components, can be made by using the data of calcium and sulfur from the sequential extraction. In anoxic, sulfide-containing sediments the two elements were 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 one mole of iron sulfide will produce 3 [H$^+$]-ions; by reaction with one mole of carbonate 2 [H$^+$]-ions are buffered. Without going into detailed discussions, it should be mentioned that there is a possibility for standardizing the data from elution experiments with respect to numerical evaluation. Here examples are given for an "elution index" based on the metal concentrations exchangeable with 1 N ammonium acetate at pH 7 (Table 1). These metal fractions are considered to be remobilizable from polluted oxic and anoxic sediments at a relative short term under more saline conditions, for example, in the estuarine mixing zone. Comparison of the release rates from oxic and anoxic sediments indicates, that the oxidation of samples gives rise to a very significant increase in the overall mobilization of the metals studied. This effect was particularly important for Cd. When proceeding further in the extraction sequence, more long-term effects can be estimated, but generally with a reduction of prognostic accuracy.

Table 1. Elution-index as determined from exchangeable fractions (1 N ammonium acetate solution at pH 7) related to back-ground values from old sediments from Rhine River: Cu = 51 mg/kg, Pb = 30 mg/kg, Zn = 115 mg/kg, Cd = 0.3 mg/kg (values multiplied by factor 100)

	Neckar	Main	Rhine	Elbe	Weser
Copper	0.2	-	1	1	-
Lead	1	1	2	1	1
Zinc	7	9	28	36	9
Cadmium	30	30	230	30	-
Total oxic	**38**	**40**	**261**	**68**	**10**
(anoxic	0.5	0.3	8	>4	4)

The relative low carbonate content of the Elbe River sediments, which is consumed during several months or years, has several practical implications: 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). Metals are easily transferred to crops, and permissible limits of cadmium have been surpassed in as much as 50% of wheat crops grown on these materials (Herms & Tent, 1982). The situation in the Elbe River estuary is particularly critical since low buffer capacities of the sediments coincide with a relative long residence time of suspended particles (Tent, 1987).

Metal release from tidal Elbe River sediments by a process of "oxidative remobilization" has been described by Kersten (1989). Short (30 cm) sediment cores were taken from a site, where diurnal inundation of the fine-grained fluvial deposits takes place; subsamples were analyzed with sequential extraction according to the methods described above. In the upper part of the sediment column, total particulate cadmium content was approximately 10 mg kg^{-1}, whereas in the deeper anoxic zone the total particulate concentration of Cd was 20 mg kg^{-1}. The results of the sequential extractions of the core sediment samples separated at 2-cm levels (Figure 4) indicate, that in the anoxic zone 60-80% of the Cd was associated with the sulfidic/organic fraction. In the upper - oxic and transition - zone the association of Cd in the carbonatic and exchangeable fractions simultaneously increase up to 40% of total

Cd. Thus, high proportions of mobile cadmium forms correlate with the reduction in total cadmium contents. This distribution of total and partitioned Cd in the "Heukenlock" sediment profile suggest that the release of metals from particulate phases into the pore water and further transfer into biota is controlled by the frequent downward flux of oxygenated surface water. In the oxic zone, Cd is leached from the labile particulate-binding sites, where the predominant mechanism controlling the availability of Cd is adsorption/desorption. With the downward flux of pore water, the mobilized metal moves into the anoxic environment, where Cd is reprecipitated by the formation of sulfidic associations. From the observed concentrations, it would be expected that long-term transfer of up to 50% of the Cd from the sediment subsurface would take place in the anoxic zone located further below the sediment-water inerface. By this process of "oxidative pumping" (Kersten & Förstner 1987) a maximum downward flux of 0.4 g Cd/m^2 per year can be estimated in the Heukenlock sediments.

Outlook

Recent investigations by Calmano et al. (1992) 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.

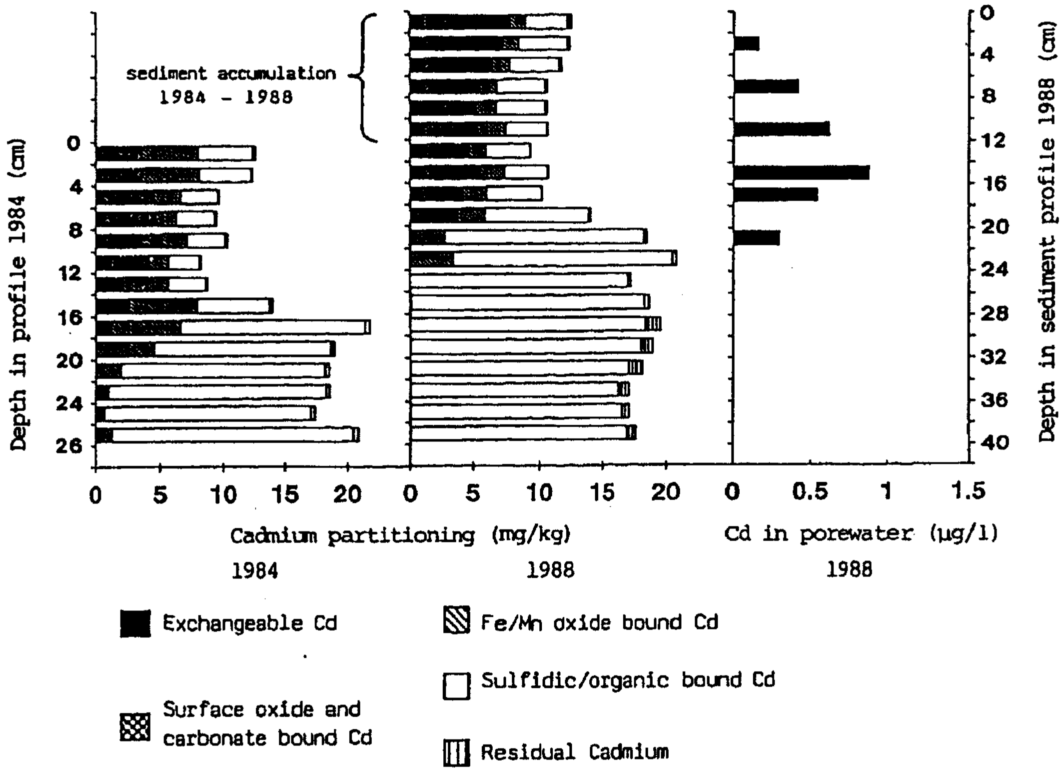

Figure 4. Total concentrations and partitioning of cadmium in a tidal flat sediment profile in the Heuckenlock area sampled in 1984 and 1988. Sedimentation rates were determined by the ^{137}Cs-method. Cd pore water profile was determined at low tide (Kersten, 1989)

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