

CHEMICAL SPECIATION AND FRACTIONATION IN SOIL AND SEDIMENT HEAVY METAL ANALYSIS: A REVIEW^(*)

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ABSTRACT

Today it is generally recognized that the particular behaviour of trace metals in the environment is determined by their specific physicochemical forms rather than by their total concentration. Several chemical speciation and fractionation methods for heavy metal analysis in soils and sediments have been and are still being developed and applied. They primarily are intended to understand the particular environmental behaviour of metals, present in a variety of forms and in a variety of matrices.

Analytical developments, modifications of existing methods, and recent new approaches are reviewed and discussed. Techniques used include chemical extractions, ion-exchange/gel chromatography, filtration, centrifugation and sieving, selective solvent extraction.

Moreover, the application of these various techniques in different research fields over the last years is explored. The value and the limitations of speciation and fractionation techniques applied in specific experimental work is outlined. It is discussed to what extent these methods have, up to now, satisfied the expectations or have been satisfactory in particular applications.

KEY WORDS: heavy metals, speciation, fractionation, soil, sediment

INTRODUCTION

In soils and sediments, elements of interest exist in several different forms and are associated with a range of components¹⁻³. It is generally recognized that information about the physicochemical forms of the elements is required for understanding their environmental behaviour (mobility, pathways, bioavailability)⁴⁻⁷. Although no generally accepted definition of the term exists, speciation can broadly be defined as the identification and quantification of the different, defined species, forms or phases in which an element occurs⁷. The term "fractionation" is frequently used interchangeably with speciation but emphasizes the concept of subdividing a "total content". Also, the analytical preparations for separating metal species are referred to as "fractionation".

The behaviour and fate of metals are governed by a range of different physico-chemical processes, which dictate their availability and mobility in the soil or sediment system. In the water phase, the chemical form of a metal determines the biological availability and chemical reactivity (sorption/desorption, precipitation/dissolution) towards other components of the system^{8,9}. The binding form in the solid phase is related to the kinetics and equilibria of metal release to the liquid phase and hence the likelihood of remobilization and bioavailability^{9,10}.

For the determination of metal species in soil solutions, methods are used which generally are based on a more profound analytical background¹¹. The complexity of possible reactions

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and often unknown reaction kinetics in natural soil and sediment systems restricts studies of metal species distribution in solid phases mainly to operationally defined analytical procedures^{11,12}. An overview of techniques used in chemical speciation analysis is given in Table 1.

Table 1 Analytical methods applied for chemical speciation of metals

Method	Metal species determined
LIQUID PHASE	
<i>Electroanalysis</i>	
Ion selective electrodes	Free ionic concentrations
Voltammetry	Free ions and labile complexes
<i>Spectroscopy</i>	
Spectrophotometry	Specific forms
Hydridegeneration	Inorganic and organometallic species; different oxidation states (Sn, As, Sb, Bi, Se, Te)
<i>Chromatography</i>	
HPLC	Cations, anions, metal complexes, inorganic species
GC or LC	organometallic compounds of mercury, tin, and lead
<i>Physico-chemical fractionation</i>	
Ion-exchange resins	Free ions and labile complexes
UV-irradiation	Organic complexes
Solvent extraction	Organic complexes
<i>Size fractionation</i>	
Filtration	Dissolved and suspended matter associated
Centrifugation	Dissolved and suspended matter associated
Dialysis	Different charge, different molecular size
Ultrafiltration	Molecular size
Gel filtration chromatography	Free forms and complexes of different molecular size
<i>Computing</i>	
SOLID PHASE	
Single reagent leaching	Reagent soluble fractions
Sequential extractions	Geochemical fractions
Ion exchange resins	Labile fractions

There is experimental uncertainty associated with all presently available methods of metal speciation⁸. Especially solid phase fractionation schemes suffer from serious limitations: besides conceptual problems related to the specificity of the techniques used, operational problems like sample handling, reagent selectivity and specificity, interferences are not yet overcome¹³.

This paper explores the development and application of chemical speciation techniques in the fields of geochemistry, marine chemistry and agricultural sciences. Recent applications of speciation techniques are reviewed and examined. It is observed that a lot of efforts were dedicated to the further development of analytical chemical speciation techniques. Methods were refined and new combinations of existing techniques were applied.

DEVELOPMENTS IN CHEMICAL SPECIATION TECHNIQUES

An important effort in speciation analysis continues to go into the further development of chemical speciation techniques. Fractionation procedures and detection techniques are being refined. Modifications and new combinations of established techniques are tested. Lund⁶ recently reviewed methods applied.

Ion selective electrodes

The use of the ion selective electrode (ISE) remains severely limited. The sensitivity is too low to be useful for metal speciation in environmental samples and may also suffer from interferences^{6,14,15}. Shuttleworth¹⁶ studied the influence of metal speciation on bacterial growth. The Cu-ISE was subject to interferences that required the elimination of some growth medium components. For the determination of ionic Cu in soil percolates, the ion selective electrode, ion-exchange separations and gel-filtrations were used¹⁷. In a slightly acidic soil sample, free copper was largely overestimated, due to interferences of H⁺.

The lower working range of the specific Cd-electrode is around 10⁻⁶ M¹⁷⁻¹⁹. Hirsch avoided the sensitivity problem in chemical speciation by spiking the sample with Cd(NO)₃. This approach however assumes that 1) the speciation of a 10⁻⁶ or more concentrated solution remains the same, 2) that the increased ionic strength does not significantly alter the speciation pattern.

Voltammetry and polarography

Differential pulse anodic stripping voltammetry (DPASV) is a very sensitive and specific polarographic technique. It is a dynamic method that requires that the kinetics of "stripping in" to the Hg electrode and "stripping out" from it are fast compared to the kinetics of dissociation or desorption of the bound metal ions. The signal depends on the kinetic characteristics of the metal species in solution and may therefore be used to determine free metal forms^{16,20}, to differentiate between strong and labile complexes²¹⁻²⁴, and to study metal-organic ligand reaction kinetics^{25,26}. Larsen and Svensmark²² stressed the need of using specific reduction potentials for each element when discerning free metal forms from labile complexes. Too low reduction potentials result in increasingly less labile complexes being reduced. This leads to an overestimation of the free ionic form.

Agraz *et al.*²⁷ applied differential pulse voltammetry using a carbon paste electrode, modified with an Amberlite cation exchange resin. As with the mercury electrode, highly sensitive measurements could be done and the method offers a similar potential to be used for speciation analysis. By using this approach, the need of adding an electrolyte to the sample that may induce changes in speciation was avoided.

Donnan Dialysis

During the preconcentration step, the free metal concentration may be overestimated due to dissociation of labile species. To avoid this, Berggren²⁰ developed a system in which the sample was equilibrated with a perm-selective membrane. Only free Cd²⁺ exchanges through the membrane and the final equilibrium concentration in the receiving solution is related to

the original free Cd^{2+} concentration in the sample. Again, however, the system was not sufficiently sensitive for the analysis of soil solutions.

Ion exchange resins

Ion exchange is frequently used to differentiate between metal species, based on the electrostatic charge²⁸ or on the lability of complexes²⁹. For speciation of free and complexed metal forms, the ion exchange technique is rapid and sensitive. It is also insensitive to interference of high concentrations of electrochemically active compounds, like humic substances³⁰. Because of on-column reactions of labile complexes, ion-exchange is only suitable for the speciation of metals that form relatively stable organic complexes. The ion exchange procedure compared well to the equilibrium dialysis method for Cu and Al, but not for Pb and Cu³⁰. For Al, the ion exchange procedure compared favourably with a solvent extraction method³¹.

Size fractionation

Size fractionation may constitute a preliminary step in a speciation scheme. Sample contamination and adsorption on the filter membranes are possible problems. Also the speciation may be altered. Applying successive filtration and tangential flow systems could minimize these alterations³².

Combinations of techniques

Several techniques may be combined in a scheme for metal speciation. Chakrabarti *et al.*³³ presented a scheme combining filtration, ultrafiltration, batch- and column ion-exchange, and anodic stripping voltammetry. It integrates physical speciation by size fractionation with the chemical speciation by characterization of metal complexes. However, the definition of the metal forms is highly operational.

Problems connected with separation methods - time-consuming, contamination, losses of analytes - may be overcome by direct coupling techniques³⁴. This coupling is nowadays mainly done for the speciation of organometallic compounds. Chromatographic techniques (GC, HPLC) are coupled to detection systems. Recent developments were reviewed by Chau and Wong³⁵.

Computer programs

Soil solution speciation may be estimated using computer programs like GEOCHEM and its progeny SOILCHEM^{36,37}, MINTEQ2³⁸ or MINTEQL³⁹.

Perfect agreement between analytical and predicted speciation is an unrealistic expectation⁴⁰. Discrepancies may arise due to the limitations of both the analytical approach and the modelling approach. Analytical limitations include insufficient sensitivity and high uncertainty on the obtained value, interferences, operational character of the method, and sensitivity to slight pH-changes. From the computational side, limitations include the uncertainty about the most appropriate equilibrium constants and the measured input data, and the fact reaction kinetics are not considered¹⁶.

Speciation of solid phase associated metals

For the speciation of solid phase associated elements, either single or sequential extraction techniques are applied^{2,6,7}. The scheme of Tessier *et al.*⁴¹ is widely used (Table 2). The application of sequential extraction is still subjected to much controversy. Nonselectivity of the extractants and trace element redistributions among phases during extraction are the main problems of sequential extraction procedures⁴²⁻⁵¹. Serious redistribution effects (Pb, Cu) and nonselectivity (Zn) have been observed in experiments with synthetic sediments^{46,47,52,53} and with spiked metals in uncontaminated sediments⁴². Some model experiments however may lead to overestimate the postextraction readsorption⁴⁴. These validation studies point out the importance of sample to sample differences. They argue against the indiscriminate use of selective extractions and the operationally defined phase associations⁵⁴. Despite all these restrictions, sequential extraction procedures have proved to be useful in the field of environmental analytical chemistry⁵⁵. It is in any case very important to accept a common scheme so that results from different scientists can be compared and a common database on the mode of occurrence of metals in soils and sediment can be build-up⁵⁶.

Other research has been carried out to improve the selectivity of extracting reagents or to design alternate reagents. Slavek and Pickering⁵⁷ examined the ability of selective extractions to remove metals from hydrous aluminum oxides, because most schemes do not attempt to identify this metal/phase association. They concluded that it is an unattainable goal due to lack of true selectivity of suitable reagents. Warden & Reisenauer⁵⁸ were more successful in designing a fractionation procedure for soil Mn (readily soluble Mn, weakly adsorbed Mn, carbonate-bound Mn, specifically adsorbed Mn, and oxide Mn). Rauret *et al.* modified the Tessier procedure to obtain a more thorough dissolution of the fractions of highly contaminated sediments^{59,60}. Sequential extraction schemes used for metal partitioning were found not to be applicable for the fractionation of As and Se⁶¹.

Table 2 Sequential extraction scheme of Tessier *et al.*⁴¹ for soils and sediments

Step	Fraction	Extraction
1	Exchangeable	1 mol/L MgCl ₂ (pH 7), 20°C
2	Acid-soluble (‘Carbonate-bound’)	1 mol/L NaOAc + HOAc (pH 5), 20°C
3	Reducible (‘Fe/Mn-oxide bound’)	0.04 mol/L NH ₂ OH.HCl + 25% HOAc, 95°C
4	Oxidizable (‘Organically bound + sulphide-bound’)	30% H ₂ O ₂ + 0.02 mol/L HNO ₃ (pH 2), 85°C; 2 mol/L NH ₄ OAc + 20% HNO ₃
5	Residual (‘Residual/Silicate’)	HF/HClO ₄

An alternative way of carrying out sequential extraction was presented by Scokart *et al.*⁶². They applied sequential extraction in a continuous on-line system, coupled with ICP-spectrometry. Gupta *et al.*⁶³ developed a simultaneous extraction scheme to give similar results as the sequential extraction procedure of Stover *et al.*⁶⁴. The major advantage is that it is less time consuming.

Sample handling and storage before analysis is a problematic aspect of every speciation technique. Sample preservation (e.g. freeze drying, oven drying) critically influences the results of sequential extraction⁶⁵. For anoxic sediments, the necessity of maintaining anoxic

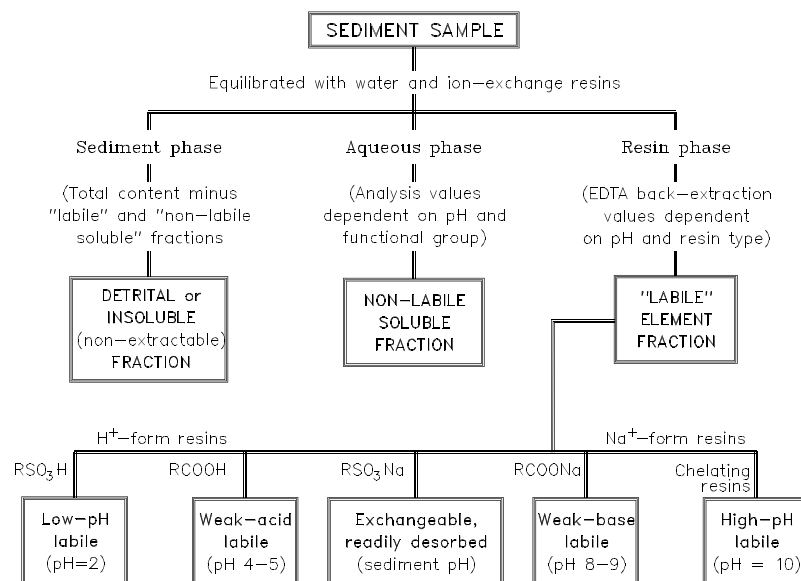


Figure 1 Fractionation scheme based on ion-exchange resins for the determination of "labile metals"⁶⁹

conditions during sampling, sample treatment and extraction has been clearly evidenced^{65,66}.

Pickering and coworkers⁶⁷⁻⁶⁹ presented an alternate approach to differentiate metal fractions in the solid phase (Figure 1). Ion exchangers were contacted with sediment suspensions. The adsorbed metals were stripped and determined. Distinction is made between the non-labile and the labile fraction. Using resins with different properties, the labile fraction was differentiated into a low-pH labile, a weak-acid labile, and a readily desorbed fraction⁶⁹. Contrary to chemical extraction, this technique would be more selective towards the element forms that are of biological importance. Disadvantages are that the procedure is more time-consuming than direct chemical extraction and that matrix attack can be greater than with salt solutions. Anyhow, this approach defines yet another series of operationally defined fractions, whose interpretability needs testing⁷⁰.

UNDERSTANDING BASIC PROCESSES

Speciation techniques were useful in studies of metal partitioning, distribution, accumulation, and mobility in water and sediment systems⁷¹⁻⁷⁷, and soil⁷⁸⁻⁸² to support hypotheses and to gain a better understanding on the different processes and mechanisms hypothesized.

Role of organic matter on metal behaviour

Speciation clearly evidenced the role of organic complexes in metal mobilization in soils. Using gel permeation chromatography, the important role of organic matter in solubilizing heavy metals in sewage sludges⁸³ and in agricultural soils amended with liquid manure^{24,78} can be clearly shown.

Aluminium mobilization in podsoils was demonstrated to be largely determined by the formation, solubilization, migration and subsequent precipitation of organic complexes⁸¹. In a

cambisol, inorganic Al forms were predominant.

Copper mobilization in forest soils was, in cases where the soluble organic carbon (DOC) concentration was low, affected by solution pH. An increased pH seemed to increase the amount of Cu bound per g DOC⁸⁰. A high mobility of Cu was observed by Domergue and Védry¹⁴ in lysimeter experiments. This was related to the fact that most of the Cu was complexed by dissolved organic matter.

Geochemical behaviour of elements

Sequential extraction data supported the study of the biogeochemical cycling of Fe and S in sediment cores⁷⁴. Highly enriched zones of iron oxyhydroxides largely resulted from localized bacterial cycling of Fe in the region of the peak. In the more reduced zones, the increase of Fe in the oxidizable fraction (sulfides) supported this hypothesis. Similarly, sequential extraction data were used to elucidate the observed distribution of both Fe and Mn with depth⁷². Mn was shown to exhibit an important postdepositional migration, both in the surface and in deeper sediments. This appeared also from Mn, associated mainly with the labile (adsorbed, exchangeable and reducible) fractions. The importance of iron oxyhydroxides in scavenging heavy metals was also clearly illustrated, more than 50% of the metals being associated with the reducible fraction.

Chemical processes and mineralogical alterations occurring during leaching of highly acidic cole pile runoff were investigated in a column experiment. Processes that occurred were identified from mass balance calculations and sequential extraction data, obtained at different stages during the leaching process⁷⁶. Several processes were fairly apparent from the chemical extraction data. The increase of Fe in the reducible fraction could be related to the retention of Fe within the soil column. As the soil buffer capacity was exhausted and the pH dropped to near 2, additional native crystalline Fe phases were destabilized and resulted in an increase in reducible Fe, in excess to the amounts predicted from mass balance calculations. The most important reactions governing transport within acid run-off percolating through the subsoil were shown to be simple partitioning between aqueous and exchange phases.

Arsenic in reducing sulfidic sediments was partitioned into oxyhydroxide bound arsenic, an organic fraction, and a sulfide associated fraction⁸⁴. Solid phases of arsenic, copper, and zinc changed from dominantly oxyhydroxide and organic phases to sulfide phases with depth. Solubility of As was low in the upper layers, due to arsenic being in the oxidized form and adsorbed on the oxyhydroxides. In the reduced layers, arsenic was accumulated in sulfide forms. In solution, higher levels of arsenic, in the oxidized and mainly in the reduced form, were maintained.

Modelling

Tessier *et al.*⁷¹ described the partitioning of Zn between the overlying water and the superficial sediments by sorption processes. They fitted either the distribution coefficient model or a simplified version of the surface complexation model. Values of the distribution coefficient for Zn were assessed using the dissolved Zn²⁺-concentrations, estimated from thermodynamical calculations, and concentrations in the ironoxyhydroxide compounds, estimated from sequential extraction data.

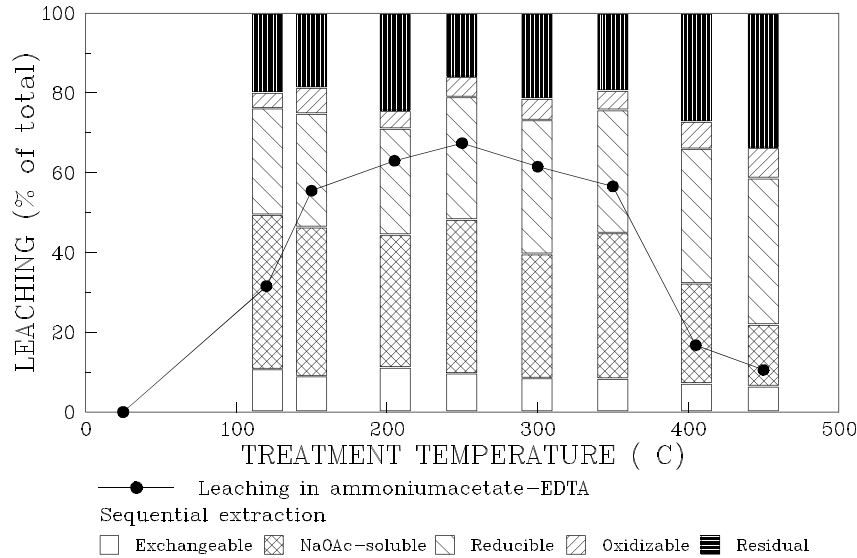


Figure 2 Leaching behaviour in $\text{NH}_4\text{OAc-EDTA}$ ¹ and sequential fractionation⁴¹ of a sediment, heated at different temperatures¹⁰²

IDENTIFICATION OF POLLUTION AND POLLUTION SOURCES

Fractionation of total metal contents may give indications of the origin of the metals. High levels in the exchangeable, acid soluble and easily reducible fractions may indicate pollution from anthropogenic origin⁸⁵⁻⁸⁹. Even high contents in the more resistant fractions, except the residual, may be significant in the long term⁹⁰.

Analysis and speciation of metals in sediments and overlying waters in estuaries allowed to track the fate of pollutants^{91,92}. Specific metal forms could be useful indicators: Méranger and Lett⁹³ suggested that monomeric aluminium could be a useful indicator for the recent effects of acidic deposition.

High Cu and Zn levels were found in the exchangeable and acid soluble fractions of coastal sediments as compared to ocean sediments, suggesting a pollution problem arising from discharges. Higher percentages of Cu and Zn (20-80%, and 45-93% resp.) were found in the more resistant reducible fraction and indicated the inclusion of pollutants in manganese and iron nodules⁸⁵. In riverine clay minerals of the Yangtze river, high total contents were found. However, the metals were mainly extracted in the residual fraction, emphasizing the importance of natural weathering and erosion in the drainage basin⁸⁷.

For surveying soil or sediment contamination, a partial, single step extraction that is not phase-selective but affects a variety of labile and relatively stable trace metal associations may be easier to apply and more suited to carry out when many samples are involved. Mesuere *et al.*⁸⁹ investigated the characteristics of a fast and simple method that involved $\text{HNO}_3/\text{H}_2\text{O}_2$ extraction on Cu-contaminated sediments. They found the method reliably extracted Cu in excess of native levels.

ASSESSMENT OF METAL MOBILITY

Metal mobility can be estimated by comparing sequential extraction results before and after treatment of the solid material by controlled intensification of relevant release parameters like

pH, redox-potential and temperature. In this context, extrapolation from sequential extraction data before and after such an experiment could provide an estimate of the endpoint of release⁵¹. This approach was illustrated for thallium in a waste from high-temperature incineration processes⁹⁴.

Sequential extraction gives at most a qualitative idea about the reactivity and mobility of total contents present, both in soils⁹⁵⁻⁹⁷ and sediments^{86,98-101}. The relation between leaching behaviour and solid phase fractions is not always univocal⁴⁵. Tack and Verloo¹⁰² demonstrated that the quantities leached from a sediment changed drastically when the sediment was heated at different temperatures. In contrast, this observation was almost not reflected by changes in the solid fractionation (Figure 2). Sediments with a similar solid phase fractionation may exhibit a different leaching behaviour. This, combined with the lack of specificity and selectivity associated with sequential extraction^{44,52,54,55,103} limits the capability of sequential extraction in quantitatively predicting metal release.

From metal speciation in solution, apparent discrepancies, arising from considering only total concentrations, may be resolved. In lysimeter experiments, metal mobility was assessed by measuring 1) uptake in plants, 2) accumulation in the underlying soil, and 3) leaching with gravity water¹⁴. This leads to opposite conclusions about the mobility order of the considered metals (Cu < Pb < Zn in plants and subsoil, Pb < Zn < Cu in leachate). The particular behaviour of Cu was explained by the high association with organic matter. This example also illustrates that the notion of "metal mobility" can have different meanings and therefore must be properly defined.

ASSESSMENT OF BIOAVAILABILITY

Speciation of metals largely determines their bioavailability and toxicity⁴. Speciation techniques were used to relate observed metal behaviour in soil and sediment systems to their chemical forms and to provide additional evidence for explaining observations. Attempts to quantitatively predict bioavailability and toxicity from speciation data, however, were essentially unsuccessful. This is not only due to limitations of analytical speciation techniques, but also to the complexity of the interactions between heavy metals and biota.

Uptake by plants

Geochemical methods for assessing the potential bioavailability of metals in the field are largely empirical and depend on chemical extraction techniques¹⁰. Single reagent leaching tests are most often used and correlated with plant uptake or toxicity^{104,105}. Frequently used single reagents are 0.1M NaNO₃¹⁰⁶⁻¹⁰⁸ and 0.005 M DTPA¹⁰⁹⁻¹¹⁶. They were related with plant uptake on soils, amended with sewage sludge^{97,104,111,117,118}, and manure¹¹².

No single approach is available for the adequate prediction of plant uptake. Jung Jin and Logan¹¹⁹ correlated different estimates of bioavailability (total Cd extracted in different extractants and the Cd²⁺-forms in those extracts, estimated with the program GEOCHEM³⁶) with uptake by Sudax in soils, amended with a range of sludges. Total contents were not significantly correlated with uptake. All indices of sludge bioavailability were significantly correlated but explained only about 60% of the variability. Only in a homogeneous system (same soils), high correlations were obtained, but with different predictors for different metals

and different parts of the plant.

The use of sequential extraction does not provide benefits in this context. A relation between sequential extraction data and metal mobility and phytoavailability may be observed but is difficult to quantify^{114,115,120}. Positive correlations between fractions obtained by sequential extraction and Cu uptake were found. However, the best equation included DTPA-extractable Cu and clay content, showing DTPA to be a good predictor of Cu-availability in prairie soils. For Zn however, DTPA was not successful because of diverse soil properties. Sequential extractions carried out before and after the experiments showed Zn-uptake was from the exchangeable, acid soluble and possibly residual fractions¹¹⁴. Sims and Kline¹¹⁸ did not observe consistent correlations between the total content or individual metal fractions and plant concentration. However, significant multiple regression models between metal fractions, pH and plant metal uptake were found.

Martin *et al.*¹³ reviewed the "promises and problems" of extraction procedures and concluded that " . . . some useful information has been obtained in the field of engineering and geoscience. However, the original idea, which led to the development of the methods, ie. the estimation of trace elements bioavailability, generally failed."

Uptake by biota

Bioavailability, accumulation and effects of heavy metals in sediments were reviewed by Bryan and Langston¹⁰. The use of geochemical leachates has, so far, yielded the best practical means of deriving predictive relationships between metal burdens in benthic organisms and their sedimentary environment. These relationships are of an empirical nature only¹⁰. For example, EDTA and dilute HCl were good predictors for the concentration of metals in invertebrates, but only within similar sediments. Using a range of sediments, only Pb was predicted well¹²¹.

In particular, metal fractions obtained from sequential extractions may correlate with concentrations in microorganisms. Exchangeable, weak acid soluble, reducible and oxidizable fractions are considered the fractions that are more or less available to aquatic biota^{21,122}.

Some of the better relationships between concentrations of metals in deposit-feeding organisms and those of the sediments depend on normalizing extracted metal concentrations with respect to a particular sediment fraction (e.g. metal/Fe or metal/% organic matter ratios). This clearly indicates that the bioavailability of the metal not only depends on its own concentration, but also on those of the sediment components (e.g. oxides of Fe or organics) to which it is sorbed¹⁰. For example, Pb content in mussels and sequential fractionation data improved strongly when the data were normalized with respect to total S, suggesting the role of sulfides in controlling Pb availability¹²².

Relations between metals in solution and metal levels in organisms are more difficult to assess because of the local and temporal variability of dissolved metal concentrations. Results from speciation between total metals and ASV-labile metals varied unpredictably between metals and between sampling day. These variations were related to mixing currents, varying temperature, and sedimentary input²¹. In model systems on the other hand, good correlations were found between toxicity of metals to the freshwater ciliate *Tetrahymna* and ASV-labile metals²². Another factor, rendering the correlation with dissolved metal concentrations less straightforward is that other factors, e.g. ingestion of sediments, may control the uptake of metals^{10,22}.

Metal speciation in metal toxicity studies may help in explaining observed toxicity of

different media. However, the interpretation is rendered difficult, because besides metal speciation, several other factors influence the toxicity of metals: (1) the relative stability constants of the various ligands for the metals, (2) the affinity of the organisms for the metals, (3) the release of metals by biological degradation of metal containing ligands, (4) the physiological condition and viability of the organisms and (5) competitive action of calcium and other ions, which do not necessarily affect the speciation of the heavy metals¹⁶.

CONCLUSIONS

Chemical speciation of metals in soils and sediments is still in the early stage. Most of the papers concentrate on method development. When speciation techniques are applied in research, an array of analytical chemical problems makes data difficult to obtain and uncertain, rendering interpretation unsure.

Until now, almost no methods are undisputed or established. Only for particular cases, f.i. the determination of Cr(VI) or As(III), or organometal compound of metalloids (Sn, As), well-defined species can be determined convincingly. For metal speciation in solution, only broad categories may be discerned (different charge, molecular size, complexed or uncomplexed). A detailed speciation has to be guessed from thermodynamical calculations. The latter approach suffers from a limited knowledge of equilibrium constants, incomplete knowledge of the studied system and the lack of taking kinetics into account. However, sensitivity, rather than selectivity and specificity, is the main analytical problem concerning speciation in solution.

The differentiation of total contents in solid matrices remains largely operationally defined. Nevertheless, sequential extraction has proven its value in the field of geochemistry. When combined with other data, sequential extraction results can help in supporting hypotheses. The information however is too uncertain to provide hard evidence and always must be interpreted with extreme care and in the context of other observations.

Methods should be further developed to be more sensitive, specific and selective, allowing quantification of well-defined species. For speciation in solution, increasing the sensitivity is a main challenge. Development of solid phase speciation techniques primarily should be aimed at increasing selectivity and specificity. Further automatization of techniques is for now not a priority.

More attention should be focused towards appropriate sampling, sample handling and conservation, which is indispensable for obtaining reliable results. The influence of sampling should be quantified to provide a support for the development and standardization of appropriate techniques.

Because chemical speciation will remain time consuming and expensive, computer programs are of great help. Kinetic aspects should be included. Mainly for the solid phase, models are very limited, and particularly in that phase, kinetics are extremely important.

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