

## Utilization of Selective Extraction Techniques for Element Speciation in Soils and Sediments - Critical Evaluation of the Contemporary State

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**Abstract.** Requirements for environmental quality assessment and management have necessitated the development of selective chemical extraction procedures to evaluate trace metal mobility in soils and sediments, and uptake by biota. Although extraction procedures have been widely used on atmospheric particulates, dust and fly ash, street dust and roadside soils, sewage sludge, incinerated sludge ash, and soils and sediments, their status as useful analytical tools is controversial. This article reviews the major extraction techniques in use, and considers criticisms, and the suitability of these methods, in light of recent research findings. It concludes the review with recommendations for further developments to improve the validity of extraction techniques and understanding of the important biogeochemical phases and processes in soils and sediments.

**Key words:** speciation, soil, sediment, sequential extraction procedures

### Introduction

Sequential chemical extraction techniques have been used to characterize chemical forms of elements in soils and sediments, which helps to predict elemental environmental availability, toxicity, and hazard to living organisms. Selective extraction procedures, consisting of subjecting a given sample to a series of increasingly strong reagents under specified conditions, have been extensively employed. They are based both theoretically and experimentally on more than 100 years of research (Jackson, 1985). These have been used to determine the „species“ of particulate metals and radionuclides in soils and other natural particulate phases and to predict the extent to which contaminants may become mobilized should sediments be resuspended, and geochemical conditions change.

The metals in soils and sediments may be present in several geochemical phases that act as reservoirs or sinks of trace elements in the environment. Factors affecting the distribution of an element among different physicochemical forms include pH, ionic strength of the solution, the solid and solution components and their concentrations and affinities for an element, and time (Ritchie & Sposito, 1995). Elements may sorb to clays, metal hydrous oxides, silicates, carbonates, soil or sediment organic matter, or sulphides. In solution, elements may be in the solvated form (solvation complex) or complexed with organic and inorganic ligands. Speciation may also consider the type of bonding between an element and other solid components. For example, an element in ionic form may bind to clay minerals or organic matter by coulombic forces, whereas covalent bonds may be formed with surface ligands on hydrous oxide surfaces (Fendorf et al., 1994). Ligands can form inner or outer-sphere complexes with cations, either in solution or on an adsorbent (Ritchie & Sposito, 1995).

Total concentration was generally used to assess the potential effects of soil and sediment contamination. Tessier et al. (1979) stated that this implied that all forms of a given metal had an equal impact on the environment and pointed out that such an assumption was clearly untenable. Many methods have been employed to fractionate elements depending on the composition of the substrate and the portions of the substrate considered most important. Jones and Hao (1993) reviewed and evaluated 60 papers concerned with sequential extraction methods for natural systems and concluded that these methods have proven useful for metal speciation. The development of selective extraction procedures, as distinct from simple measurements of „total“ metal in environmental samples, has been gradual.

The numerous reagents used and sequential schemes proposed in the literature, however, illustrate the difficulty in selecting the best method for the study of the different metal phases. The specificity and reproducibility of methods depend strongly upon the chemical properties of the element, the chemical composition of the samples, and various experimental factors. There is no general agreement in the literature on the solutions preferred for the various sediment and soil components to be extracted, due mostly to the „matrix effect“ involved in the heterogeneous chemical processes. The most appropriate extractants are determined by the aim of the study, by the type of solid material (sediment or soil, sewage sludge, fly ash, dredged harbour mud, street dusts, manganese nodules, and so on), and by the element of interest. A vast literature exists on specific research areas, with appropriate extractant formulations for a selected problem. Reviews exist in such fields as geochemical prospecting, trace metal speciation in soils in general or more specifically in sewage sludge-amended soils, sediments, deep sea geochemistry, fly ash characterization, and solid



waste (e.g. Pickering, 1986; Förstner et al., 1990; Förstner, 1986). These papers usually give many experimental details as a basis of evaluation of the selectivity and effectiveness of reagents, such as solid to solution ratios, treatment times, specific extraction chemistry and matrix effects of many of the different reagents, and similar suggestions.

During the last decade, a great effort was devoted to the problems and to the further development of chemical analytical speciation techniques. Fractionation procedures and detection methods are being refined and new combinations of existing techniques were applied (Broekaert et al., 1990; Ure & Davidson, 1995).

The aim of this article is to evaluate the most recent extraction techniques in use, their suitability for most applications, the criticisms of these methods in light of the most recent research findings, and to recommend further developments for improvements of extraction techniques.

### Definition of Speciation

There is no generally accepted definition of „speciation“, and various meanings have been attributed to the term by different workers. Here, the broad definition evolved under the auspices of the Commission of the European Communities, Community Bureau of Reference, BCR (Ure et al., 1993a, b) is used. In this context, speciation may be defined as either (a) the process of identifying the different, defined species, forms or phases present in a material; or (b) the description of the amounts and kinds of these species, forms or phases present. Whichever approach is taken, the species, forms or phases are defined (a) functionally, (b) operationally, or (c) as specific chemical compounds or oxidation states.

### Why the Need for Speciation in Soils ?

The existence of an element in different chemical forms in the gaseous, solid, or aqueous solution phases provides the conceptual basis for speciation in soils. More specifically a „chemical species“ in soil refers either to a specific molecular arrangement of the atoms of an element or, quite often, to the result of an operational process of detection and quantification aimed at elucidating the chemical forms. A comprehensive review of the species in soils can be found in the monograph by Schlesinger (1991).

The existence of an element in a soil is transitory, because the soil is only one „compartment“ in the biogeochemical cycling of elements in an ecosystem. The residence time of an element, however, varies considerably, depending on the mobility of its predominant species and the rate of soil evolution (Sposito & Page, 1984). For example, aluminium, iron and silicon are the most abundant elements in soils, but < 1 % of their soil chemical species cycle in one year because most of their chemical forms are extremely immobile. This slow cycling is fortunate, considering the toxicity of Al to plants and animals, but unfortunate if iron nutrition is thereby limited. Thus,

slow cycling becomes a problem if it can lead to soils being deficient in elements that are required for plant growth (e.g. Fe, Cu and Zn).

The soil solution is the medium through which dissolved species are transported to a root surface and carried to groundwaters or surface waters. In addition, it acts as an important link between solid soil phases and other components of an ecosystem involved in biogeochemical cycling. The general behaviour and properties of the soil solution have been reviewed (Sposito, 1986), as have the reactions of trace elements in soil solutions (Kabata-Pendias & Pendias, 1992). The total dissolved concentrations of trace elements vary quite widely depending on several factors, such as soil type and use and the proximity to potential pollution sources (Kabata-Pendias & Pendias, 1992). Ionic strength, pH and electron activity (pE) are the three major characteristics of the soil solution commonly recognized as affecting metal speciation. However, reaction kinetics and the relative concentrations and complexing affinities of cations and anions may be equally important (but are sometimes overlooked). The kinetics of reactions in solution are well documented from a theoretical perspective (Sparks, 1989). The kinetics of reactions between components in solution are considered to be so fast, if compared to solid-solid or solid-solution reactions, that it is justifiable to assume that solution equilibrium exists. In many cases, this is a reasonable assumption - for inorganic complexes in particular - but it may not be so for metal complexing by multidentate organic ligands, such as humic and fulvic acids, and some inorganic ligands (Sposito, 1986; Hering & Morel, 1990). For example, humate and fulvate ligands often have been treated in experimental study as monodentate ligands when considering their reactions with metal ions (e.g. Hering & Morel, 1990). In reality, this is unlikely to be the case and it is not possible to predict the net effect on reaction rates. Given the importance of metal-humate/fulvate reactions to plant uptake, it is an area that warrants further research to establish the importance, if any, of kinetics in the availability of metal cations to plants.

Metal cations may be soluble, readily exchangeable, complexed with organic matter or hydrous oxides, substituted in stoichiometric compounds, or occluded in mineral structures (see reviews by Beckett, 1989; Förstner, 1991). The chemical factors that affect the retention of a specific chemical form of a trace metal (e.g. effects of pH and ionic strength on „specific adsorption“) are well documented (Alloway, 1990; Förstner, 1991). Increasing soil pH (or I) increases the number of sorption sites available on clay minerals, hydrous oxides, or organic matter, but will not necessarily increase the amount of a trace metal adsorbed by a soil component unless that specific component binds the metal most strongly and there are sufficient sites for adsorption. For example, increasing the pH of a soil that contains mainly hydrous oxides and kaolinite may only increase the fraction of total Cd („% Cd“) bound to hydrous oxides (Mann & Ritchie, 1993). If sufficient Cd is added, however, the amount of total Cd that is in an exchangeable form can increase at lower pH values because of a lack of adsorption sites on hydrous



oxides. By contrast, raising the pH of a lateritic podzol (which contain mainly kaolinite) from 4 to 5 at both application rates of Cd increased % Cd in the exchangeable form because it was the major form present. The application rate did not affect % Cd in the exchangeable form, which indicated an excess of sites, even at pH 4. At higher pH values, exchangeable Cd decreased, possibly because Cd was adsorbed onto sites that were less accessible and could be displaced only by acid extraction, i.e. the residual form. In the same study, increasing the pH of a sandy soil increased exchangeable Cd at the expense of soluble Cd. The more Cd present, the smaller was the decrease in soluble Cd because of a lack of cation exchange sites.

The distribution of trace metals among soil components is important for assessing the potential of soil to supply sufficient micronutrients for plant growth or to contain toxic quantities of trace metals, and for determining amelioration procedures for soils at risk of causing the trace metal contamination of waterways.

### Why the Speciation in Sediments ?

The tendency of an element to be accumulated by organism depends in particular upon the capacity of a sediment - water system to resupply trace elements removed from solution by biotic and abiotic processes. Solid components in sediments govern the dissolved levels of these elements via sorption-desorption and dissolution-precipitation reactions. Thus, particular trace metal species identification tends to be far more instructive than any total elemental concentrations. In order to assess the environmental impact of a given pollutant the following points must be addressed in contaminated sediment-water systems (Kersten & Förstner, 1995):

- 1.) What is the reactivity of the metals introduced with solid materials from anthropogenic activities (hazardous waste, sewage sludge, atmospheric deposits, etc.) by comparison with the natural components ?
- 2.) Are the interactions of critical metals between solution and solid phases comparable for natural and contaminated systems ?
- 3.) When the solid inputs or the solid-solution interactions lead to weaker bonding of certain metal species, are the factors and processes of remobilization effective in contaminated sediments, as compared with natural systems ?

While most direct physico-chemical speciation approaches are too insensitive for the trace amounts of environmentally relevant metals encountered in sediment, wet chemical extractions have been shown to provide a convenient means to determine the metals associated with the principal accumulative phases in sedimentary deposits and to elucidate the mechanisms of their diagenetic transformation. A general goal of all studies involving selective chemical extraction is the accurate determination of the partitioning of elements of environmental concern among different discrete phases of a sample. Mineralogical constituents of sediment considered important in controlling metal concentrations in sediment are hydrous

oxides of iron and manganese, organic matter, and clays. Fractionation is usually performed by a sequence of „selective“ chemical extraction techniques which include the successive removal or dissolution of these phases and their associated metals. Despite the clear advantages of a differentiated analysis over investigations of the bulk chemistry of sediments, verification studies conducted in recent years indicate that there are many problems associated with „operational“ speciation by partial dissolution techniques. It is common for studies in wet chemical extraction to point out that the various extractants used are not as selective as expected. Van Valin & Morse (1982) concluded that „the concept of an operationally defined element reactivity is generally used rather than attempts to characterize each phase individually“. In recent years, some reviewers came to conclusions as pessimistic as „these techniques represent nothing but an operational tool and complementary approach until physical techniques are available with the new generation of microprobes and other sophisticated instruments“. On the other hand, the results of the comparative study performed by Lion et al. (1982) suggest that „the role of sediment components may be evaluated from the perspective of competitive adsorption phenomena and that sediment adsorption characteristic and extractant-determined component-metal associations yield consistent information on the binding of metals“.

### A Review of the Most Frequently Used Sequential Extraction Techniques for Soils and Sediment Fractionation

#### The Tessier Method

In this landmark work, Tessier et al. (1979) proposed a five-step scheme consisting of selective extractants used in a sequence, to determine the forms in order of their decreasing solubility. The solids are extracted with  $MgCl_2$  (Exchangeable metals),  $NaOAc$  (Carbonate-bound metals),  $NH_2OH \cdot HCl$  in  $HOAc$  (Fe+Mn-oxide-bound metals),  $H_2O_2$ ,  $HNO_3$ , followed by treatments with  $H_2O_2$ ,  $NH_4OAc$  and  $HNO_3$  (organically-bound metals), and finally  $HF-HClO_4$  digestion (metals in the residue). Solids are rinsed with distilled water between extraction steps and the rinse water is discarded.

*Exchangeable:* In the Tessier scheme, the first or „exchangeable“ fraction is obtained with a magnesium chloride solution (1 mol/L, pH=7.0) or a sodium acetate solution (1 mol/L, pH=8.2). According to Chapman (1965), the solubility of  $CaCO_3$  in sodium acetate is low. The  $CaCO_3$  fraction solubilized in relation to the total  $CaCO_3$  content of the sample. A sodium acetate solution (1 mol/L) adjusted to pH=8.5 and a 0.5 g sample was chosen for the first fraction by Orsini and Bermond (1994) to minimize the loss of carbonates. Water soluble and exchangeable phases are regarded as mobile and readily bioavailable, whereas other forms are of minor importance for uptake (Chlopecka, 1993; Dudka & Chlopecka, 1990). The reagents found to give the best correlations to plant uptake in different studies include



water, 1 M  $\text{MgCl}_2$ , 0.05 M  $\text{CaCl}_2$ , 1 M  $\text{NH}_4\text{OAc}$ , 0.1 M  $\text{NaNO}_3$ , 1 M  $\text{KNO}_3$ , 1 M  $\text{NH}_4\text{NO}_3$ , acidified ( $\text{NH}_4$ ) $_2$  $\text{C}_2\text{O}_4$ , 0.1 N  $\text{H}_3\text{PO}_4$ , 0.1 N  $\text{HCl}$  and DTPA (diethylenetriaminepentaacetic acid), indicating that several alternate reagents to those of Tessier have proven useful.

**Bound to carbonates:** Tessier et al. (1979) used 8 mL of 1 M  $\text{NaOAc}$  adjusted to pH 5 with acetic acid. The complete dissolution of  $\text{CaCO}_3$  can be limited by its solubility in the extract and by the dissolution kinetics. The dissolution time depends upon several parameters related to the sample: the grain size, the  $\text{CaCO}_3$  content, the nature of the carbonates and the sample size. Orsini and Bermond (1994) found that a 1 M  $\text{NaOAc}$  solution adjusted to pH=5 with acetic acid completely dissolved the  $\text{CaCO}_3$  while dissolving little or none of the iron and manganese oxides after 5 h. Tack & Verloo (1995) determined that the conditions of the acid extractable step in the Tessier sequential fractionation scheme are not suited to dissolve selectively carbonates and associated metals if the sediment has a high carbonate content (>10 %). From thermodynamics, it is expected that large amounts of Fe would dissolve in these conditions. Experimentally, this solubilization of Fe does not occur, but the solubilization of carbonates is incomplete for kinetic reasons.

**Metals associated with manganese and iron oxides:** Tessier et al. (1979) extracted this fraction with 20 mL of either 0.3 M  $\text{Na}_2\text{S}_2\text{O}_4$  plus 0.175 M Na-citrate plus 0.025 M H-citrate or 0.04 M  $\text{NH}_2\text{OH} \cdot \text{HCl}$  in 25 % (v/v)  $\text{HOAc}$  at  $96 \pm 3^\circ\text{C}$  with occasional agitation for as long as required. A reducing solution of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  solubilizes iron ( $\text{Fe}^{3+}$  into  $\text{Fe}^{2+}$ ) and manganese ( $\text{Mn}^{4+}$  into  $\text{Mn}^{2+}$ ) oxides. Chao (1972) found 0.1 M  $\text{NH}_2\text{OH} \cdot \text{HCl}$  was specific for Mn oxides. Others concur (Hickey & Kittrick, 1984; Gibson & Farmer, 1986), although Gupta and Chen (1975) found it did not dissolve all of the Mn oxide nodules. Some workers have discriminated between metals bound to amorphous Fe oxides and crystalline Fe oxides. Gupta and Chen (1975) used hydroxylamine to extract metals from amorphous Fe oxides, yet the same reagents, at a greater concentration, did not dissolve magnetite (Singh et al., 1988). Oxalate [ $(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{H}_2\text{C}_2\text{O}_4$ , in the dark] was used by Miller et al. (1986) for extracting metal from Fe oxides. Other reagents used to dissolve the crystalline iron oxides are sodium dithionite - citric acid and oxalate with ultraviolet irradiation (Gupta & Chen, 1975; Miller et al., 1986; Singh et al., 1988). Tessier et al. (1979) report that  $\text{NH}_2\text{OH} \cdot \text{HCl}$  dissolves some silicates in sediments; however, silicate dissolution seems to be negligible in soil. Heron et al. (1994) have more recently suggested several extractants for Fe under different redox environments.

**Organically bound metal:** Tessier et al. (1979) add 3 mL of 0.02 M  $\text{HNO}_3$  and 5 mL of 30 %  $\text{H}_2\text{O}_2$  adjusted to pH 2 with  $\text{HNO}_3$  to the soil or sediment and heat the mixture to  $85 \pm 2^\circ\text{C}$  for 2 h with occasional agitation. A second 3 mL aliquot of 30 %  $\text{H}_2\text{O}_2$  (pH 2 with  $\text{HNO}_3$ ) is

then added and the sample is heated again to  $85^\circ\text{C}$  for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M  $\text{NH}_4\text{OAc}$  in 20 % (v/v)  $\text{HNO}_3$  is added the sample diluted to 20 mL and agitated continuously for 30 min to prevent readsorption of heavy metals to the oxidized sediment. Hydrogen peroxide is the commonly used extractant for this fraction (Gupta & Chen, 1975; Gibson & Farmer, 1986) even though it dissolves Mn oxides (Keller & Vědy, 1994) and does not dissolve all forms of organic matter. Hydrogen peroxide seems to be more efficient when used after the oxide extraction step. Orsini and Bermond (1994) found the kinetics of destruction of organic matter was slower than originally specified by Tessier and took 24 h.

**Metals in the residues:** Tessier et al. (1979) recommended the solubilization of the metals bound to the residue using a 5:1 mixture of HF and  $\text{HClO}_4$  in a platinum crucible, however, many have successfully used polypropylene tubes. Orsini and Bermond (1994) show that a duration of 24 h is sufficient to achieve the complete solubilization of Cu. The method used by Miller et al. (1986) digests the residue with concentrated  $\text{HNO}_3$  (65 %), but only  $\approx 60$  to 80 % of the metals dissolved under these conditions (FAC, 1989). Aqua regia dissolves all the metals in the residue except those in the silicates; the percentage extracted varies between 60 and 100 % depending on the metal (Keller & Vědy, 1994). In general, aqua regia, HF and  $\text{HClO}_4$  have been used in that order, though the order has been varied and the reagents combined. After HF treatment of the extraction residues, newly formed fluorides may be found (Hirner, 1992).

These and similar sequential extraction protocols have been applied to atmospheric particulates, dust and fly ash (Hirner, 1992), street dust and roadside soils (Gibson & Farmer, 1986), sewage sludge (Legret, 1993), incinerated sludge ash (Förstner, 1993), as well as soils and sediments (Gupta, 1989; Sheppard & Thibault, 1992). Other extraction schemes have been proposed (Salomons & Förstner, 1980; Towner, 1985) and multistep extractions involving various reagents have been described by many authors (McLaren & Crawford, 1973; Gupta & Chen, 1975; Chang et al., 1984; Miller et al., 1986; Singh et al., 1988; Oughton et al., 1992). Some authors have coupled this technique with physical fractionation (Keller & Vědy, 1994).

### The BCR Extraction

The BCR method (originating with the European Community Bureau of Reference, Quevauviller et al., 1994, 1998) consists of three sequential extraction steps using (1) acetic acid, (2) hydroxylammonium chloride, and (3) hydrogen peroxide/ammonium acetate. Between extracting reagents, the solids are rinsed with distilled water; rinses are discarded.

Results from the BCR extraction protocol, intended to harmonize and standardize selective extraction techniques (Lopez-Sanchez et al., 1993) were compared with results



of the Tessier extraction procedure on the same sediments. Although both methods gave reproducible results, substantial differences were found between the metals extracted by similar reagents. In particular, the BCR consistently extracted more metals (Cd, Cr, Cu, Ni, Pb and Zn), assumed to be associated with organic matter or sulphides, than did the Tessier procedure. Whalley and Grant (1994) used the BCR procedure to analyze mineral phases previously equilibrated with metal-spiked (Cu, Ni, Zn) artificial seawater and found that the results were acceptably precise in comparison with real river sediments. In another study using the BCR procedure, Davidson et al. (1994) summed up the yields of metals in the three fractions to ensure they equalled the „total“ metals as measured by acid digestion. The results of an initial study on the stability and reproducibility of metal „speciation“ in a standard reference material, using the BCR extraction for Cd, Cr, Cu, Ni, Pb and Zn, showed generally stable distributions among the extraction fractions over a period of eight months (Fiedler et al., 1994). The results of an interlaboratory comparison study using another reference material, however, were less promising (Quevauviller et al., 1994). In this study, many contributing laboratories were unable to submit qualifying results.

#### Other Notable Selective Extraction Methods

Bendell-Young et al. (1992) proposed a method intended to reduce the complexity and robustness of selective extraction procedures, while maintaining comparability with the Tessier method. Another sediment method uses the Acid Volatile Sulphide (AVS) fraction, the solid phase sediment sulphide fraction that is soluble under cold acid conditions, to determine biological availability and toxicity. It has been proposed (Ankley et al., 1991) that this fraction is capable of binding an equimolar quantity of trace metals such as Cd and Ni, and that bioavailability and toxicity in sediments do not commence until the sediment metal : AVS ratio exceeds unity. Solubilization of organics using complexing reagents, such as pyrophosphate, EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid), that competitively desorb metal, or by oxidizing reagents ( $H_2O_2$ ,  $NaClO_4$ ) that destroy the binding sites in the organic matter, is also common (McLaren & Crawford, 1973; Miller et al., 1986; He & Singh, 1993).

#### Limitations of Selective Extraction Methods

The Tessier method has been extensively criticized since its inception (Accomaso et al., 1993; Förstner, 1993; Gupta & Chen, 1975; Heron et al., 1994; Kheboian & Bauer, 1987; Miller et al., 1986; Nirel & Morel, 1990; Orsini et al., 1994; Pickering, 1986; Riise et al., 1994), yet it remains a widely-used extraction procedure. Criticisms include: the extractions are not as selective as they were hoped to be, a problem recognized by Tessier et al. (1979); minor variations in analytical procedures have significant effects on the results; metals released by the

dissolution of one solid phase may be re-sorbed during the extraction process by remaining solid phases; metals may be mobilized and lost when distilled-water rinses are discarded; the overall procedure is imprecise and poorly reproducible; and labile phases may be transformed during the procedure, leading to an incorrect assessment of metal distribution in sediment (this point applies particularly to anoxic sediments). Lack of standardization and reference materials, lack of analytical sensitivity to detect metals in the extracted fractions, concern about background contamination in reagents and labware or during the many manipulation steps, and matrix interferences between some extraction reagents and trace metals being analyzed are also cited as problems.

We can discuss seven areas where sequential extraction procedures have been criticized. Many of these issues occur at the same time and confound the interpretation of the results. These include: 1) sample handling and preparation methods, 2) failure to sample pore water, 3) non-specificity of the extractant for a particular contaminant of concern in a specific media, 4) readsorption and redistribution of the heavy metal of interest during the extraction, 5) insufficient procedure duration for the kinetics of the expected reaction, 6) surface occlusion causing inefficiency of the extractant, 7) quality assurance, analytical sensitivity, and matrix interferences.

#### Sample Handling, Preparation and Storage

The preparation and storage of samples for qualitative and quantitative determinations of species of one or several elements has always required special attention. The nature of this task differs from procedures adopted for total elemental analyses. However, it is essential to keep in mind that data on total elemental concentrations are often necessary in many investigations. Any procedure adopted for the preservation of samples between the time of collection in the field and the opportunity for analysis in the laboratory should not disturb the equilibria among the species. Contaminated solid materials are not necessarily stable (Whalley & Grant, 1994) and correct sample handling and storage prior to manipulation, extraction and analysis are critically important. Rubio and Ure (1993) discuss and compare approaches to sampling, sample pretreatments, contamination control, and consider the suitability of the extracting solution matrix for the analytical technique. Definitive protocols for sampling and sample pretreatment are required to prevent changes from reducing to oxidizing conditions, transformations of sulphides, pH shifts, light catalysed reactions, reactions with the sample container, time delays before analysis with biologically active samples, etc. Förstner (1993) reviewed concepts in sediment metal speciation and emphasized the sensitivity of sequential extraction techniques to artifactual changes in sediment geochemistry between sampling and analysis. A sequential extraction of sediments from Hamburg harbor, performed under oxygen-free conditions, indicated that essentially all of the Cd associated with anoxic mud was bound in a sulphidic fraction. In contrast, samples exposed to oxygen or dried before ex-



traction showed completely different distributions of Cd, a shift towards the reducible, carbonate-bound, and exchangeable phases. Maintaining strictly anaerobic conditions between the moment of sampling and analytical procedure can be a daunting challenge.

Sequential extraction of soils from the vicinity of a Polish copper smelter suggested a high proportion of Cu and Pb could be mobilized from the exchangeable and carbonate fractions of the soil (Rybicka et al., 1994), yet Scanning Electron Microscopy/Energy Dispersive X-ray (SEM/EDX), spectroscopy of soil particle size fractions indicated that both metals were mainly associated with sulphides and/or sulphates. The explanation put forward was that oxidation reactions during handling and/or extraction had converted much of heavy metal sulphides to soluble hydrous sulphates. However, SEM preparation is not benign and must also be considered as a manipulation of the sample.

Reliable and generally applicable methods for the preservations of the original distribution of the species in natural sediment and soil samples do not yet exist. Thus, it is important to be aware of the kinds and degrees of changes taking place in the soils or sediments while they are actually being studied. Whatever the extraction procedure chosen, the validity of selective extraction results will, however, be primarily dependent on the ways in which the samples are collected and preserved prior to analysis.

#### Failure to Sample Pore Water

Soluble contaminants in sediments may be transported to the water column with discharging groundwater, by diffusion, or through the pumping action of burrowing invertebrates. Although transport in the water column is rapid, transport in bulk sediments is typically dominated by molecular diffusion and concentration gradients. Thus, bioavailability, toxicity, and environmental mobility can be assessed from pore-water concentrations. However, sediment contaminant pore-water concentration gradients are rarely measured despite being technically feasible (either using „peepers“ or by squeezing or centrifuging of core material). Sediment (soil) pore water concentrations also permit determination of the sediment (soil) - solid : pore-water partition coefficient,  $K_d$ . Stephenson et al., 1995 determined cadmium  $K_d$  values and they found that the highest  $K_d$  values are in the organic sediment cores from 8–9 m of water and the lowest are from a shallow (3 m) sandy core, which also had the highest sediment pore water Cd concentrations. The lower  $K_d$  values at depth in all cores imply that post-depositional mobility of free Cd is likely: the high  $K_d$  near the sediment-water interface suggest that natural enrichment of total Cd in surface organic sediment can be expected. These results show that sediment pore water contaminant concentrations can provide direct and relevant evidence for the assessment of biological impacts, and trace element fluxes and fate, in the environment.

Partition coefficients determined from soil pore water and solids, extracted from cores that were allowed to

freeze in-situ in a long-term field study, are preferred to  $K_d$  values measured in the laboratory using batch  $K_d$  methods (Sheppard et al., 1993).

The use of pore water analysis for realistic  $K_d$  determination is important in soils where solid to solution ratios are normally large and anoxic pockets exist even in well-aerated profiles. This is especially important for very mobile elements such as I and As, and for elements such as Tc or U, that are strongly influenced by redox potential. Pore water measurements are certainly as important as chemical extraction results, yet the importance of pore water is ignored in all major extraction schemes.

#### Nonspecificity of the Extractants, Readsorption and Redistribution

Two major experimental problems with sequential procedures have been recognized: nonselectivity of extractants, and trace element redistribution among phases during extraction (Kheboian & Bauer, 1987; Nirel & Morel, 1990; Kim & Fergusson, 1991; Tessier & Campbell, 1991; Bermond & Eustache, 1993; Förstner, 1993; Xiao-Quan & Bin, 1993). Generally it is difficult to associate a given extractant reagent with a particular physicochemical phase. Instead, the specificity of an extractant is operationally defined according to what it extracts; e.g. acetate buffer extracts the „acetate-buffer-extractable“ phase. Although it is often believed that this particular phase includes carbonate minerals, these minerals may not be uniquely attacked by this reagent. This is the nonselectivity problem. For the other problem - redistribution - trace elements liberated by one extractant have an opportunity to reassociate with remaining undissolved sediment (soil) components before recovery of the extract. Both processes scramble the true phase association of the trace elements thus complicating interpretations.

Lack of geochemical specificity was reported in experiments where Kheboian and Bauer (1987) studied metal spike recovery from mixed model phases. Kim and Fergusson (1991) studied the extent of Cd redistribution between phases by sequentially extracting and comparing a range of „synthetic“ soils with a real soil. Shannon and White (1991) examined the selectivity of the Tessier method for FeOOH, FeS and FeS<sub>2</sub> minerals in sediment. Although the method worked reasonably well for amorphous FeOOH, sulphide minerals (particularly FeS) tended to be extracted prematurely. Tessier et al. (1990) reported a modification of the internal structure of ferrous smectites after a reduction treatment. Peroxide, in this case, seemed to act as a strong solubilizing reagent for the clay minerals (smectites and chlorite) that had become less resistant to this reagent by the action of hydroxylamine, used as a reducing agent, in the previous step. Jarvis (1984) showed that it was difficult to precisely define whether Cu or Cd was associated with either one or the other oxide in an Fe-Mn oxide mixture. Beckett (1989) presented the survey of the extractants most commonly used and listed the groups of compounds it is presumed that they extract. This survey also discusses the



efficiency of extractants at mobilizing iron, manganese, and aluminium, with the implication that an extractant that dissolves a particular category of iron oxide, etc., also mobilizes any trace metals that it contains.

The problems with nonspecificity of used extractants are also connected with the natural tendency of nonspecialists to adopt published extractant sequences as standard procedures, without appreciating the reservations of their proposers. For example, the effects of acid ammonium oxalate extractant have been shown to depend on the nature and degree of illumination of the reaction mixture (e.g., dark, daylight, or ultraviolet light), yet many publications do not specify which illumination was employed, and some workers at least appear to have worked under the undefined illumination of an open laboratory. Other workers have not recorded the pH, concentration of their extractants, reaction times or ratio of extractant to sample.

Bermond and Benzineb (1991) have studied readsorption and reagent selectivity. Their soil experiments showed a strong effect of acidity on the extraction of Cu and Zn. They suggested a high pH may reduce the extent of the readsorption or its kinetics.

Kheboian and Bauer (1987) observed significant redistribution of Cu, Pb and Zn between phases when using the sequential extraction scheme of Tessier et al. (1979). Others have reported redistributions of As, Cd, Ca, Cu, Pb and Se among various phases of soils and sediments (e.g. Qiang et al., 1994a). The extent of redistribution depends both on the affinity of the remaining undissolved phases for the metal ion involved, and the ability of the extractant used to inhibit the adsorption of the metal by those phases (Kheboian & Bauer, 1987). Qiang et al. (1994b), concluded that the occurrence and extent of redistribution is determined by both the soil composition and the chemistry of a given metal. Unfortunately, the extent of readsorption and /or redistribution is difficult to quantify for individual elements and for individual geochemical phases.

### Speciation Based on Calculation Methods

In view of the errors that can be associated with sampling and sample preparation, and the limitations of many of the experimental procedures used in speciation, many investigators prefer to calculate the most likely species distribution pattern. Data inputs required include the total levels of cations, anions and ligand species present, and equilibrium constant values for all possible interactions between the various species. This approach is not new, e.g. a model for seawater was developed 38 years ago (Sillen, 1961).

In recent years with the proliferation of PCs several computer models have become widely available and are used for a variety of applications. Some of the commonly used models include GEOCHEM (Mattigod & Sposito, 1979) and its updated version SOILCHEM (Sposito & Coves, 1988); HYDRAQL (Papelis et al., 1988); ECOSAT (Keizer, 1991) and MINTEQA2 (Allison et al., 1991). These approaches involve solution of multiple si-

multaneous equations, some describing the competing chemical equilibria and other defining mass balance relationships. Perfect agreement between analytical and predicted speciation is an unrealistic expectation. Discrepancies may arise due to limitations of both the analytical approach and the modelling approach. From computational side, limitations include the uncertainty about the most appropriate equilibrium constants and the measured input data, and the fact reaction kinetics are not considered. In spite of this, because chemical speciation will remain time consuming and expensive, computer programmes are of great help.

### Role of Organic Matter for Metal Behaviour

Speciation clearly evidenced the role of organic complexes in metal mobilization in soils (Frimmel & Christman, 1988). Ziang et al. (1994) showed that the reduction of manganese oxides and amorphous iron oxides by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  can be hindered by a covering or occlusion of organic matter. These components can behave as a combined phase rather than as discrete phases, making selective dissolution of these entities in soils impossible. Robbins et al. (1984) showed that the failure to remove organic matter prior to reduction of ferromanganese oxyhydroxides caused the organic fraction value to be artificially high, and oxyhydroxide values to be low. Removal of carbonates and organic matter „clean up“ oxyhydroxide coatings, and facilitate the retrieval of any metal ions associated with this fraction. Occlusion, however, is very dependent on soil or sediment type and chemistry.

### Quality Assurance, Analytical Sensitivity, Accuracy and Matrix Interferences

The need for quality control in speciation studies is important not only for the „absolute“ reasons of scientific precision and accuracy but also to assist in achieving analytical methodologies that are robust enough to be used in different laboratories with comparable results. Universally applicable, validated methodologies make it possible for results from different scientists and different laboratories to be compared and provide the basis for the establishment of international databases on the occurrence and distribution of elemental species in the environment. However, the lack of uniformity in the different procedures and only few suitable certified reference materials (CRMs) do not permit the results to be compared worldwide nor the procedures to be validated. With a view to improving and ensuring a good quality control of speciation analysis, the Community Bureau of Reference BCR (now The Measurements and Testing Programme) of the European Commission has organized a series of interlaboratory projects over the last decade, as well as the production of CRMs (Quevauviller et al., 1994, 1996; Ure et al., 1993). The preparation of reference materials certified for the contents of element species is, however, a difficult task. This is because, firstly, the fractionation of the total content of an element in a material into its different species means that the species concentrations are low,



with all the consequent requirements for higher analytical sensitivity and greater care in avoiding contamination. Secondly, the species concentrations in the reference material must be preserved in such a way that they remain constant over the several year's life of a reference material. The informations about the preparation, homogeneity and stability studies of commercially available soils, and sewage sludges CRMs, certified for species defined operationally are included e.g. in Quevauviller et al. (1997, 1998).

### Conclusions and Recommendations

The differentiation of total contents in solid matrices remains largely operationally defined. Problems in published studies using sequential extraction include lengthy delays between coring, sectioning and analysis, failure to obtain pore water composition, failure to maintain anoxic samples under inert atmosphere during processing, excessive sample drying, failure to use N<sub>2</sub>-purged reagent solutions for anoxic samples, insufficient analytical sensitivity, and lack of quality assurance. 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. Chemical extractions can help to elucidate the long-term stability of contaminants in soils and sediments under changing environmental conditions.

Recommendations for further developments to improve the validity of selective chemical extractions are:

- design extraction sequences with improved selectivity for a particular soil or sediment sample
- use rigorous procedures for sampling, storage and manipulation
- readsorption effects can be reduced significantly when substituting the conventional static extraction system by a dynamic extraction process in a flow cell
- because of mutual inclusion effects between inorganic and organic phases, it may be necessary for certain samples to repeat the extraction steps several times
- washing solutions between adjacent extraction steps should be analysed, and not discarded
- use analyte spikes, standard reference materials, thermodynamic modelling and surface analysis to assess and confirm the specificity of metal release from substrates
- use corroborative evidence from sediment and soil pore water sampled under appropriate natural conditions.
- use the methods that require the minimum number of steps in sample preparation, or the minimum amounts of chemicals

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