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TRACE ELEMENT SPECIATION IN SOILS AND SEDIMENTS USING SEQUENTIAL CHEMICAL EXTRACTION METHODS

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Several commonly used sequential chemical extraction procedures of heavy metals in soils and sediments are compared, and their advantages and disadvantages are discussed focusing on selected case studies. In particular, problems caused by handling of anoxic samples, and of specific phases (e.g. organic fractions and sulfides) are addressed.

Eventually, recommendations for the improvement of extraction selectivity as well as the reduction of readsorption effects are given.

KEY WORDS: Trace elements, speciation, sequential extraction, soil, sediment.

INTRODUCTION

Soils and sediments constitute concentrated reservoirs of trace metals; the concentrations in these compartments are orders of magnitude higher than those found in the adjacent overlying phases, the water and air, respectively.

Measurement of the total metal concentration of bulk samples will provide little indication of the metal's potential interactions with the biotic and abiotic components present in the environment. Therefore, the kind of association of the metal with particular environmental phases is to be determined.

Besides direct methods using an electron microscope/microprobe or certain surface sensitive instrumental techniques¹, thermodynamic calculations and partial extraction procedures are the only two indirect methods presently available for estimating trace metal partitioning in soils and sediments².

Metal ion associations in soil and sedimentary systems are very complex like those segments released by different chemical treatments^{3,4}. Thus, with the aid of chemical sequential extraction methods just operationally (and not strictly chemically) defined fractions can be separated. Nevertheless, they may enable to estimate the relative strengths of the various processes leading to associations of metals and solids, e.g. chemical bonding, (co)precipitation, specific and non-specific adsorption, solid state diffusion, coating, and flocculation^{1,5,6}.

In this study, some pertinent schemes of sequential chemical extraction procedures are presented, and recommendations for their further improvement are given. In

particular, first results of hitherto unpublished work applying a modified extraction scheme developed at the University of Mainz are discussed.

PRINCIPLES AND PROCEDURES

In principle, the dried bulk soil or sediment sample is sequentially extracted by n different solvents in n steps, yielding n extract solutions as well as $(n - 1)$ intermediate and one final solid extraction residue (Figure 1). The resultant extract solutions are usually analysed by instrumental techniques suitable for the chemical multielement analysis of liquids, i.e. atomic absorption (GFAAS) and emission (ICP/AES), or mass spectrometry (ICP/MS). However, the complementary approach (i.e. analysis of the solid extraction residues by X-ray fluorescence spectrometry = XRS) is also possible⁷.

In the literature, speciation studies of soils and sediments are reported independently. This is because most natural soils are characterised by oxidised conditions (oxide minerals), whereas unpolluted sediments are usually deposited under oxygen-deficient conditions (reduced mineral assemblages). In the environment however, different circumstances as a consequence of the anthropogenic action may occur as well. In this regard, waste deposits with high coal ash content may show high-density surface layers, resulting in reducing conditions underneath; or dredged anoxic sediments may be deposited under aerobic conditions. Thus, it is desirable to

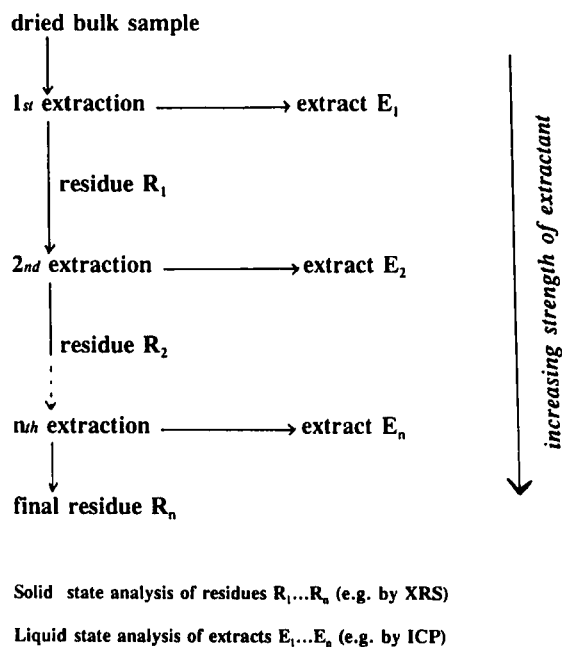


Figure 1 General scheme of sequential chemical extraction of sediments and soils.

compare sequential extraction methods including oxidised as well as reduced soil and sediment constituents. This has been done in Table 1 where six frequently used extraction schemes as described in the pertinent literature^{2,8-16} are presented. The extraction sequence used by Tessier *et al.*¹² had been most widely used, and applied not only to sediments and soils, but also to atmospheric particulates (dust, fly ash)¹⁷⁻¹⁹.

Developed on the basis of studies with model trace compounds, Sposito *et al.*¹³ presented an extraction scheme for arid-zone field soils enabling an experimental precision at any extraction step of better than 5%. Systematic differences with respect to mass balance were explained as result of the 4M HNO₃ extraction in the sequential

Table 1 Selected sequential extraction procedures

extraction sequence ↓	<i>EXTR COMP (SE)</i>		<i>EXTR COMP (SE)</i>	
	B	exchangeables	D	exchangeables
	K	carbonates	K	carbonates
	O	oxides	M	Mn-oxides
	Q	organics	V	Fe-oxides (amorph.)
	XY	residuals	Q	sulfides + organics
			Z	residuals
	Tessier <i>et al.</i> (1979)		Kersten and Förstner (1986)	
	<i>EXTR COMP (SE)</i>		<i>EXTR COMP (SO)</i>	
	A	water solubles	E	exchangeables
	D	exchangeables	I	sorbed components
	G	soluble organics (<i>s.e.</i>)	R	organics
	H	soluble organics (<i>h & f</i>)	Z	carbonates + sulfides
	L	mineral matrix (<i>e.s.</i>)		
	X	mineral matrix (<i>h.s.</i>)		
	LYZ	insoluble organics		
	Hirner and Kritsotakis (1989)		Sposito <i>et al.</i> (1982)	
	<i>EXTR COMP (SO)</i>		<i>EXTR COMP (SO)</i>	
	F	exchangeables	C	unspec. adsorpt.
	J	organics	D	spec. adsorpt.
	N	Mn-oxides	N	Mn-oxides
	T	Fe-oxides (amorph.)	S	organics
	U	Fe-oxides (cryst.)	T	Fe-oxides (amorph.)
	LXZ	residuals	U	Fe-oxides (cryst.)
			XYZ	residuals
	Shuman and Hargrove (1985)		Zeien and Brümmer (1989)	

EXTR = extractant; COMP = main component extracted; SE = sediment; SO = soil; *s.e.* = solvent extractables; *h & f* = humic & fulvic acids; *e.s.* = easily soluble; *h.s.* = hardly soluble; insoluble organics = (proto)-kerogen.

A: H₂O B: MgCl₂ C: NH₄NO₃ D: NH₄OAc E: KNO₃ F: Mg(NO₃)₂ G: benzene/methanol H: benzene/methanol/KOH I: NaOH J: NaOCl K: NaOAc/HOAc L: HCl M: NH₂OH.HCl/HNO₃ N: NH₂OH.HCl + NH₄OAc O: NH₂OH.HCl/HOAc Q: H₂O₂/HNO₃/NH₄OAc R: EDTA S: NH₄-EDTA T: (NH₄)₂C₂O₄ U: ascorbic acid/oxalate buffer V: oxalate buffer X: HF Y: HClO₄ Z: HNO₃

procedure, which is more effective than the direct 4M HNO₃ extraction of the bulk metal, because of preconditioning of the soil sample by NaOH and EDTA in the sequential procedure.

The procedure of Zeien and Bruemmer¹⁵ was developed mainly to avoid problems inherent to frequently used routine methods^{9,12-14}. The extractants were based on NH₄⁺ and nitrate, acetate, and oxalate as anions to constitute a solution matrix suited for atomic absorption spectrometry. In the course of the elution sequence the acidity of extractants is increasing. The heavy metals are fractionated according to their mobility during the first two steps of the extraction sequence, whereas steps three to seven fractionate according to their binding characteristics. However, this method is only applicable to oxidised soils with <5% CaCO₃; in the second step carbonates are dissolved by titration with HCl. The weight sum of all seven fractions ranged between 88 and 107%, indicating a fairly good recovery rate (quantitative mass balance) of this elution sequence. While the fraction of the exchangeable metals is more or less identical to the non-specifically adsorbed metal fraction, specific metal adsorption by soil minerals is mainly related to metal ion hydrolysis⁶.

Based on the observation that significant amounts of heavy metals may enter the organic phase of sediments under certain geochemical circumstances^{20,21}, Hirner and Kritsotakis proposed an extraction sequence concentrated on the specific isolation of soluble (by solvent extraction) and insoluble organic constituents (by demineralisation). In the meantime, this scheme had been applied to soils²² as well as to sediments^{23,24}. The main results of these studies will be discussed in the following section.

The last step of any sequential extraction procedure is the quantitative dissolution of the final extraction residue. Bomb or microwave digestion procedures with strong mineral acids and oxidising agents at elevated pressures and temperatures are usually effective to dissolve inorganic and organic residues except for a few uncommonly resistant minerals which require alkaline fusion²⁵.

Modifications of the usual extraction sequence concentrating on the more mobile fractions have been proposed for Cd²⁶, in the sense that sequential extractions are performed with H₂O, CaAc₂, NaAc, NaOH, and Na-citrate. For marine sediments, extraction of the organic-bound fraction by hot (100°C) sodium dodecylsulfate-sodium bicarbonate at pH 9.2 has been recommended²⁷.

Many other sequential extraction schemes similar to those selected in Table 1 are in practical use. More bibliographic data together with descriptions of the method of parallel chemical extractions can be found in Calvet *et al.*²⁸

SELECTED CASE STUDIES

An extraction sequence proposed by Hirner and Kritsotakis²⁰ was applied to Rhine sediments by Siering²³ and Giesemann²⁴ as well as to selected soil samples by Streck²².

Metal concentrations in the separated fractions were determined by ICP/AES, and ICP/MS. Lead concentrations were measured by GFAAS, and the stable isotopes of

lead by thermal ionisation MS as described in the literature²⁹. Mass balance calculations showed the metal sum of fractions being roughly comparable to bulk metal content in most cases, sometimes lower, especially for Pb.

The results of these studies clearly demonstrate that high amounts of toxic metals brought into the Rhine by the heavily polluted Schwarzbach are concentrated in the more mobile species when compared to the relatively unpolluted background levels of the Altrhein canal³⁰. This observation is consistent with the distribution of stable lead isotopes. Anthropogenic lead is isotopically light and concentrated in the exchangeable fraction, whereas isotopically heavy geogenic lead is found in the silicate fraction, the latter being characterised by isotopic ratios similar to those in rocks from the Black Forest. Although the absolute amount of metals associated with organic substances was found to be generally low (sum of heavy metals less than $10 \mu\text{g g}^{-1}$ with the exception of Zn in humic/fulvic acids, and Fe and Ti in the protokerogen), the relative partition within organic fractions was often substantial for Cr, Ni, As, and Pb.

As the low metal concentrations in the humic/fulvic acid fraction reported in these studies²²⁻²⁴ contrast with the usual metal enrichments observed for this fraction in other studies^{20,31}, during the extraction procedure appreciable quantities of metals may be retained by the solid extraction residues, resulting in unusual high concentrations in the subsequent carbonate fraction. Low metal concentrations in the protokerogen fraction indicate a possible demetallation of the insoluble organic polymers by HCl/HF acid treatment. Thus, the separation procedures for organic fractions definitely require further improvements.

DISCUSSION

Advantages of the sequential extraction method

The best argument for applying sequential extraction methods is in the field of environmental chemical research. The preparative procedures applied during sequential extraction are comparable to those occurring in nature. In natural environments soils and sediments are subject to similar leaching procedures by natural and anthropogenic electrolyte solutions. As the main difference between laboratory extraction and natural leaching is the time, extrapolation of long-term extraction experiments may be necessary.

Sequential extractions will yield more information than single extractions (elution tests).

As all fractions should sum up to near 100% (mass balance), no sample material should be lost. Thus, compound transformations within the sample can be traced. For example, heavy metals added to soils as soluble salts or deposited by pollution processes may become immobilised and less available with time because of slow diffusion of trace metals into minerals under natural conditions⁶.

With respect to geochemical speciation studies, sequential extraction methods are an essential tool in establishing element partitioning within natural samples (e.g. oil

shales), especially when complemented by other methods as well as by different approaches for modelling their chemical composition⁷.

Stable (²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb) and unstable isotopes (²¹⁰Pb) are used to trace the origin and age of lead in the environment^{29,32–34}. It has been demonstrated in the case of Rhine sediments, that even in cases where a differentiation of natural vs. anthropogenic lead could not be made when analysing bulk samples, clear indications of association of anthropogenic constituents to mobile fractions and of natural constituents to immobile fractions exist when applying sequential extractions²⁴. When dating peat deposits by ²¹⁰Pb, it is assumed that Pb is immobile and not subject to diagenesis³⁴. However, over a three-year period of study Pb losses of more than 30% were observed in a peat bog, leading to significant errors in age determination³². The latter could be avoided when analysing immobile fractions only.

Disadvantages of the sequential extraction method

The main problems with sequential extraction procedures are nonselectivity of extractants and trace element redistribution among phases during extraction^{10,28,35}. This has been demonstrated by Kheboian and Bauer³⁵ in the course of experiments with synthetic sediments. Serious redistribution effects (esp. for Pb and Cu) and nonselective extraction (esp. for Zn) leading to inconsistent results had been observed, although some model experiments may lead to overestimate the postextraction readsorption³⁶. In the case studies reported in the preceding section the separation between the soluble humic/fulvic acid fraction and the carbonates seem to be problematic. Special care should be taken with the preparation of anoxic samples, where oxygen-free conditions are to be maintained^{10,37}.

Certain sulfides and organic compounds are distributed between several fractions. Acid labile sulfides are already partly dissolved in the course of the first three extraction steps³⁸. Extraction of organic matter by oxidative agents is unsatisfactory because (i) refractory organic matter is not completely destroyed, and (ii) sulfides are oxidised, too. Na₄P₂O₇ and NaOH extract organic material, but attack clays and other alumino-silicates²⁷. The scheme proposed by Hirner and Kritsotakis (see Table 1) avoids oxidative reagents, and thus offers advantages in separating organic and sulfidic matter.

Under high pH conditions—e.g. during humic acid extraction by sodium hydroxide—basic metal oxides may be formed. After HF treatment of the extraction residues, neoformed fluorides may be found.

Between adjacent extraction steps washing procedures are required. These solutions are usually discarded, although they may frequently contain dissolved metal ions³⁵.

Mobility and bioavailability of metals

Mild extractants like distilled water or neutral salt solutions (usually a 0.1M CaCl₂ solution), together with the knowledge of pH and clay content, are best suited to estimate the mobile and bioavailable heavy metal fractions³⁹. The other metal

fractions are more or less immobile⁶. Lindsay and Norvell⁴⁰ proposed a solution consisting of 0.005M DPTA, 0.1M triethanolamine, and 0.01M CaCl_2 (pH 7.3) for the determination of available Zn, Fe, Mn, and Cu in soils. CaCl_2 seems a promising extractant in order to predict the actual Cd and Zn availability for plant uptake from different soils⁴¹. Neutral salt solutions (CaCl_2 or $\text{Ca}(\text{NO}_3)_2$) as soil extractants, however, did not prove to represent a suitable measure for the Pb and Cu uptake in plants⁴².

It could be demonstrated by statistical analysis⁴³, that the water and CaCl_2 soluble, mobile and bioavailable fraction is correlated with the reservoir concentration extractable by EDTA and DTPA⁴⁰, and pH. For Cd, Zn, and Mn the metal concentrations in wheat corn are correlated with those in the water and CaCl_2 soluble fraction⁴⁴. In the case of Cd the ecologically most effective constituents are apparently to be found in the water soluble fraction⁴⁵.

Elements introduced with solid waste material (e.g. sewage sludge) are usually less stably bound than those in natural systems^{10,13}. Thus, mobilisation of toxic elements by acidity, complexing agents, increasing salt concentrations, or redox changes, may be significantly increased⁴⁶. Eventually, chemical extraction sequences can be used for the estimation of the potential remobilisation of metals under changing environmental conditions¹.

CONCLUSIONS

At present sequential extraction procedures have proved their potential in the field of environmental analytical chemistry. However, they are not particularly recommended in fundamental physico-chemical research. The use of sequential extraction techniques appears to be an efficient method for making comparative studies between natural and contaminated areas, as well as between areas characterised by different types of contamination. Chemical extractions can help to elucidate the long-term stability of contaminants in soils and sediments under changing environmental conditions.

Eventually some recommendations for further developments will be given, by which the method of sequential chemical extractions may be considerably improved:

—With the aid of Table 1 it should be possible to design extraction sequences with improved selectivity for a particular soil or sediment sample.

—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 for several times.

—Washing solutions between adjacent extraction steps should be analysed, and not be discarded.

Efforts are made in our laboratories to incorporate these improvements into sequential extraction schemes as well as to gain additional insights by comparing the

results obtained with various methods applied to a single particular soil or sediment sample.

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