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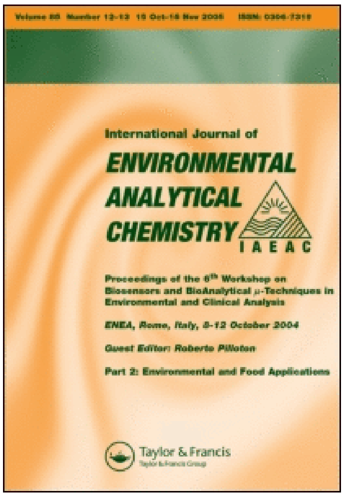

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Metal Speciation - General Concepts and Applications

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METAL SPECIATION - GENERAL CONCEPTS AND APPLICATIONS

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Several aspects of metal speciation in sediments are reviewed: (1) Due to the instability of polluted solid materials, sample handling and storage prior to analysis is problematic. In particular, changes from reducing to oxidizing conditions, which involve transformations of sulfides and a shift to more acid conditions, increase the mobility of critical metals. (2) Simple "standard" leaching tests can be used for easily soluble components such as halides or sulfates, but in most cases are not adequate for assessing mobility of trace metals. With sequential extraction procedures rearrangements of specific solid "phases" can be evaluated prior to their actual remobilisation. (3) Estimation of long-term release of metals from solids can be made using a test procedure, which combines data from column experiments applying controlled intensivation of parameters such as pH-value, redox potential and temperature with results from sequential extraction of the contaminated solids before and after exposure. (4) Partitioning studies on materials from core profiles are particularly useful, since they provide information on relative variations of elemental phases irrespective of the method applied, and thereby an insight into diagenetic processes taking place after deposition of the sediment components. (5) The leachable fraction does not necessarily correspond to the amount available to biota. Studies on the prediction of the trace metal levels in benthic organisms have shown, that the prognostic value of sequential extraction data is improved, when the trace metal concentrations are normalized with respect to the iron (hydrous oxide) and/or organic content of the sediments.

KEY WORDS: Metal speciation, sample handling, leaching tests, long-term release, sediment cores, bioavailable fraction.

INTRODUCTION

The present review on metal mobility in relation to their "speciation" in typical examples of soils, sediments and solid waste materials is a follow-up study to our earlier compilations, e.g. from the NATO Advanced Research Workshop on Trace Element Speciation[1] held at Nervi/Italy in 1981, the Dahlem Konferenzen on Chemical Speciation in Environmental Processes[2] held at Berlin in 1984, from an International Symposium on Metal Speciation, Separation and Recovery[3] held at Chicago in July 1986, from an International Workshop on Speciation of Metals in Water, Sediment and Soil Systems[4] held at Sunne/Sweden in October 1986, a book edited by Graeme Batley[5] on Trace Element Speciation: Analytical

Methods and Problems, and from the NATO Advanced Study Institute on Metal Speciation in the Environment[6] held at Cesme/Turkey in October 1989.

CONCEPTS IN SOLID SPECIATION

Among the criteria to assess which element or elemental species, beside its toxic potential, may be of major concern in ecological evaluations, one question deserves primary attention[7]: Is the element mobile in geochemical processes because of either its volatility or its solubility in natural water, so that the effect of geochemical perturbations can propagate through the environment? In this context, "mobility" mostly deserves a negative aspect of environmental "speciation", in that faster transfer from one environmental medium into another generally involves greater reactivity and bioavailability of potentially toxic elements. The term speciation is used here in the meaning of "describing the distribution and transformation of metal species in various media"[2].

Problems with solid "speciation" are connected to the complexity of heterogenous systems, e.g. of soils, sediments and aerosol particles, and to disequilibria between dissolved and particulate fractions. The term speciation is now used in the second meaning of "operational procedures for determining typical metal species in environmental samples"[2]. Particularly in polluted solid systems, an even greater increase of "entropy" will induce a concominant increase in instability in both physical and chemical context; this can mainly be seen in the difficulties in sample handling and storage prior to analysis[8]. On the other hand, it are just these systems, where action is immediately needed and where for an assessment or prognosis of possible adverse effects the species and the transformations of pollutants have to be evaluated.

In addition to the manifold procedural aspects of "speciation", we consider it as an important challenge in this new field of environmental research that the findings established on the molecular level are transferred into a macroscopic scale, where practical action can take place.

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Accelerating and inhibiting factors

Typically for systems involving solution/solid interactions, "*speciation*" reflects the flux of metal species in a certain medium, which contains both accelerating and inhibiting factors and processes. The former influences comprise effects of pH-lowering, redox changes, inorganic and organic complexation, and microbially mediated species transformations such as biomethylation. Among the spectrum of "barriers", physical processes include adsorption, sedimentation, and filtration; chemical barriers comprise mechanisms such as complexation and precipitation; biological barriers are often associated with membrane processes, which can limit translocation of metals, for example, from plant roots to the shoots and fruits. "Complexation" in its various forms can both inhibit and accelerate metal fluxes, particularly in biological systems consisting of different types of membranes.

Assessment of metal mobility in dynamic environments

Coming from this general concept, four different ways can be envisaged for the assessment of metal mobility in typical environmental compartments:

1. The most comprehensive approach involves evaluation of all species changes along the pathway of the element through the system ("full-system speciation").
2. For many objectives, e.g. for studying effects on biota, determination of the elemental species distribution at a critical section within the system or at its efflux may be sufficient ("part-system speciation").
3. Model considerations, which are aimed to generalize typical distribution or transformation processes, need data on dominant species combined with typical mobilizing/inhibiting parameters such as pH, and pH_2S in the dissolved phase and surface properties of the solid phase ("model species/mobility approach").
4. Long-term prognosis 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 conditions in a dynamically evolving medium ("prognostic mobility/species approach").

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In the present contribution we will mainly discuss the two latter approaches, which typically include solid/solution interactions of metal species. As will be shown later, long-term prognosis of such interactions (approach 4) at this stage is still based mainly on characteristic changes of total metal fluxes, i.e. on mobility variations derived from laboratory experiments, rather than on informations on real "speciation".

Among the various "macro-environments" typical conditions can be considered, where the assessment of metal mobility is of particular relevance for estimating both the actual and future effects of critical components. Such "dynamic" sites include: (1) Excessive treatment of soil with organic-rich agricultural waste materials; (2) transformation of metal-rich components in mining residues in tropical regions; (3) behaviour of polluted particulate matter in the estuarine mixing zone; (4) long-term development of municipal and industrial waste materials. In these dynamic environments characteristic factors and processes are acting as "driving forces":

- High-energy mechanical processes, such as resuspension of particles by wave action, bioturbation, and dredging activities.
- Strong chemical gradients, e.g. of salinity, as well as of redox conditions, pH-values, and organic ligand concentrations, the latter three variables mainly induced by the degradation of organic matter.
- Distinct temporal variations and developments, such as seasonal changes of biological activity in aquatic systems and typical successions in metabolic transformations, for example, reductive processes in waste materials.

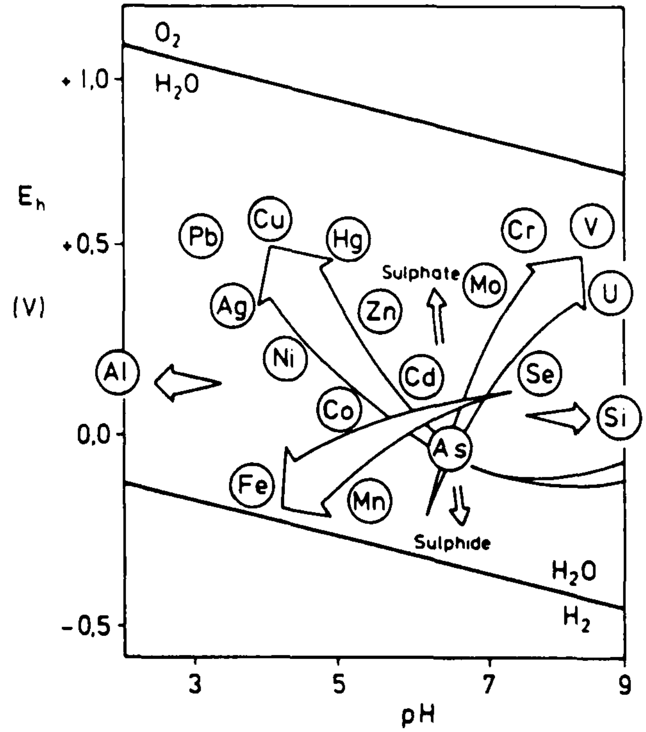

Figure 1 Schematic presentation of major trends for increasing element mobilities (broadening arrows) as a function of redox and pH changes in solid waste material[11].

Redox- and pH-variations

Regarding the potential release of metals from sediments changes the pH and redox conditions are of prime importance. It can be expected that changes from reducing to oxidizing conditions, which involve transformations of sulfides and a shift to more acidic conditions, increase the mobility of typical "B-" or "chalcophilic" elements, such as Hg, Zn, Pb, Cu, and Cd. On the other hand, the mobility is characteristically lowered for Mn and Fe under oxidizing conditions. Elements exhibiting anionic species, such as S, As, Se, Cr, and Mo are solubilized, for example, from fly ash sluicing/ponding systems at neutral to alkaline pH-conditions[9,10] (Figure 1).

The major process affecting the lowering of pH-values (down to pH 2 to 3) is the exposure of pyrite (FeS_2) and of other sulfide minerals to atmospheric oxygen and moisture, whereby the sulfidic component is oxidized to sulfate and the acidity (H^+-ions)

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is generated. Bacterial action can assist the oxidation of Fe^{2+} (aq) in the presence of dissolved oxygen.

Acidity is perhaps the most serious long-term threat from metal-bearing wastes. Water seeping from mine refuse has been passing increased metal concentrations into receiving waters for decades. The threat is especially great in waters with little buffer capacity, i.e., in carbonate-poor areas, where dissolved-metal pollution can be spread over great distances. The acidity production can develop many years after disposal, when the neutralizing or buffering capacity in a pyrite-containing waste is exceeded. High concentration factors have been determined in inland waters affected by acidic mine effluents, where the levels of dissolved Ni, Mn, and Fe exceed the normal surface water concentrations by factors of more than 10,000.

Primary emissions of high metal concentration occur from waste rocks and tailings, secondary effects on groundwater take place from the ponds. An important and long-term source of metals are the sediments reworked from the floodplain, mainly by repeated oxidation and reduction processes.

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LEACHING PROCEDURES

Initial estimation of potential release of metal from contaminated solids is mostly based on elutriate tests, which - apart from the characterization of the reactivity of specific metals - can provide information on the behaviour of metal pollutants under typical environmental conditions. Common single reagent leachate tests, e.g. U.S. EPA, ASTM, IAEA, ICES, and DIN use either distilled water or acetic acid[12]. A large number of test procedures have been designed particularly for soil studies. These partly used organic chelators such as EDTA and DTPA, both as single extractants or in sequential procedures[13]. Physiological solutions have been applied, e.g. for the estimation of organ-specific effects of atmospheric particulates[14].

A "mobility test" procedure for soils based on variations of pH-values has been proposed by Kiekens and Cottenie[15]. Application to a large number of polluted and non-polluted soils indicate that typical mobilisation patterns are obtained for the different heavy metals. Beside the nature of the element, the pH-curves reveal typical textural features of different soil substrates. Best results with respect to the estimation of middle-term effects can be attained by "cascade" test procedures at variable solid/solution ratios: A procedure of the U.S. EPA[16] designed for studies on the leachability of waste products consists of a mixture of sodium acetate, acetic acid, glycine, pyrogallol, and iron sulfate. For the study of combustion residues a standard leaching test has been developed by the Netherland Energy Research Centre[17]. In the column test the material under investigation is percolated by acidified demineralized water (pH = 4; for evaluating most relevant effects of acid precipitation) to assess short-term leaching (< 50 years). In the cascade test the same quantity of material is extracted several times with fresh demineralized water (pH = 4) to get an impression of medium-term leaching behavior (50-500 years). As a time scale the liquid/solid ratio (L/S) is used[18].

Table 1 Sequential extraction scheme for partitioning sediment samples[21,22].

Fraction	*Extractant*	*Extracted Component*
Exchangeable	1 *M* NH_4OAc, pH 7	Exchangeable ions
Carbonatic	1 *M* NaOAc, pH 5 w/ HOAc	Carbonates
Easily reducible	0.01 *M* NH_2 OH HC1 w/ 0.01 *M* HNO_3	Mn-oxides
Moderately reduc.	0.1 *M* oxalate buffer pH3	Amorphous Fe-oxides
Sulfidic/organic	30% H_2H_2 pH 2 w/ 0.02 HNO_3 extr. w/ 1 *M* NH_4OAc-6% HNO_3	Sulfides together with organic matter
Residual	hot HNO_3 conc.	Lithogenic material

Sequential extraction

In connection with the problems arising from the disposal of solid wastes, particularly 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 remobilisation of certain proportions of an element into the dissolved phase[19]. One of the more widely applied extraction sequences of Tessier and co-workers[20] has been modified by various authors (Table 1).

The widely used extraction sequence of Tessier and collaborators[20] consists of five steps. Applications of these methods have been given for atmospheric particulates (e.g., Lum et al.[23]), street dust and roadside soils[24], sewage sludge[25], incinerated sludge ash[26]: With respect to the different substrates, the extreme leachability of both cadmium and lead in the urban particulate matter and street dust is particularly relevant for subsequent interactions with acid, complexing, or salty solutions (the high cation and chloride concentration used in the exchange solution may reflect conditions in soils contaminated with deicing salt.

Despite the relatively low concentration of cadmium in the sewage sludge sample (activated sludge; Landau/Pfalz), there is a significant shift to higher percentages in the carbonate fraction, whereas lead is typically enriched in the organic/sulfidic and residual forms. The general experience that the (anthropogenically) more enriched elements are also the more reactive ones seems to be valid only for waste material, which has not been treated by high temperature processes; this is exemplified by the data from incinerated sludge ash (Hamilton municipal incinerator), where the remaining metals are highly enriched but rather stably bound in the "residual fraction". Better efficiency of emission control, however, of stack gases from combustion processes will recycle higher percentages of atmospheric particulate matter into the residues to be deposited; these materials are expected to contain higher fractions of leachable metals, as shown in the first two columns of Figure 2.

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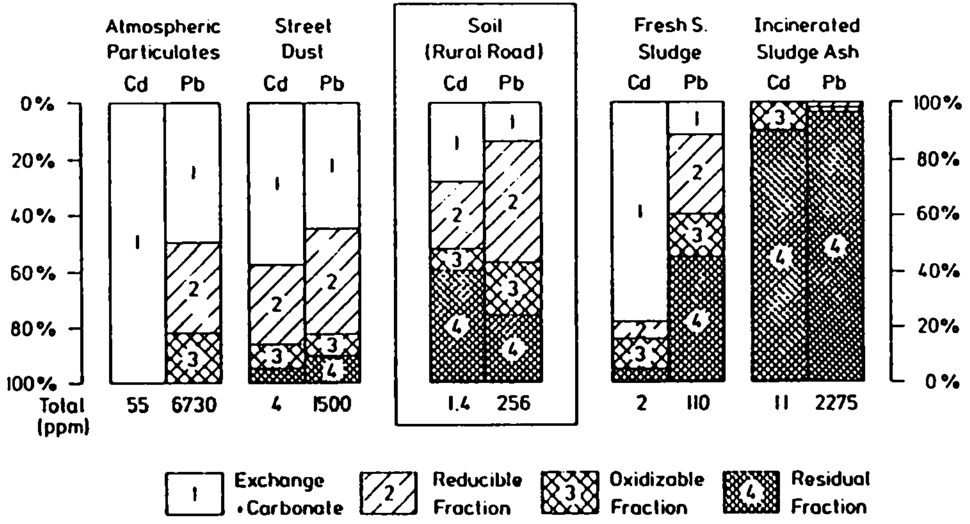

Figure 2 Chemical fractionation of cadmium and lead in solid waste particles (Urban Particulate Matter Standard Reference Material (SRM 1648); street dust; fresh sewage sludge; incinerated sewage sludge ash).

Extractants:

(1a) 1 M $MgCl_2$ (Exch.); (1b) 1 M sodium acetate (Carb);

(2) 0.04 M hydroxylamine hydrochloride/25% acetic acid;

(3) 0.02 M nitric acid/30% hydrogen peroxide at pH 2;

(4) conc. nitric acid digestion.

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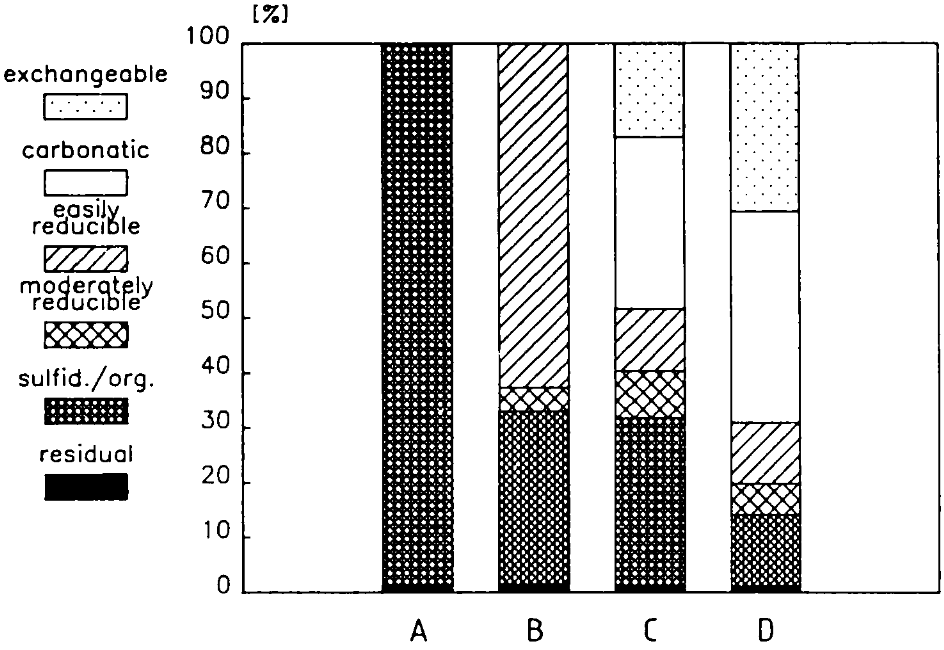

Figure 3 Partition of cadmium in anoxic mud from Hamburg Harbor in relation to the pretreatment procedures[22]: (A) Control extracted as received under oxygen-free conditions; (B) after treatment with elutriate test; (C) freeze-dried; and (D) oven dried at 60°C.

Problems associated with extraction procedures

Despite the advantages of a differential analysis over investigations of total metal concentrations and the fact that sequential chemical extraction is probably the most useful tool for predicting long-term adverse effects from contaminated solid material, it has become obvious that there are still many questions and uncertainties associated with these procedures[21,27], for example:

- Reactions are not selective and are influenced by the duration of the experiment and by the ratio of solid matter to volume of extractants. An excessive solid content, together with an increased buffer capacity may cause the system to overload; such an effect is reflected, for example, by changes of pH-values in time-dependent tests.
- Labile phases could be transformed during sample preparation, which can occur especially for samples from reducing sites.

In this respect, earlier warnings have been made by various authors, not to forget changes of the sample matrix during recovery and treatment of the material. The first indicates, that even oxic materials are not free of changes caused by manipulations during treatment[28]. The

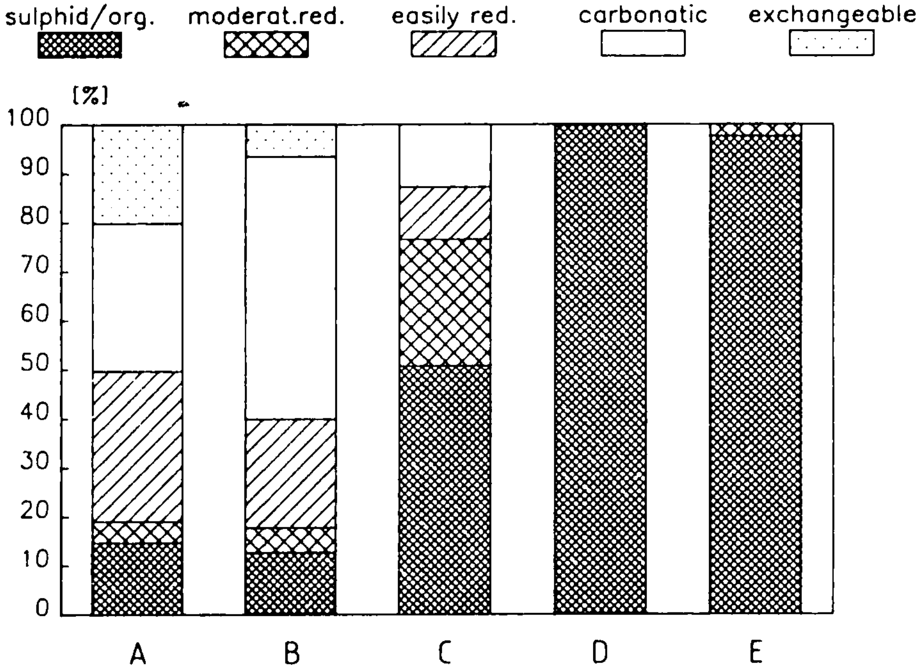

Figure 4 Fractionation results of cadmium from samples of different early diagenetic stages[22]: (A) Estuarine suspended matter; (B) oxic surface sediment from the Elbe Estuary; (C) postoxic subsurface core sediments; (D) marine sulfidic; and (E) freshwater methanic mud samples.

second relates to the anoxic sediment material, where changes are quite obvious. "The integrity of the samples must be maintained throughout manipulation and extraction"[29]. A detailed description of the procedures necessary to fullfil these requirements, including extraction under inert atmosphere in a glove box using deaerated reagents, is given by Kersten and Förstner[30].

Although these problems, particularly for anoxic sediments, are well known since many years, we have clearly underestimated the effects for a long period. It was realized, when we have been trying to separate iron forms in dredged sediments. Our results were totally different from the model calculations, which claimed for a very considerable percentage of iron carbonate. When we tried to produce artifical iron carbonate, we failed as the originally white material was disintegrating to form red iron oxide within short time periods. It became obvious, that these materials were highly sensitive to aeration. Cadmium typically changes from sulfidic forms to easily reducible, carbonatic and exchangeable forms (Figure 3).

In the pretreatment scheme, which was developed from this experience[31], anaerobic dredged samples were taken immediately from the center of the material with a polyethylene

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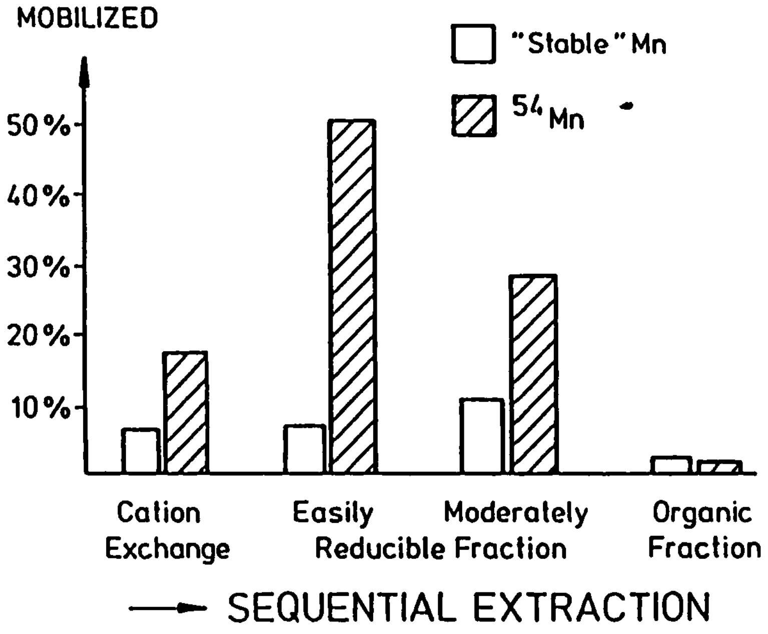

Figure 5 Comparison of chemical extractability of artificial and stable isotopes of manganese from a sediment sample of the Rhône River[34].

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spoon, filled into a polyethylene bottle until the surface. Immediately after arriving at the laboratory, sediments were inserted into a glove box prepared with an inert argon atmosphere. Oxygen-free conditions in the glove box were maintained by purging continuously with argon under slight positive pressure. Extractants were deaerated prior to the treatment procedure.

APPLICATIONS

Surface-related studies on solid materials have been performed or are aimed for

Assessment of sources by characterization of typical inputs

There are as yet only few studies in this field. We have performed a regional survey on the distribution of thallium in soils in an area, where two point sources were effective[32]: One was an abandoned lead-zinc mine, the other was the chimney of a cement factory which had

Table 2 Elution-index for selected river sediments[35], as determined from exchangeable proportions (1 *M* ammonium-acetate). Calculated relative to background data from Elbe River sediments. These values are multiplied by a factor of 100.

	Neckar	*Main*	*Elbe*	*Weser*
Copper	<1	—	1	—
Lead	1	1	1	1
Zinc	7	10	40	10
Cadmium	22	22	25	—
Total oxic	*30*	*33*	*67*	*11*
(Anoxic	0.5	0.3	>44	4)

used sulfidic roasting residues as additives to special cement. Results from leaching experiments with ammonium acetate showed statistically highly significant differences. In the mine area, the extractable portion was in the range of 4%, whereas in the soils affected by the cement plant emissions approx. 18% could be extracted. The lower absolute concentrations in the latter area were therefore more available, leading also in some cases to increased concentrations of thallium in plants.

Different geochemical environments

Diagenesis involves processes in the interstital water and gases, which are strongly affected by changes of redox conditions. The sequence of "redox titration" is comprising the major reactions "respiration" , "manganese reduction", "nitrate reduction", "iron reduction" and "sulfate reduction" mediated by bacteria. In ancient sedimentary deposits, these zones can be identified from characteristic mineral assemblages: The oxic environment contains oxyhydrates of Mn and Fe at low contents of organic matter (which is mostly degraded); the post-oxic environment is characterized by the presence of manganese carbonate, both oxides and carbonates of iron, and low organic matter as well. Under anoxic conditions two branches can be distinguished: In the marine milieu reduction of sulfate provides sufficient sulfide ions to form iron sulfide, whereas in the freshwater environment there is a tendency to form carbonate of iron, when the sulfide ions are consumed; the general tendency of diagenesis in anoxic freshwater sediments is the formation of methane. Sediments collected on four campaigns represent different early diagenetic environments according to the before-mentioned classification. Cadmium is associated in the oxic environment with reducible phases, carbonates and to some extent with exchangeable forms. Higher percentages of sulfides are found already in the post-oxic environment and in both anoxic milieus. These findings reflect the strong affinity of cadmium to the sulfidic phase, even in such environments, where the concentration of sulfide ions is limited (Figure 4).

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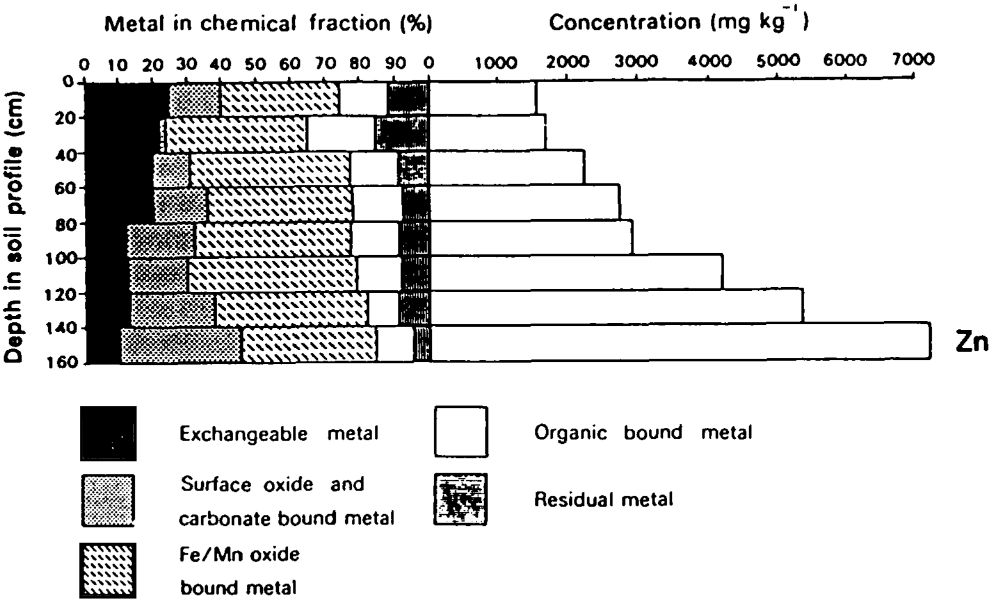

Figure 6 Total concentrations and partitioning of zinc in a floodplain soil profile in the Manifold catchment[38].

Evaluation of diagenetic effects

The typical effects of the earliest stages of "diagenesis" (involving transformations of organic matter, "aging" of mineral components and formation of new equilibria between solid and dissolved species) have been demonstrated by Salomons[33] with respect to the behaviour of trace metals at the sediment/seawater interface. When addition of cadmium and zinc to suspended matter was performed at longer absorbing periods, desorption by saline water was significantly lower. An extrapolation can be made to geologic time scales by a comparison of the bonding intensity of stable metal isotopes and their unstable counterparts—the latter supplied from radioactive emissions of nuclear power and reprocessing plants. In Figure 5 the effects are shown of sequential leaching of a sediment sample from the lower Rhône River in France. The reducing agents hydroxylamine (pH 2) and oxalate buffer (pH 3) only extract 15% of the natural stable manganese while the artificial isotope Mn-54 from the reprocessing plant is mobilized at more than 80% by these treatments (Figure 5).

Sediment quality criteria

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 approaches are based on (1) accumulation, (2) pore water concentrations, (3) solid/liquid equilibrium partition (see above), and (4) elution properties[35].

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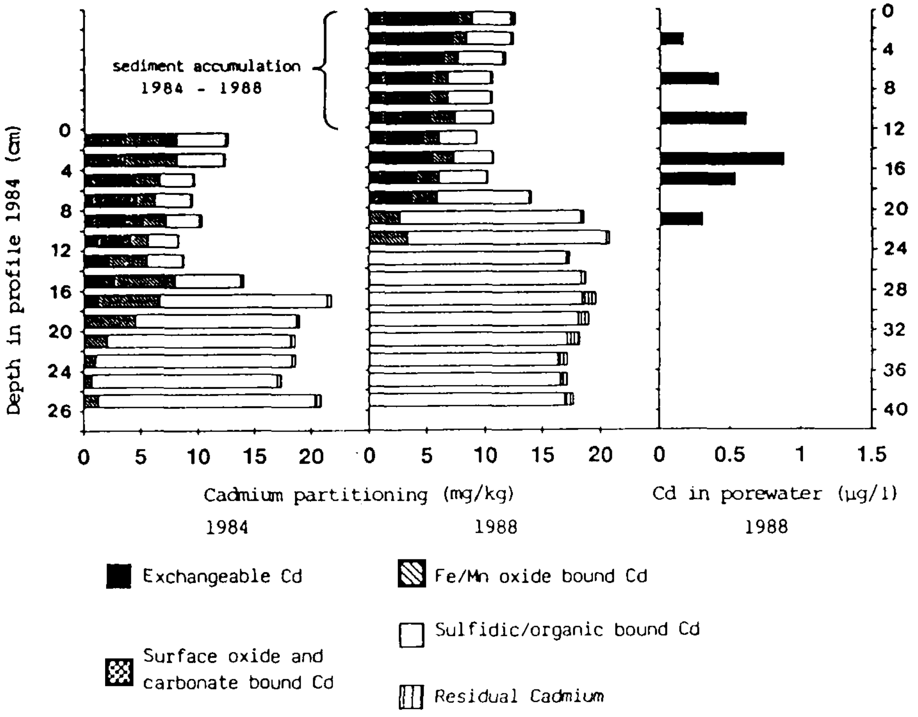

Figure 7 Total concentrations and partitioning of cadmium in a tidal flat sediment profile in the Heuckenlock area sampled in 1984 and 1988. Sedimentation rates were determined by the ^{137}Cs-method. Cd pore water profile was determined at low tide[39].

In Table 2, 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 Germany is based on the metal concentrations exchangeable with 1 N ammonium acetate at pH 7. These metal fractions are considered to be remobilizable from polluted 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 clearly indicates, that the oxidation of samples gives rise to a very significant increase in the 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 2).

Study of sediment core data I—Flood-plain soil

Partitioning studies of sediment from core profiles are particularly useful, since they provide information on relative changes of elemental phases irrespective of the method

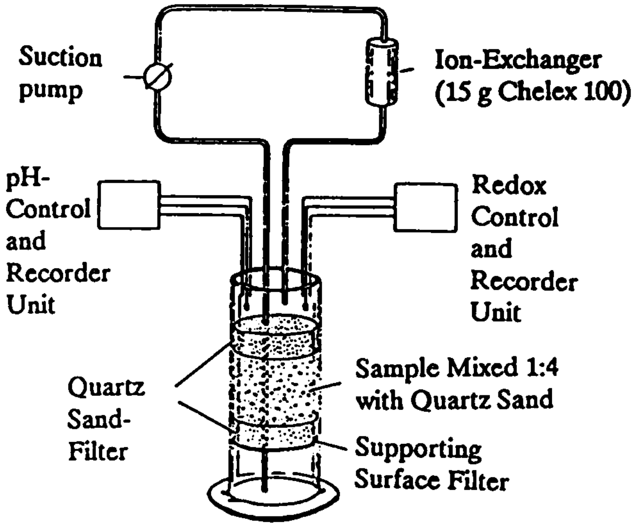

Figure 8 Experimental design for long-term prognosis of metal release[42].

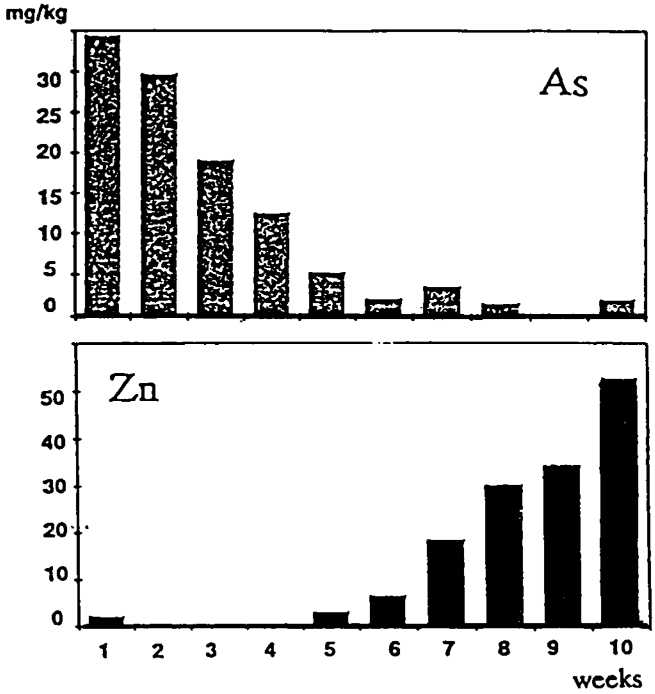

Figure 9 Kinetic of release of arsenic (above) and zinc (below) from industrial waste treated with a high-pH additive. Experiments were conducted with pH 5 solutions[43].

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applied, and thereby an insight into diagenetic processes taking place after deposition of the sedimentary components. Two examples are presented here, both indicating significant changes in the partition of zinc and cadmium during a relative short period of time.

Floodplains on the River Manifold contain sediments with large metal concentrations[36, 37]. The sedimentary units described were deposited during concerted mining, and as mining ceased in 1870, pedogenic processes have influenced these sediments for over 100 years. A general decrease of total Zn concentrations over time, which can primarily be interpreted as the result of improvements in the processing of ores, is given here (Figure 6, right bars). Phase differentiation (Figure 6, left) indicate that there has been a significant temporal increase of the percentage of exchangeable Zn. These changes can be interpreted from pedogenic processes. Since these transformations will result in a reduction of the bonding strength, it cannot be excluded, that the decrease of total metal concentrations is partly due to a diagenetic remobilisation of metals from the floodplain deposit. However, Pb concentrations have decreased similar to Cd and Zn, without the respective changes of chemical fractions. Thus, it is suggested that the process of diagenetic release generally is not a significant factor in this environment.

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Study of sediment core data II—Oxidative pumping

Metal release from tidal Elbe River sediments by a process of "oxidative remobilization" has been described by Kersten[39]. Short (30 cm) sediment cores were taken from a site, where diurnal inundation of the fine-grained fluvial deposits takes place; sub-samples were analyzed with sequential extraction. 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 7) 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

Table 3 Some examples from *in situ* studies for prediction of trace metal availability to benthic organisms from sediment characteristics[45].

Organism	*Metal*	*Best predictor in the sediment*	*Ref.*
Scrobicularia plana	Pb	[Pb]/[Fe] extracted with 1 N HCl	46
Scrobicularia plana	As	[As]/[Fe] extracted with 1 N HCl	47
Scrobicularia plana and Macoma balthica	Hg	[Hg] extracted with HNO_3/organic content (%)	48
Anadonta grandis	Cu	[Cu]/[Fe] extracted with $NH_2OH \cdot HCl$	49
Elliptio complanata			50

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. By this process of "oxidative pumping"[30] a maximum downward flux of 0.4 g Cd/m^2 per year can be estimated in the Heukenlock sediments.

Long-term prognosis of metal-release from polluted solid material

Because many of these approaches do not involve kinetic considerations, they are of limited value with regard to prediction of long-term effects in waste-deposits. This lack can be avoided by an experimental approach, originally been used by Patrick et al.[40] and Herms and Brümmer[41]. Metal mobility can be estimated by comparing sequential extraction results before and after treatment of waste material by controlled significant intensivation of relevant release parameters such as pH-value, redox-potential and temperature using an ion-exchanger system for extracting and analysing the released metals at a adequate frequence (Figure 8).

This system was used for the evaluation of the long-term behaviour of metal contaminants (including arsenic, cadmium, thallium and vanadium) in various waste materials. Elements such as arsenic are released at an initial phase during changes of pH and redox conditions; remobilization of elements such as zinc takes more time, since lower pH-values resulting from the oxidation of sulfide is required (Figure 9).

In particular for the elements for which the endpoint of release cannot be estimated from the respective cumulative curves of the water concentrations, extrapolations from sequential extraction data on the solid material are needed.

Bioavailability of sediment-bound metal species

Estimation on the remobilization of metals under changing environmental conditions and on the potential uptake by biota are two major objectives of species differentiation on particle-bound trace metals. However, many authors have shown that with respect to bioavailability, as distinct from geochemical mobility, the present state of knowledge on solid matter speciation of metals is still somewhat unsatisfactory. The leachable fraction does not necessarily correspond to the amount available to biota.[44] This handicap is primarily due to a lack of information about the specific mechanism by which organisms actively translocate trace element species. In the case of plant root activities interactions with soil and sediment components include redox changes, pH alterations and organic complexing processes.

Studies on the prediction of the trace metal levels in benthic organisms have shown, that the prognostic value of sequential extraction data is improved, when the trace metal concentrations are normalized with respect to the iron (hydrous oxide) and/or organic

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content of the sediments[45] (see Table 3). Depending on the main route for accumulation of trace metals in the benthic organism of concern, at least three mechanisms could explain an inverse relationship between metal concentrations in the organism and the concentration of a potential sink in the sediments:

Mechanism 1. If it is assumed that the major route for accumulation of trace metals in the organism involves the digestive system, and that acidic and/or reducing conditions prevail in the intestinal tract, one can envisage the simultaneous solubilization of both the cations (Fe, Mn, Ca) and the trace metals associated with some sinks (e.g., Fe/Mn oxides). The cations thus released could then compete with the trace metals fro uptake sites in the digestive system and reduce their uptake.

Mechanism 2. If it is again assumed that accumulation of trace metals occurs predominantly via the digestive system, but that conditions prevailing within the gut (pH, pE, residence time) are such that the sink remains unchanged during the digestion, then the unreacted sink could compete with the uptake sites in the intestinal tract for the solubilized trace metals.

Mechanism 3. Alternatively, the main route for accumulation of the trace metals may involve the uptake of dissolved trace metals (e.g., via the gills and mantle). In this case, the protective role of the sink could be explained by invoking adsorption in the external medium as the principal factor controlling the dissolved metal concentrations to which the organisms are exposed. Clearly, as the concentration of adsorbing substrate increases, the concentration of dissolved metals will decrease.

It has been inferred by Tessier and Campbell[45] that a strong dependence of trace metal accumulation upon sediment characteristics does not imply that the main route of entry of trace metals is necessarily via ingestion of particulate metals; it can be explained by a control through adsorption reactions of the dissolved trace metal concentrations in the solution to which the organisms are exposed, such as in the case of filter-feeders where high levels of trace metals were found associated with the gills and mantle[50]. For the latter pathway the study of the intermediate water phase—e.g., pore water—and the different forms and availabilities of metals in this medium seems to be particularly promising.[51]

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