Effects of Redox Variations on Metal Speciation—Implications on Sediment Quality Criteria Assessment

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Summary

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. Numerical criteria approaches, which are based on pore water concentrations, and the accumulation, solid/liquid partition, and elution properties of contaminants, usually do not imply variations of chemical interactions with solid matrices. Regarding the potential release of metals from sediments, changes in pH and redox conditions are of prime importance. To incorporate new experience with non-linear and time-delayed processes, special emphasis should be put on the characteristics of the mineral and organic solid matrices, *e.g.* to capacity controlling properties, and in particular, the buffer capacity against pH-depression.

1 Introduction

Sediment quality criteria were developed in the mid-eighties for the following reasons.

(i) In contrast to the strong temporal variability in the water phase, sediments integrate contaminant concentrations over time. One can, therefore, reduce the *number of samples* in monitoring, surveillance, and survey activities.

(ii) Long-term perspectives in water management need *'integrated strategies'*, in which sediment-associated pollutants have to be considered as well; generally, the contaminant level in the sediment may have greater impact on the survival of benthic organisms than do aqueous concentrations.

(iii) Management plans have increasingly been based on the *assimilative capacity* of a certain receiving system, and this requires knowledge of the properties of sedimentary components as the major sink.

(iv) Finally, there is the wide spectrum of problems with dredged sediments: permission for *dredging activities* and *deposition of dredged material* have to be based on standardized sampling protocols and test procedures. In this context, the conventions for the marine environment—Oslo and London—should be mentioned.

Predictions of the short-, middle-, and long-term effects of metal contaminated particulates, in the framework of sediment quality objectives and criteria development, have to consider the environmental 'speciation' of critical metals, which in this context means 'describing the distribution and transformation of metal species and various media'.[1] Long-term prognosis, in particular, of the behaviour of metals at critical sites requires both the knowledge of interactions of element species in solid matter and solution, and an estimation of the future borderline (particularly 'worst case') conditions in a dynamically evolving medium.[2] In sediments, typical driving forces for intensified matrix–element interactions are strong chemical gradients of redox conditions, pH-values, and organic ligand concentrations, all three factors being mainly induced by the degradation of organic matter.

2 Redox Variations: Implications for Sediment Quality Criteria

Numerical approaches for the assessment of the environmental impact of sediment-associated pollutants are based on: (i) accumulation; (ii) pore water concentrations; (iii) solid–liquid equilibrium partition (both sediment–water and organism–water); and (iv) elution properties of contaminants.[3]

Background Data Comparisons: This procedure compares data from the test area with that of natural or insignificant pollutant concentrations. Particularly useful are samples from deeper layers of the sediment sequence at a given site, for example, from drill holes, since this material is derived from the same catchment area and usually is similar in its substrate composition. Nonetheless, standardization with respect to grain size distribution is indispensable.

Porewater Analysis: This is based on the experience, that the composition of interstitial waters is the most sensitive indicator of the reactions that take place between pollutants on particles and the aqueous phase which contacts them. There is the advantage of a direct recovery and analysis of water-borne constituents. However, there are several disadvantages, mainly arising from the sampling and sample preparation, which need considerable precautions, such as for exclusion of oxygen, which could alter redox states during storage.

Equilibrium Partition Studies: These approaches are related to the broad toxicological basis of food and water quality data and as such, offer a very important advantage. On the other hand, there are the effects of sample preparation, *e.g.* the drying procedures; the separation techniques, *e.g.* filtration or centrifugation; there are strong effects of grain size composition and the influence of suspended matter concentration in the aquatic system, which is even more important, if the kinetics of sorption and desorption are too slow for equilibria to be achieved in a given time of interaction. Unlike non-ionic organic chemicals, the K_D-values of *metals* are not only correlated to organic substances but also with other sorption-active surfaces. Hence, the equilibrium partition approach exhibits strong limitations for metallic elements.

Remobilization: Short-term effects may be studied from water–sediment suspensions, medium-term effects from experiments using tanks, and long-term effects by applying chemical extractants, either singly or in sequence. Field observations often do not show clear effects, as has been demonstrated for the release of metals from anoxic sediments during oxidation. Such implications for future criteria development, particularly important for dredging and the management of dredged material, will be discussed on the basis of experience from metal speciation studies on soils and sediments.[4]

Effects of Redox and pH Variations on the Mobility of Metals

Acidity is perhaps the most important long-term factor in the mobilization of metals from metal-bearing wastes and, in some instances, sediments. The threat is especially great in waters with little buffer capacity, *i.e.* in carbonate-deficient areas where dissolved-metal pollution can be spread over great distances. The acidity production can develop many years after disposal, *e.g.* when the neutralizing or buffering capacity in a pyrite-containing waste is exceeded.

The major process affecting the lowering of pH-values (down from pH 2 to 3) is the exposure of pyrite (FeS_2) and other sulfide minerals to atmospheric oxygen and moisture, whereby the sulfidic component is oxidized to sulfate and acidity (H^+-ions) is generated. Bacterial action can assist the oxidation of Fe^{2+}(aq) and precipitation as $Fe(OH)_3$ in the presence of dissolved oxygen.

The acidification problem in a sediment–water system arises after hydrogen ions are generated during oxidation, *e.g.* during dredging or resuspension of mainly fine grained material containing less carbonate than needed for long-term neutralization.[5,6] Primary emissions of high metal concentration occur from waste rocks and tailings and secondary effects on ground-water take place from ponds. An important and long-term source of metals are the sediments reworked from the floodplain, mainly by repeated oxidation and reduction processes.[7]

If anoxic sediments are exposed to the atmosphere, redox conditions will change and a new distribution and transformation of heavy metal species bound to the sediments takes place. Periodic changes, for example, are typical for the sediments of older fluvial or marine terraces in monsoon regions, which have a seasonally changing water level caused by submergence with rain water. Under these conditions, hydrology favours either lateral or vertical drainage and leads to a variation in redox potential.[8]

Tidal currents lead to daily periodic redox changes in coastal and estuarine sediments. In some coastal plains the sediments and soils are seasonally flooded.

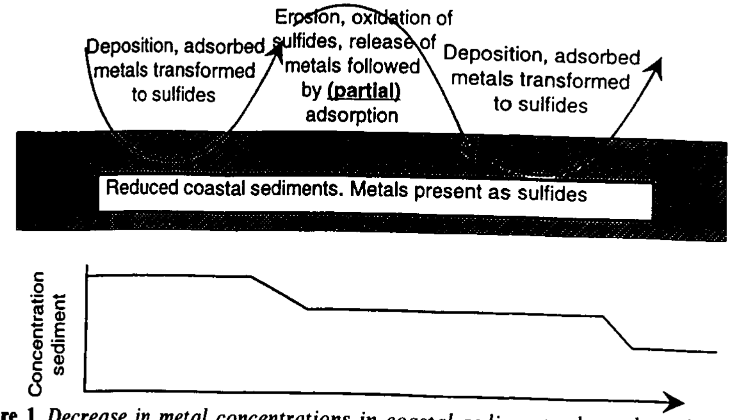

Figure 1 *Decrease in metal concentrations in coastal sediments through cyclic processes of erosion and deposition (Dr. W. Salomons, Haren/Netherlands, unpublished results)*

By these processes, the chemical properties of sediment compounds are changed. For example, iron(II) sulfide (or pyrite) is formed by reduction of sulfate from sea water, while dissolved hydrogen carbonate is partly removed by diffusion or convection. Over several years or decades appreciable amounts of sulfide can be accumulated in tidal sediments.[9]

For coastal marine environments, such as the Wadden Sea coast, the possible implications of cyclic processes on metal concentrations in sediments have been modeled schematically by Salomons.[10] Figure 1 suggests, that after deposition and during storage in reduced coastal sediments, adsorbed metals are transferred to sulfidic bonding forms. During erosion processes, oxidation can take place involving remobilization of a certain proportion of the sediment-associated metals, which may subsequently be readsorbed in part by particulate matter. Under marine conditions, the extent of adsorption will mainly depend on the stability of complexes formed by chloride and competition for adsorption sites by cations like Mg^{2+}, Ca^{2+}, and Na^{+}. Such oxidative events are relatively short compared to the longer periods of reduced conditions during deposition. However, it can be expected that through repeated, though irregular (in contrast to the tidal interactions mentioned before) cyclic processes of erosion and deposition, a significant release of metals from coastal sediments will take place.

During the last two decades, transformation of heavy metal binding forms under changing redox conditions has received much attention. Examples have been given for seasonally changing cadmium mobilities in Corpus Christi Bay Harbour,[11] for releases of Hg, Pb, and Zn from estuarine sediments of Mobile Bay,[12] for the transformation of Cd compounds in Mississippi River sediments under controlled redox and pH conditions,[13] for the removal of sulfide from pore waters and subsequent Cd mobilization via ventilation of the upper sediment layers,[14,15] and for the release of Pb and Cd from contaminated dredged material after dumping in a harbor environment.[16] Typical early diagenetic geochemical changes and subsequent element mobilization via the porewater, as a result of effects of oxidation during dredging activities, were studied by Darby *et al.*[17] in a man-made estuarine marsh.

From enclosure experiments in Narragansett Bay it has been estimated by Hunt and Smith[18] that, by mechanisms such as oxidation of organic and sulfidic material, the anthropogenic proportion of cadmium in marine sediments is released to the water within approximately three years; where as for remobilization of copper and lead, approximately 40 and 400 years, respectively, is needed, according to extrapolations.

Chemical extraction experiments, for estimating characteristic particulate binding forms of metals in anoxic marine and freshwater sediments, were carried out by Kersten and Förstner,[19] both in the presence and absence of atmospheric oxygen during the experiments. By drying the sediments under oxygen, the proportion of sulfidic bound metals was significantly decreased.

In Table 1, an example is given for the possibilities of standardizing the data from elution experiments with respect to numerical evaluation. An 'elution index' for sediment samples from various rivers in West Germany is based on the metal concentrations exchangeable with 1 M ammonium acetate at pH 7. Higher values imply greater mobility. These metal fractions are considered to be remobilizable from polluted sediments, in the relative short term, under more saline conditions, for example, in the estuarine mixing zone. Comparison of the release rates from oxic and anoxic sediments clearly indicates that the oxidation of samples gives rise to a very significant increase in the mobilization of the metals studied.

Limitations of Available Test Procedures

It is clear that when considering the mobilization of heavy metals from sediments, there are two dominant variables: redox potential and pH, with the latter directly influenced by the former. For the practice of criteria development and application, available test procedures should be checked regarding their relevance for predicting the middle- and long-term behaviour of metal-bearing sediment matrices under changing redox and pH conditions.

Table 1 *Elution Index for Selected River Sediments, as Determined from Exchangeable Properties (Extracted with 1 M Ammonium Acetate)*

	Neckar	*Main*	*Elbe*	*Weser*
Copper	<1	—	1	—
Lead	1	1	1	1
Zinc	7	10	40	10
Cadmium	22	22	25	—
Toxic oxic	*30*	*33*	*67*	*11*
(Anoxic	0.5	0.3	>4	4)

Thermodynamic Models. With respect to the possible implications of sediment-bound metal species, *e.g.* in the framework of sediment quality assessment studies, it seems that thermodynamic models are still of limited use for 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 and ageing processes; (ii) influences of organic ligands in the aqueous phase can rarely be predicted as yet; (iii) the effects of competition between various sorption sites should be considered; and (iv) the reaction kinetics of the individual constituents cannot be evaluated in a mixture of sedimentary components.

Pore Water Chemistry. As mentioned previously, the composition of pore water is a highly sensitive indicator for reactions between chemicals on solid substrates and the aqueous phase which contacts them. For fine-grained material, in particular, the large surface area compared with the small volume of its entrapped interstitial water, ensures that minor reactions with the solid phase will be indicated by major changes on the composition of the aqueous phase. While the direct recovery and analysis of water-borne constituents can be seen as a major advantage of this approach, there are several disadvantages, particularly arising from sampling and sample preparation, which are not yet routine procedures, and usually involve considerable precautionary measures, such as exclusion of oxygen.

Elutriate Tests. To estimate short-term chemical transformations, the inter-relations between solid phases and water have been increasingly subjected to laboratory studies. The advantage of such experiments is that especially important parameters can be directly observed and particularly unfavourable conditions simulated. The US Army Corps of Engineers and the US Environmental Protection Agency have developed an elutriate test that is designed to detect any significant release of chemical contaminants in dredged material. This test involves the mixing of one volume of the dredged sediment with four volumes of the disposal site water for a 30 min shaking period. If the soluble chemical constituent in water exceeds 1.5 times the ambient concentration in the disposal site water, special conditions will be imposed and will govern the disposal of the dredged material.

Sequential Extraction. In connection with the problems arising from the disposal of solid wastes, particulary of dredged materials, chemical 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. The undisputed advantage of this approach with respect to the estimation of long-term effects on metal mobilities lies in the fact that rearrangements of specific solid 'phases' can be evaluated prior to the actual remobilization of certain proportions of an element into the dissolved phase.

3 Prognostic Tools for Long-term Behaviour of Metals in Sediments

Redox and pH variations and their effects on metals in natural systems are typical non-linear and delayed—'chemical time bomb'—processes, *e.g.* toxic metals can 'break through' once the specific buffer capacity of a sediment system has been surpassed. Within a scientific perspective of the chemical time bomb concept, the aspect of the storage capacity controlling properties (CCP's) of solid substrates is playing a key role.[20] There are two mechanisms for potential time bomb evaluation. The first is direct saturation, by which the capacity of a sediment for toxic chemicals becomes exhausted; the second way to 'trigger' a time bomb is through a fundamental change in a chemical property of the substrate, that reduces its capacity to adsorb (or keep adsorbed) toxic materials. In the aquatic environment, such effects are mainly induced by redox variations and it is, in particular, the carbonate buffer capacity of the sediments, which controls the pH values and the most significant interactions between solid and dissolved metal phases, as well as transfer processes of trace metals between inorganic and organic solid substrates.

A typical example, dredged material from Hamburg Harbour, indicates typical differences in the kinetics of proton release from organic and sulfidic sources.[21] Recent deposits are characterized by low concentrations of nitrate, cadmium, and zinc; when these low-buffered sediments are oxidized during a time period of a fews months to years, the concentrations of ammonia and iron in the pore water typically decrease, whereas those of cadmium and zinc increase (with the result that these metals are easily transferred into agricultural crops!). The different steps are schematically given in Figure 2. Oxidation of sulfides during stage B strongly increases the concentrations of cadmium and zinc in a relative short time. When acidity is consumed by buffer reactions (phase C), cadmium and zinc concentrations drop, but are still higher than in the original sulfidic system. In phase D, oxidation of organic matter again lowers pH values and can induce a long-term mobilization of Zn and Cd. The latter development, in particular, can rarely be predicted with available procedures.

Criteria for the prognosis of the middle- and long-term behaviour of metals should include the abilities of sediment matrices for producing acidity and for neutralizing such acid constituents.

Acid Producing and Consuming Capacity of Sediments

The concept of the acid-producing capacity (APC) was initially developed as part of the prediction and calculation of acid mine drainage and waste tailings management.[22] Periodic redox processes can cause an increase or decrease in APC or pH in a sediment-water system.[23] In a *closed* system, periodic redox processes can lead to a change or transfer between APC(s) and APC(aq), but the total APC of the system does not change. The processes are reversible. The hydrogen ions produced in the oxidation cycle will be consumed by the following reduction cycle. However, in an *open* system, the total APC of the system will

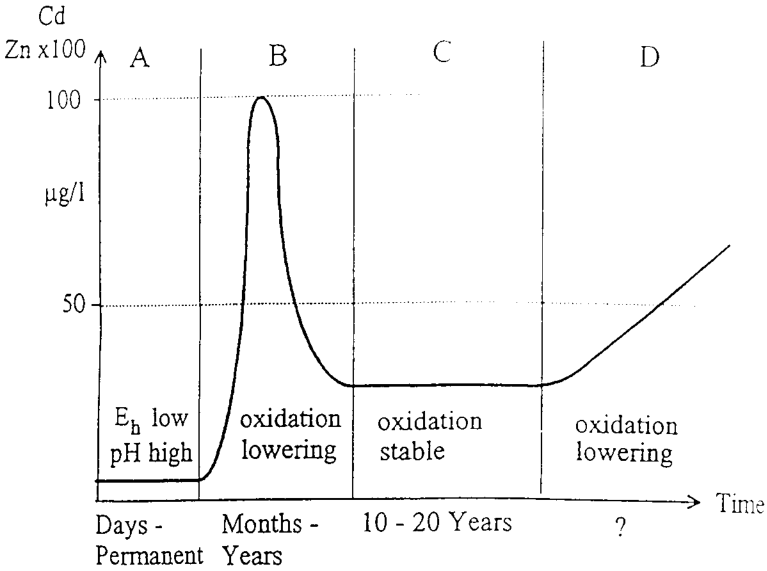

Figure 2 *Schematic diagram illustrating different phases of metal release from land-disposed (low-carbonate) dredged material (Maaß and Miehlich,[21] modified)*

change depending on the properties of the system and the reaction processes. Under certain conditions, the total APC in the system increases, where as under other conditions, the total APC in the system decreases. Some processes are irreversible. The components producing or consuming H^+ leave the system and cause the changes in APC(s), APC(aq), and the permanent acid consuming capacity (ACC). Important acid-producing oxidation reactions, leading to a decrease of pH in low buffered sediments, are listed in Table 2.

Table 2 *Important Acid-Producing Oxidation Reactions in Aquatic Systems*

Elements		*Reactions*	*Acid formation coefficient, f*
inorganic	S	$H_2S + 2O_2 = SO_4^{2-} + 2H^+$	2
	S	$S^0 + 3/2O_2 + H_2O = SO_4^{2-} + 2H^+$	2
	S, Fe	$FeS + 9/4O_2 + 3/2H_2O = FeOOH + SO_4^{2-} + 2H^+$	2
	S, Fe	$FeS_2 + 15/4O_2 + 5/2H_2O = FeOOH + 2SO_4^{2-} + 4H^+$	4
	Fe	$Fe^{2+} + 1/4O_2 + 5/2H_2O = Fe(OH)_3 + 2H^+$	2
	N	$NH_4^+ + 2O_2 = NO_3^- + H_2O + 2H^+$	2
	N	$NO_x + 1/4(5 - 2x)O_2 + 1/2H_2O = NO_3^- + H^+$	1
organic	N	$R{-}NH_2 + 2O_2 = R{-}OH + NO_3^- + H^+$	1
	S	$R{-}SH + H_2O + 2O_2 = R{-}OH + SO_4^{2-} + 2H^+$	2

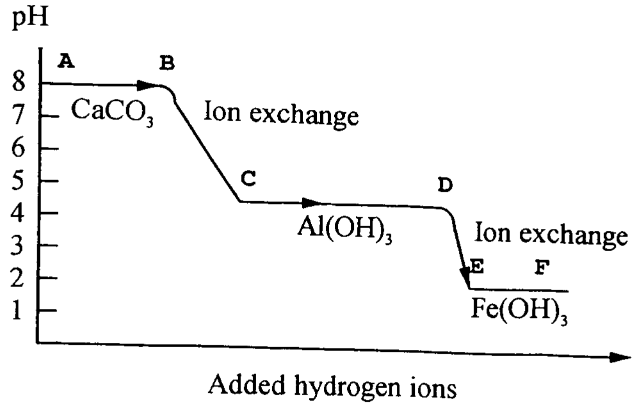

Figure 3 *Acid buffering processes in soils.*[25] *This curve summarizes important aspects of acidification in a soil–water system*

The acid-producing capacity is not only related to the oxidation of sulfides, but oxidation of organic matter must be considered as well. For example, the contribution of protons from organic nitrogen and organic sulfur in a sample containing approximately 5% organic carbon is equivalent to the acid-producing capacity of 1% FeS_2.[24] In total, APC can be defined as the largest amount of hydrogen ions (H^+) produced by the oxidation of the components per unit weight of sediment, each unit volume of water, or in the whole sediment–water system.

Acid consuming processes in terrestrial and aquatic ecosystems include:[23] (i) mineralization of cations; (ii) assimilation of anions; (iii) protonation of anions; (iv) reductions; (v) weathering of metal oxide components; (vi) reverse weathering of anions; and, in particular, (vii) dissolution of carbonate minerals. A schematic curve of different buffering levels in soil–water systems (Figure 3 after Prenzel[25]) combines two factors: the horizontal axis, which usually refers to the 'capacity' factor, indicating the amount of strong acid added, while the vertical axis indicates the 'intensity' factor, *i.e.* the pH or the degree of base saturation of the exchange complex. As long as $CaCO_3$ is present, added protons will be consumed by dissolution reactions, and the pH of the system will remain constant (A → B in Figure 3). Between B and C the exchangeable sites of clay minerals are displaced by hydrogen ions. Ultimately, this process leads to the dissolution of Al, *e.g.* clay minerals (C → D); due to the abundance of Al in clay minerals, the buffering capacity in this process is high. When the accessible reservoir of Al is exhausted, the dissolution of ferric oxide will consume hydrogen ions and resist the pH decrease (E → F). With regard to long-term effects, major processes consuming hydrogen ions in ecosystems include the release of basic cations by decomposition of organic matter, specific anion adsorption, mineral weathering, and unbalanced reductions of oxidized compounds.[26] The process of specific anion adsorption in sediments mainly refers to interactions of sulfate and phosphate with aluminium and iron sesquioxides.[27]

Estimating Acid Producing and Consuming Capacities

Experimental approaches for calculating APC and ACC for sulfidic mining residues have been summarized by Ferguson and Erickson.[28] A test described by Sobek *et al.*[29] involves the analysis of total pyritic sulfur; potential acidity is then subtracted from the neutralizing potential, which can be obtained by adding a known amount of HCl, heating the sample, and titrating with standardized NaOH to pH 7. Bruynesteyn and Hackl[30] calculated APC from total sulfur analysis; here the acid-producing capacity was subtracted from the acid-consuming capacity, obtained by titration with standardized sulfuric acid to pH 3.5. The APC-relationships of sediments are more complex than those in sulfidic ores because the APC of organic matter must be considered; also, the time scale plays a major role in sediments (Figure 2).

The acid neutralization capacity of a natural aquatic system is composed of the acid consuming capacity of the solids ACC_s and that of the dissolved phase ACC_{aq}:

$$ACC = ACC_s + ACC_{aq}$$

The ACC_{aq} of the dissolved phase (in aquatic systems this is always much smaller than ACC_s) may be described by the following equation:

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

A similar rule applies to the ACC_s of the solids at $pH > 5$:

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

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

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

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

For example, for an anoxic Elbe River sediment with an original pH_o of 7.03 and a pH_e of 3.29, an APC_{eff} of 5.12 mmol kg^{-1} was calculated after an oxidation time of 35 days. Such simple test procedures allow better statements of the sediment quality than simple considerations of limiting values.

4 Implications for Metal-related Sediment Criteria

While the actual focus in sediment criteria is on individual pollutant concentrations and their biological effects, inclusion of data on potential matrix variations by redox and pH changes has not been considered, as yet, to any significant extent. The only exception is the initiative of the United States Environmental Protection Agency to introduce the acid volatile sulfide (AVS) procedure as a measure for the non-availability of critical metals at a surplus of reactive sulfide ions.[31] Such effects have been investigated experimentally with a multi-chamber device, where the individual components are separated by membranes.[32] Metal transfer processes observed in the experimental device, usually cannot be measured under field conditions, due to the complexity of natural systems and short residence time of released metals in the water phase. Extrapolation of such findings, therefore, into quantitative models seems to be nearly impossible, and this may also restrict their incorporation into criteria. Three approaches are given below for providing a basis for the decision-making processes.

Mobilization of Metals Following Resuspension of Anoxic Sediments

As has been shown in previous sections, metals can be released into the dissolved phase, but may subsequently be readsorbed or precipitated, in part, to solid phases. Resuspension of sediments from the Elbe River, which were characterized by a high acid producing potential and low neutralizing capacity, was studied from a regional and long-run perspective. Experiments were undertaken at constantly neutral pH values, and both total release and scavenging rates were extrapolated from time series of measured net release values over 630 h.[33]

The example in Figure 4 shows that the initial lead release was high, but then decreased continuously due to readsorption. After about 100 h the relative equilibrium between release and readsorption was reached. Curves for copper indicate continuous release until about 350 h, when the scavenging rate became faster than the release rate. With respect to cadmium and zinc, release was

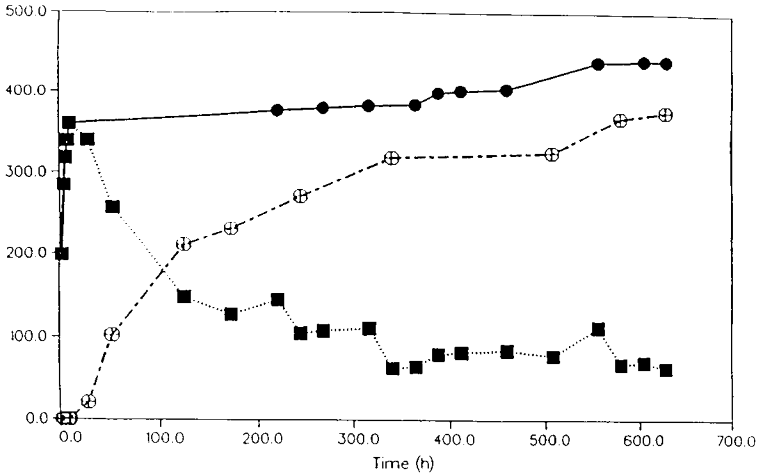

Figure 4 *Laboratory simulation experiments on wet sediments in a reaction cell indicate typical time evolution of interactive release and scavenging processes: lead release from Elbe sediments.*[33] *Full quadrangles: net release; full circles: total release; open circles: scavenging (adsorption/coprecipitation). y-axis denotes Pb concentration released from sediment* (μg kg^{-1})

found to be higher than the scavenging rate during the whole experiment.

Based on these experimental results and relevant literature data, a four stage interaction model has been developed for metals in anoxic sediments subsequent to oxidation:

- *Release Stage*: Includes amorphous sulfide oxidation, some pyrite oxidation, and some organic detritus decomposition. At the beginning, amorphous sulfide oxidation is a dominant chemical process; the metals, which are bound to acid volatile sulfides will be released at the early stage. The second contribution is characterized by mineralization of ammonium and pyrite oxidation. (At the end of the experiment, about 50% of the pyrite content was oxidized.)
- *Transition Stage of Release and Scavenging*: Acid-volatile sulfide compounds have been exhausted; pyrite oxidation and organic detritus decomposition continued. On the other hand, readsorption becomes stronger. Phosphate, derived from the decomposed organic detritus, accumulates and then precipitates with some metals.
- *Scavenging Stage*: At this stage all processes including pyrite oxidation, organic detritus decomposition, and release from solid organic and inorganic compounds decline. Iron and manganese oxide formation continues and scavenging of trace metals becomes a dominant process.
- *Equilibrium Stage*: Release and scavenging processes have basically reached a new equilibrium, *i.e.* the release rate is equated to the scavenging rate. The metal concentration in solution will remain constant. The formation of new solid metal species and their redistribution still proceed during this period of 'early diagenesis'.

The order of total release from the sediment has been found to be Cd (5%) > Zn (1.5%) > Cu (1%) > Pb (0.3%). The percentage scavenging of released metals was in the order of Pb (85%) > Cu (53%) > Zn (35%) > Cd (30%). The order of net release percentage of total metals from the sediment is Cd > Zn > Cu > Pb. For the released amount, however, the order is Zn > Cu > Pb > Cd. At the end of the experiment this order and the magnitude of released metals, were similar to that observed in the natural waters of the river Elbe at Hamburg.

Geochemical Characterization of the Potential Metal Mobility

The most efficient fixation process within anoxic sediments for trace metals is production of free sulfide during anaerobic degradation of organic matter and reduction of sulfate (study of heavy metal associations with sulfide and carbonate formations in anoxic sediments, therefore, provides insight into early diagenetic processes[34,35]).

Whereas the ability of the sediment to produce free sulfide is determined by the sulfate reduction rates, the ability to remove all the free HS^- produced is given by the reactive metal concentrations (predominantly reducible Fe^{3+}), available to form sulfide minerals ('Available Sulfide Capacity' [ASC][36]). Simultaneous application of standard sequential leaching techniques[3

(BCR-Version: Ure *et al.*[38]) on critical trace elements and matrix components, can be used for geochemical characterization of anoxic, sulfide-bearing sediments in relation to the potential mobility of critical trace metals[39]:

Step 1	Exchangeable ions Carbonates	Ca^{2+} and Fe^{2+} from carbonates and phosphates	Shake 0.5 g sediment for 5 h with 20 ml of acetic acid (0.11 mol l^{-1})
Step 2	Reducible metals	Fe^{3+} from reactive oxides	then, shake for 16 h with 20 ml $NH_2OH \cdot HCl$ (0.1 mol l^{-1}), HNO_3 pH 2
Step 3	Sulfidic and organic bound metals	S from easily oxidizable sulfides (FeS)	then, add 10 ml hydrogen peroxide 8.8 mol l^{-1} (twice)—followed by extraction with 50 ml $NH_4Ac/HOAc$ pH 5

For determination of the acid producing capacity ('maximum APC') in anoxic sediments, both the FeS pool ('actual APC') and the maximum iron(II) sulfide-producing capacity (worst case: pyrite) upon disposal has to be taken into consideration. The latter is given by the 'sulfide binding capacity' (ASC, see above), which as determined in our example of Hamburg harbour mud (Table 3) using the Fe-concentrations in Step 2 of the sequential leaching results. The stoichiometry of the oxidizable S- and Fe-fractions of Step 3 indicate that the iron(II) sulfide extracted in this step was in the FeS form. The sum of both the ASC and the 'actual APC' gives the 'maximum "APC"' for the samples as shown in Table 3. The acid consuming capacity values for these samples was more simply determined from the Ca-concentration released from reactive carbonates by the Na-acetate solution of Step 1, which has to be multiplied by a factor of 0.5 to account for the stoichiometric ratio between pyrite and calcite within the redox reaction:

$$FeS_2 + 2CaCO_3 + 15/4O_2 + 1/2\ H_2O = FeOOH + 2SO_4{}^{2-} + 2Ca^{2+} + 2CO_2$$

The negative balance between the ACC and APC indicates that the mud sample from Hamburg harbour has a significant acidification potential.

Table 3 *Balance Between Acid Producing Capacity (APC) and Acid Consuming Capacity (ACC) Values for an Anoxic Sediment Sample from Hamburg Harbour*

Compound	*Function*	*Value*	*Parameter*	(mmol kg^{-1})
Ca in Step 1*	base potential	(×0.5 =)	ACC	90
Fe in Step 2*	ASC†	(335)		
S in Step 3*	sulfide sulfur	(+ 85 =)	max. APC	420
Balance			ACC − APC =	−330

* Steps in sequential extraction procedure.[38]
† Available Sulfide Capacity.

Assessing Long-term Mobility of Metals in Sediments

With regard to prediction of long-term effects of sediment-bound metals, chemical extraction procedures are of limited value because they usually involve neither reaction-mechanistic nor kinetic considerations. Those limitations can be avoided, by an experimental approach originally used by Patrick *et al.*[40] and Herms and Brümmer,[41] where sediments can be treated in a circulation system under controlled changes of significant release parameters such as pH, redox-potential, and temperature. Our experimental design[42] includes an ion exchange system for extracting and analysing the released metals at an adequate frequency, and compares sequential extraction results before and after treatment of the sample in the circulation apparatus. Individual metal species are released at different time intervals. By taking into account the level of elements released during the ten week experiments (equivalent to several thousand years of solid–water interaction) and those obtained by extrapolation from extraction 'pools', concentrations can be calculated for different scenarios.

These extrapolations have been made from pH 5 conditions, but titration curves for investigations on a wide spectrum of metal-bearing waste materials[43] suggest that pH 4 may be more appropriate for long-term predictions of potential metal release from contaminated sediments. In this pragmatic approach, which is outlined in Figure 5, the pH is automatically adjusted to 4 over a time period of

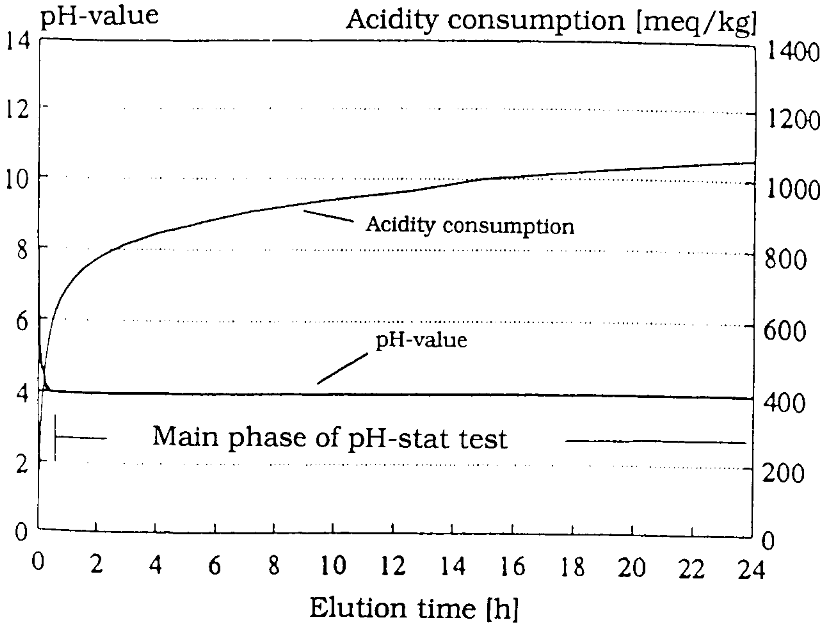

Figure 5 *Patterns of a suspension titration.*[43] *The initial phase, during which the target pH value is not attained, is followed by a 50-fold longer main phase with highly stable pH conditions*

24 hours; in addition to the release rates of metals, which can be determined from samples taken at different time intervals, the sum curve of acid consumption provides information on (a) the potential changes of the matrix composition during acidification and (b) the availability of buffer capacity at different time scales. In this respect a diagram of discrete acid additions would be valuable!

The acid consumption curve in Figure 5 reflects slow long-term metal release from sediments. Because calcite dissolution was fast, the acid consumption in the first stage increased drastically within a short period of time. Cation release and alumosilicate dissolution were dominant factors consuming acid in the later stage. The reactions can be treated as:

$$SO{\equiv}\mathrm{Me} + 2\mathrm{H}^+ = SO{\equiv}\mathrm{H}_2 + \mathrm{Me}^{2+}, \text{ and}$$

$$\mathrm{Al_2O_3} + 6\,\mathrm{H}^+ = 2\,\mathrm{Al}^{3+} + 3\,\mathrm{H_2O}$$

where $SO{\equiv}$ and Me are the reaction groups on the solid phase, and the metal ion, respectively. The reactions of the hydrogen ions with metals and alumosilicate are delayed due to the complex sediment structure and the composition, *e.g.* clay minerals coated with organic matter or biofilms. Rates of reactions can be estimated by determination of the metal concentrations in solution.

5 Final Discussion and Outlook

Regarding the potential release of metals from contaminated sediments, changes of redox and pH conditions are of prime importance. In practice, therefore, characterization of sediment substrates with respect to their buffer capacity is an indispensable step for the prognosis of middle- and long-term processes of metal mobilization.

Description of Basic Processes

Experimental studies in the multi-chamber device and reactor cell provided information on metal transfer between different sedimentary matrices and on inter-relations between mobilization and readsorption mechanisms (Section 4). Further studies should focus on the role of iron sulfides in large-scale changes in metal species, *i.e.* solid–solution interactions and the bioavailability of trace metals in aquatic systems. The combination of matrix and trace element data in sediments, extracted simultaneously with different reagents, can provide additional information, which can be used to establish models on chemical interactions occurring under characteristic borderline conditions, *e.g.* with respect to sulfide, chloride, and organic complexing agents.[44]

Reliability of long-term prognoses on the impact of metal-bearing sediments is restricted due to the dominance of non-linear and delayed processes in redox-controlled systems. While measurements of actual acid producing and consuming capacities can be undertaken with available methods (Section 3), a possible 'split' or translocation of their inventories between solid and dissolved phases renders such parameters difficult to predict in a long-term perspective. It seems that calculation of the maximum acid producing capacity (APC), involving 'available sulfide capacity', *i.e.* the reducible Fe(III) concentration (Section 4), gives a relatively safe basis for such considerations, because iron generally is less mobile than some sulfur species. From data on the long-term acid producing potential of anoxic sediments, appropriate management techniques for dredged materials can be derived (see below).

Definition of Parameters

The pragmatic pH_{stat} approach (presented in Section 4) for evaluating the behaviour of solid waste subsequent to landfilling involves the 'spot test' of lowering the pH value and, in addition, provides data on the buffer capacity of the solid matrix. Direct assessment of the acid producing capacity can be performed by ventilation with air or oxygen; our data, however, have shown that these experiments should be designed for relatively long time periods, *i.e.* for several weeks duration.[33]

Although the three parameters forming the framework of future criteria for assessing long-term effects from metal-bearing sediments, *viz.* the acid producing potential, the acid consuming capacity, and the metal concentration, are closely inter-related, regulatory activities will focus on the concentration term, mainly because its priority function as an effect parameter in biological systems. In this respect, however, the long-term prognostic approach is different from the assessment of the short-term impact by metal-contaminated sediments, which is preferentially done by applying bioassays on sediment porewater and elutriates (recent developments are directed towards solid phase bioassays). Long-term predictions, *i.e.* extrapolations of experimental or field data to a hypothetical situation, necessarily implies some type of numerical method. From the available approaches (Section 2), the group of elution techniques generally seems to be best suited for this purpose; within this group, the long-term predictive capacity is predominantly reflected by the more rigid extractants, in particular, acid solutions. Guideline values based on acid extraction data have been proposed for soil and solid waste materials. The most common pH level of about 4 was primarily aimed to simulate conditions of acid precipitation; however, as has been shown from sediment and solid waste data, internal processes such as oxidation of sulfides, can, by far, be more effective in the lowering of pH.

Usually, criteria will focus on direct effects by ionic trace metals released from polluted sediments. However, it should be mentioned that even if it is not a metal-polluted sediment, Al dissolution from clay materials should also be a matter of concern, as Al^{3+} can be classified as a toxic metal ion in aquatic and terrestrial systems.

Criteria for Dredging and Up-land Deposition of Sediments

In dredged material management, two different target areas for combined matrix/metal criteria can be distinguished: (1) sediment resuspension and (2) dredged material disposal. With respect to 'resuspension of aquatic sediments', which involves more short-term effects than the disposal of dredged material, special emphasis should be placed on the factor, 'available metal species'. Within certain categories of acid producing and consuming capacities, guideline values for individual metals should be based on elutriate data, preferentially at pH 4, for better comparison with other solid matrices (*e.g.* Swiss Ordinance for Waste Materials,[45] which includes two categories of limit values: 'Inert-Construction Materials' and 'Residue Material Deposits', the latter mainly comprising pretreated products of municipal solid waste incineration).

Environmental impact of sediment deposits is influenced by the internal chemical conditions rather than by the concentration and extractability of metals. Priority, therefore, should be given to the optimization of long-term chemical stability ('geochemical engineering').

Consequences for Technical Measures

Regarding the various containment strategies, it has been argued that up-land containment, *e.g.* on heap-like deposits, could provide a more controlled management than containment in the marine environment. However, contaminents released either gradually from an imperfect impermeable barrier (including to groundwater) or catastrophically from failure of the barrier, could produce substantial damage. Up-land disposal of contaminated sediments at least requires provision of a long-term buffer capacity against acidity, arising from the oxidation of sulfides and organic substances. Laboratory studies on the efficiency of stabilization processes, undertaken by Calmano,[46] suggest that best results are attained with calcium carbonate, since pH conditions are not changed significantly upon addition of $CaCO_3$.

On the other hand, near-shore marine containment, *e.g.* in capped mound deposits, offers several advantages, particularly with respect to the protection of groundwater resources, since the underlying water is saline and chemical processes are favourable for the immobilization or degradation of priority pollutants. In a review of various marine disposal options Kester *et al.*[47] suggested that the best strategy for disposing of contaminated sediments is to isolate them in a permanently reducing environment. Under sub-sediment conditions there is a particular low solubility of metal sulfides, compared to the respective carbonate, phosphate, and oxide compounds. Marine sulfidic conditions, in addition, seem to repress the formation of mono-methyl mercury, one of the most toxic substances in the aquatic environment, by a process of disproportionation into volatile dimethyl mercury and insoluble mercury sulfide.[48]

With regard to the immobilization of contaminants in municipal and industrial waste materials, the term 'final storage quality' has been brought into discussion.[49] Solid residues with final storage quality should have properties very similar to the earth's crust (natural sediments, rocks, ores, soil). Landfills with solids of final storage quality need no further treatment of emissions into air and water. It seems that for large-volume waste materials, such as dredged sediments, deposition under permanent anoxic conditions both provides immediate economic advantages and could fulfil the requirement of 'final storage quality'.

Outlook

The preceding discussion has shown that the potential mobility, bioavailability, and toxicity of metals in sediments strongly depend on redox conditions. From earlier chemical extraction procedures, as proposed by Tessier *et al.*[37] to more recent SEM/AVS ratio determinations,[31,50] metal speciation is a major characteristic describing its potential mobility in sedimentary environments. The inherent link between the parameters to describe 'metal speciation' is the characterization of chemical stability and bioavailability of metal compounds in sediments under certain redox conditions.

In a sulfidic anoxic environment, even if the sediment is heavily polluted by metals, organisms are considered to be safe due to the strong fixation of metal ions by S^{2-} or HS^- as a source of acid volatile sulfide. Such heavily polluted sediment, however, can behave as a time bomb which is triggered by only one factor, a redox increase to a critical point, *e.g.* by exposure to oxygen-rich overlying water or directly to the air (a possible pathway also is oxygen transfer via plant roots). Once this situation occurs, toxic metals in the sediments will be released to the water phase or transformed into more bioavailable species.[51]

At the moment, research on long-term effects of redox variations on metal behaviour in sediments is mostly based on thermodynamic considerations. Future research should emphasize studies on the kinetics of metal species transformations, hydrogen ion production, and metal release, as affected by changing redox conditions. Additional important aspects involve the bridging of the gaps between numerical criteria approaches, as reflected by matrix composition and metal mobility, and biological approaches. Assessment for bioavailability of metal species is still based on the results of water phase and elutriate analysis, mostly using acute toxicity data.[52,53,50] However, initial data on solid phase bioassays suggest good prospects for future applications in sediment quality assessment. It may well be that for such systems, which are much less disturbed than artifical sediment elutriates, relationships between matrix conditions, as reflected, *e.g.* by redox indices, and metal species bioavailability may be found, which may serve as a more solid basis for the interpretation of results from bioassays, eventually with respect to chronic toxicity.

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