

Evaluation of sequential extraction procedures for metal speciation in model sediments

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Abstract

The three-step sequential extraction protocol designed by the BCR (Community Bureau of Reference) was evaluated with regard to total recovery, reproducibility, selectivity of extractants and extent of phase exchanges or redistribution of metals during the extraction. Model sediments of known composition were developed consisting of humic acid and natural minerals like kaolin, quartzite and ochre. Synthetic compounds like calcium carbonate (calcite) and iron oxide (goethite) which could be used to simulate typical components of sediments, were used for comparison. Our results indicate that the procedure gives excellent recoveries for all 6 metals (Cu, Cr, Cd, Zn, Ni and Pb) studied. Reproducibility of 3% was achieved. Redistribution of Pb and Cu in the presence of humic acid was demonstrated. The selectivity of the reagents was insufficient to warrant interpretation of results in terms of a specific origin of a metal in a particular phase. It was shown that the chemistry of a metal can be a more important parameter than the actual phase location of the metal in the sediment in determining its response to the extractants. This was demonstrated in the case of Cr which reported to Step 3 irrespective of its location.

Introduction

Sequential extraction procedures, despite much adverse critique and controversy in the scientific literature (Kheboian and Bauer, 1987; Nirel and Morel, 1990; Martin et al., 1987; Rapin et al., 1986) over the last decade still remain popular for measuring the particulate speciation of trace metals in sediments. There seems to be an important need in especially the environmental sciences to be able to characterise the speciation of trace metals in sediments. Aquatic sediments act as sinks for trace metals in the environment and particulate speciation procedures provide useful information with regard to bio-availability and geochemical fate of trace elements. It is, however, a cause for concern that sequential extraction procedures of which more than ten different schemes (Campbell and Tessier, 1987; Salomons and Förstner, 1980; Towner, 1985; Meguellati et al., 1983) have been developed, are often used in a nondiscriminatory fashion in the belief that the procedures are selective, that phase exchanges or trace element redistribution do not occur, and that matrix effects can be ignored. This despite the fact that various attempts (Kim and Fergusson, 1991; Håkansson et al., 1989; Kersten and Förstner, 1986) to validate these procedures have provided evidence that these assumptions could not generally be made. The method most often used for sequential extractions, is that by Tessier et al. (1979). Various modifications (Lum and Edgar, 1983; Rauret et al., 1989) have been suggested to improve the original technique, none of which really solved the inherent problems associated with the interpretation of results from sequential extractions.

In the application of a sequential extraction procedure to a natural sediment the different geochemical phases which constitute a typical sediment are assumed to be present. These may include clay minerals, calcite, iron and manganese oxides, sulphides and organic matter. A fundamental problem arises because not all sediments include chemically and physically distinct phases. In such cases results from sequential extractions are essentially

meaningless if interpreted in terms of metal content in defined geochemical phases. The non-selectivity of extractants and trace element redistribution among phases during extraction further complicate this type of interpretation of results in terms of phase association of metals. Selectivity studies have been made on single phases with single reagents (Slavek et al., 1982) and redistribution studies have been performed in the presence of mixed substrates (Guy et al., 1987; Rendell and Batley, 1980; Belzile et al., 1989) using the Tessier procedure. The reported results all show that readsorption of metals released during the extraction procedure may occur to varying degrees.

In a bold step to bring some order in this field, various laboratories (Ure et al., 1993) within the EEC are collaborating to develop reference sediments which would be of crucial importance in the ultimate validation of a standard sequential extraction procedure. The ability to distinguish between the reactive load, which could be indicative of the bio-available component, and the inert part of a sediment is in our view the most important requirement of a universally acceptable or standard sequential extraction procedure. In order to achieve this, provision has to be made to accommodate three basic interaction types which could play a role in the remobilisation of metals from sediments, namely:

- acid-base equilibria
- reduction reactions
- oxidation reactions.

By applying these reactions to a sediment using extractants of the appropriate strength, the potential of the sediment to release pollutants into the environment can be estimated. A useful procedure (López-Sánchez et al., 1993) for this purpose has recently been suggested by the Community Bureau of Reference (BCR Protocol). It is basically a simplified Tessier procedure using acetic acid to provide for acid-base, hydroxylamine hydrochloride for reduction, and hydrogen peroxide (H_2O_2) for oxidation interactions.

In this work we attempted a validation of the BCR Protocol with well-defined samples. We studied this procedure for the six elements Zn, Cu, Cd, Cr, Ni and Pb with respect to total recovery, possible phase exchanges during extraction, element specificity

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and matrix effects. For this purpose we developed a number of well-characterised model sediments from natural components as well as synthetic material. The different mineral compositions included in our selected phases were: calcium carbonate as synthetic calcite, iron oxide as natural ochre or synthetic goethite, aluminium silicate as kaolin, quartzite and organic matter as humic acid. Mineral composition has an important effect on the efficiency of extraction and the extent of re-adsorption (Xiao-Quan and Chen Bin, 1993).

Experimental

Instrumentation

Sediment phases were characterised by X-ray diffraction (Philips PW 1730 Powder Diffractometer) and scanning electron microscopy (JEOL JXA-840A). The concentrations of metals in solutions obtained after sequential extraction procedures were measured by inductively coupled plasma atomic emission spectrometry (ARL 35000 ICP-AES spectrometer). Centrifugation was performed with a Heraeus Sepatech Labofuge 200.

Materials

Standards

Trace element standards were prepared from a 1 000 mg·l⁻¹ multi-element Merck ICP standard solution. 18 M Ω water from a Millipore polishing unit was used in all solutions. Spectral interferences in ICP measurements were investigated for calcium and iron using single element ICP standards.

Natural sediment phases

Typical solid phases found in South African sediments were obtained from the SA Geological Survey. These included kaolin (Serina Minerals, Cape Town), ochre mined near Albertinia (G&W Base and Industrial Minerals, Wadeville), and quartzite (N. Transvaal). Humic acid was obtained from Fluka chemicals. Natural solid phases were pulverised, dry-sieved to less than 83 μm, and washed successively with 0.1 M HNO₃ and deionised water.

Synthetic sediment phases

Calcite was prepared (Wray and Daniels, 1957) by drop-wise addition of 0.1 M Ca(NO₃)₂ into a stoichiometric amount of 0.1 M Na₂CO₃ at 37°C and aged for 24 h at this temperature. To prepare (Benjamin and Leckie, 1980) goethite, iron hydroxides were precipitated from KOH and Fe(NO₃)₂ solutions and aged at 60°C for 24 h. Similar procedures, except that one of the precipitating reagents was spiked with the required metal, were used to prepare phases containing co-precipitated elements.

Phases containing adsorbed metals

Metals were adsorbed onto natural and synthetic phases by suspending the substrate in a solution of the desired metal for 2 h with continuous magnetic stirring at an optimum pH. The pH was chosen to minimise precipitation of metal hydroxides and maximise surface adsorption. Solids were recovered by centrifugation, repeatedly washed with water to remove the supernatant solution, and then dried in an oven at 50°C and stored in a desiccator.

Substrate	Phase%	Metal	mg·l ⁻¹	Metal	mg·l ⁻¹
Metals adsorbed onto natural phases		Model A	ModelA	Model D	ModelD
Quartz	10	Pb	48	Cd	113
Ochre	10	Ni	3.4	Cr	8.8
Kaolin	75	Zn	96	Cu	53
Humic acid	5	Cu	17	Zn	11
Metals adsorbed onto synthetic phases		ModelB	ModelB		
Calcite	10	Pb	61		
Goethite	10	Ni	76		
Kaolin	75	Zn	28		
Humic acid	5				
Metals co-precipitated with synthetic phases		ModelC	ModelC	ModelE	ModelE
Calcite	10	Pb	1.1	Pb	61
Goethite	10	Ni	6.2	Ni	76
Kaolin	75	Zn	28	Zn	28
Humic acid	5				

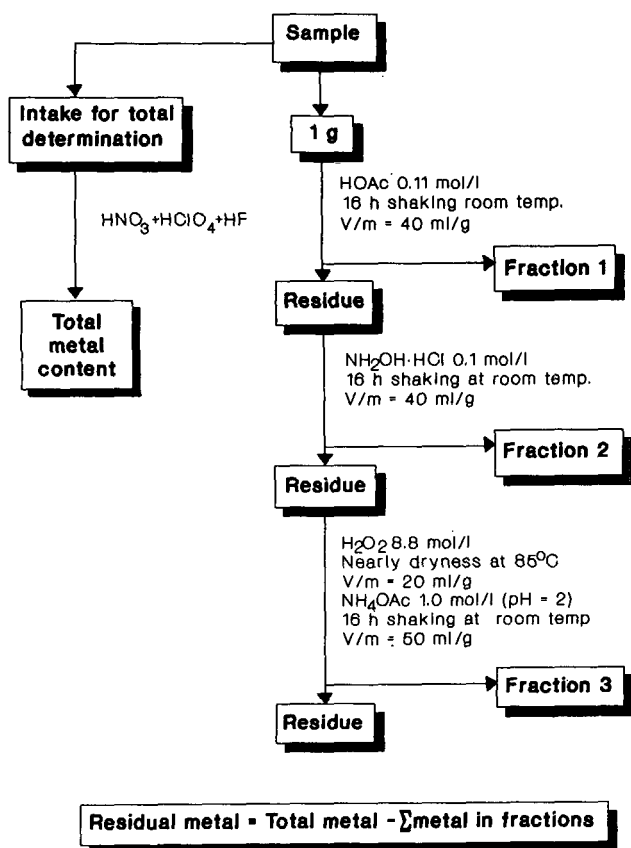


Figure 1
Schematic presentation of BCR sequential extraction protocol

Substrates were loaded with only one metal at a time to ensure that the source of the metal would be clearly defined. The actual loading was determined by treating kaolin, calcite and quartzite with 0.1 M HCl, ochre and goethite with aqua regia and humic acid with 30% peroxide (see Step 3 of sequential extraction procedure) and measuring the metals in solution by ICP. In the case of kaolin and quartzite, the substrate did not dissolve completely. It was, however, assumed that the adsorbed metals had been released quantitatively in order to calculate the loading of these substrates.

Model sediments

Model sediments were prepared by mixing a selection of phases containing one spiked element each in a Spex Industries mechanical shaker for 15 min. The composition of the model sediments is summarised in Table 1.

Procedures

Sequential extraction procedure

A summary of the basic BCR extraction procedure, shown schematically in Fig 1., is given below:

Step 1 1 g of dry sediment is extracted with 40 ml of 0.11 M acetic acid by shaking overnight (16 h) at 20°C.

Step 2 The residue from Step 1 is then extracted overnight (16 h) with 40 ml of freshly prepared 0.1 M hydroxylamine hydrochloride acidified with nitric acid to pH 2.

Step 3 The residue from Step 2 is rinsed with 10 ml 30% H₂O₂ adjusted to pH 2-3 with nitric acid in a covered beaker for 1 h at room temperature. Digest for a further 1 h at 85°C to reduce volume to a few ml. Add a further aliquot of 10 ml H₂O₂, and heat in a covered beaker for 1 h at 85°C. When the volume is reduced to a few ml, transfer the wet residue to a suitable centrifuge tube by rinsing with 50 ml of 1 M ammonium acetate adjusted to pH 2 with acetic acid, and extract by shaking overnight (16 h).

Magnetic stirring was used during all extractions. The extracts were separated by centrifugation and decantation. Extracts were filtered through 0.45 µm Millipore membrane filters into high density polyethylene bottles and stored at 4°C until analysis by ICP-AES spectrometry.

Characterisation of natural phases

Ochre is an earthy variety of the mineral limonite from which it originates by weathering and oxidation. It occurs together with kaolin and therefore contains some aluminium silicate. A chemical analysis of the ochre is: Fe₂O₃ (45%), SiO₂ (32%), Al₂O₃ (10%), loss on ignition (10%).

Kaolin and ochre consisted of particles smaller than 2µ while the average particle size for quartz was about 4µ.

Crystallographic analysis confirmed that ochre and goethite were both oxyhydroxides of the form FeO(OH). Adsorption or co-precipitation of Ni did not change the goethite crystal structure in any way detectable by X-ray diffraction. Synthetic calcium carbonate was confirmed to be pure calcite.

Blank values

Blanks were obtained for the 4 natural substrates by performing the sequential extraction procedure in triplicate and determining each of the 6 metals in the extracts by ICP-AES spectrometry. The results given in Table 2 show that the substrates were relatively clean after the wash procedure had been applied.

pH adsorption edges

The pH adsorption edges for the 6 metals were determined for the selected natural phases i.e. quartzite, ochre, kaolin and humic acid. The substrates (50 mg) were suspended in 0.01 M NaNO₃ solution to which was added 10 ml of a 1 × 10⁻⁴ M solution containing the 6 metals to give a final concentration of 2 × 10⁻⁵ M. The pH was adjusted with NaOH and HNO₃ solutions to between 3 and 10 in steps of 0.05 or 0.1 and the solutions (final volume 50 ml) then equilibrated for 24 h at 25°C in a water bath with continuous mechanical shaking.

After centrifugation the final pH was measured and the metal concentration in the solution determined by ICP. The difference between this value and the initial concentration was used as an indication of the amount of metal adsorbed by the substrate.

ICP analyses

Analytical lines, summarised in Table 3, were chosen to minimise possible interferences by Fe, Al, and Ca which could typically

Step	Element	Quartzite	Ochre	Kaolin	Humic acid
1	Cd	<0.01	<0.01	<0.01	<0.01
1	Cr	<0.02	<0.02	<0.02	0.03
1	Cu	<0.01	<0.01	0.02	<0.01
1	Pb	<0.50	<0.50	0.90	<0.50
1	Ni	0.58	0.28	0.15	0.08
1	Zn	<0.01	0.03	0.10	0.03
2	Cd	0.03	<0.01	0.05	<0.01
2	Cr	<0.02	<0.02	<0.02	<0.02
2	Cu	<0.01	<0.01	<0.01	<0.01
2	Pb	0.80	0.70	<0.50	<0.50
2	Ni	0.65	0.15	0.06	<0.02
2	Zn	0.07	<0.01	<0.06	0.05
3	Cd	<0.01	<0.01	<0.01	<0.01
3	Cr	<0.02	<0.02	<0.02	<0.02
3	Cu	<0.01	<0.01	<0.01	<0.01
3	Pb	<0.50	<0.50	<0.50	<0.50
3	Ni	0.26	0.10	0.08	<0.01
3	Zn	<0.01	<0.01	<0.01	<0.01

Element	Line	Interference
Zn	213.86	Ni
Cd	214.44	Fe,Al
Pb	220.35	Al
Ni	221.65	
Cr	267.72	Mn
Cu	324.75	Fe

Element	K _{sp}	pH 50% ADS*	pH 50% PREC**
Cr	2.0 × 10 ⁻³⁰	4.4 ± 0.2	4.4
Pb	1.4 × 10 ⁻²⁰	4.6 ± 0.3	6.7
Cu	1.6 × 10 ⁻¹⁹	4.6 ± 0.4	7.0
Zn	1.2 × 10 ⁻¹⁷	6.3 ± 0.5	8.5
Ni	5.5 × 10 ⁻¹⁶	7.1 ± 0.5	8.0
Cd	5.2 × 10 ⁻¹⁶	7.5 ± 0.5	9.2

* ADS = Adsorption
** PREC = Precipitation

be present in sediment extracts. Interference checks with 1 000 mg·l⁻¹ solutions of speccure Fe, Al and Ca salts showed negligible interference at the selected wavelengths.

Results and discussion

pH Adsorption edges

Typical pH adsorption curves are shown in Fig. 2 for the different metals for natural ochre. Figure 3 shows calculated precipitation curves to compare the effect of precipitation of metal hydroxides as a function of pH with metal adsorption in Fig. 2. The pH values at which the loading procedures were performed were chosen according to these results to minimise the contribution of precipitation to overall loading. The adsorption characteristics of the metals seem to follow their K_{sp} values with Cr, Cu and Pb

adsorbing at lower pH values than Cd, Zn, Ni. This result is typical of numerous metal adsorption studies (Tessier et al., 1979). In general it can be stated that metal cations that form strong complexes with OH also bind strongly to oxygen-containing functional groups like those found in kaolin, ochre and calcite. Table 4 compares the experimentally determined pH adsorption edges at 50% adsorption and calculated critical pH values for 50% precipitation using the equilibrium speciation modelling program MINTEQA2 (Allison et al., 1991).

The pH adsorption values are average values for the 4 substrates. Small differences were observed among the adsorption curves for the different substrates but the characteristics were essentially the same.

The precipitation of Zn begins at a slightly higher pH contrary to what could be expected on grounds of the relative K_{sp} values, if it is assumed that the adsorption of uncharged species will be

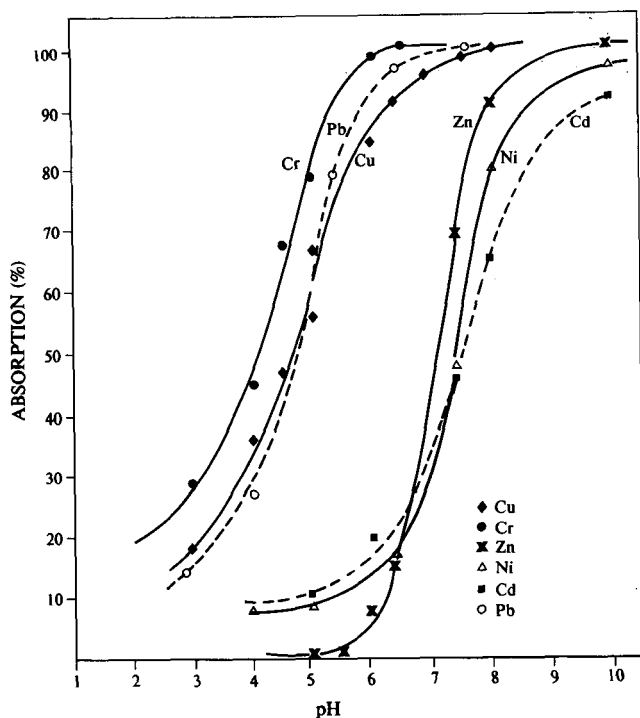


Figure 2
pH adsorption curves for ochre

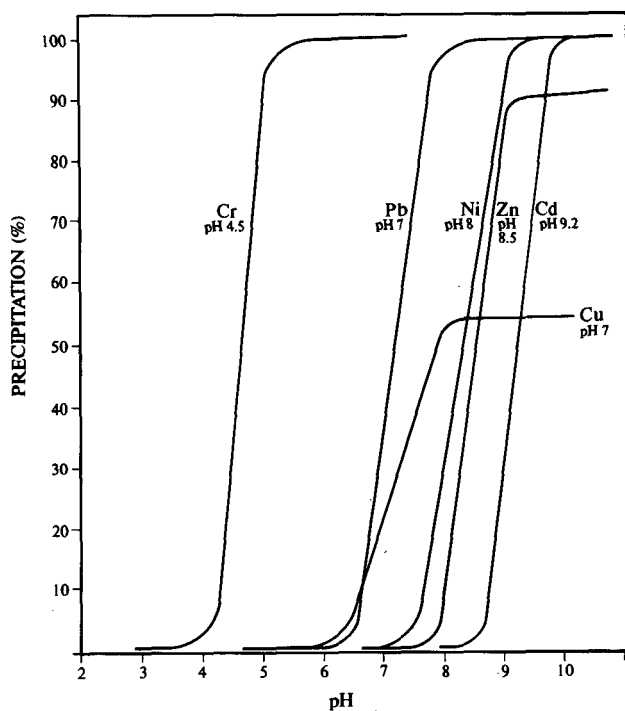


Figure 3
pH precipitation curves

considerably less than that for charged species. This contradiction could be explained in terms of the relatively high value of the molecular solubility of the $Zn(OH)_2(aq.)$ species (1.7×10^{-6} M). The presence of this species also explains why the precipitation curve for Zn shows that the maximum amount of Zn precipitated is only 90 % at the concentration (2.0×10^{-5} M) used in this experiment. The same explanation also applies to Cu with a molecular solubility of 9.12×10^{-6} M. This limits the maximum amount of Cu that will precipitate to 54% in this particular case.

Sequential extractions

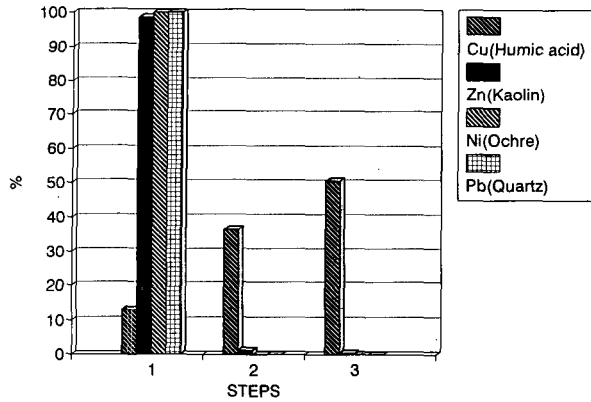
Sequential extractions were performed in triplicate on each loaded substrate and model sediment and the results are given in Table 5. Histograms showing the % recoveries in the individual steps for the different models and single phase extractions are compared in Fig. 4. Total % recoveries were calculated relative to the amount of loading determined by dissolution. Recoveries were also calculated with respect to the sum of amounts obtained during the extraction of the single element phases. These alternatives are denoted by L and S, respectively, in the captions of the last 2 columns in Table 5. Recoveries are in most cases remarkably close to 100%, particularly the values shown in the last column in Table 5 which compares recoveries in the extraction of the models with those obtained in the single phase extractions. A few deviations however, need to be accounted for: Cu and Zn on humic acid in Model A and D, respectively, show marked discrepancies. This might be attributed to the experimental difficulties encountered in working with humic acid which tended to float on the surface of the suspension during extraction or to accumulate on the sides of the centrifuge tube. Intimate contact with the solution was therefore only partially possible. In the case of Zn on humic acid the metal was predominantly released in the first extraction step whereas loading was determined by following the procedure in Step 3. The loading values for Zn are therefore suspect. In the case of co-precipitated Ni and Cr with goethite in Model C and E respectively, the high loading values relative to those obtained from sequential extraction could indicate that the extractants were not capable of completely dislodging the total amount of Ni and Cr when co-precipitated with goethite. It is known that mixed crystals often have different solubilities than the pure compounds.

Single phase extractions

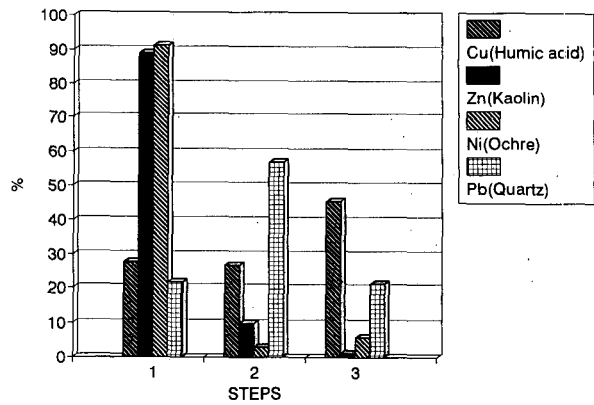
Model A and D (adsorption onto natural phases): The histograms for Model A single phases shown in Fig. 4(a) show that the adsorbed metals Ni (ochre), Zn (kaolin) and Pb (quartzite) were quantitatively recovered in the first step despite the fact that the substrates were not dissolved to any significant extent. This observation would indicate a surface complexation and/or surface precipitation model for loaded metals. In the case of copper loaded onto humic acid most copper was released in Step 3 which is in accordance with the reported results (Håkansson, et al., 1989) obtained using the Tessier scheme. This could be explained if cognisance is taken of the fact that Cu readily forms complexes with humic acid. These complexes are obviously more stable than the copper-acetate complexes expected to form in Step 1. The copper-humic acid complex is probably partially destroyed in Step 2 due to the low pH used in this extraction.

The most interesting feature of the bar chart for Model D single phases shown in Fig. 4(b) for extraction recoveries in the single phases of model D is the fact that Cr (ochre) reports

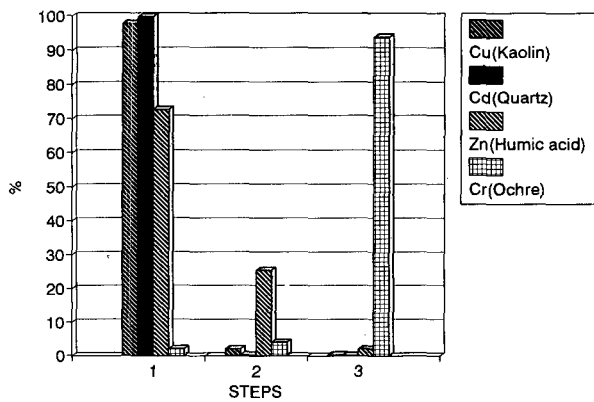
4(a) Model A Single phases



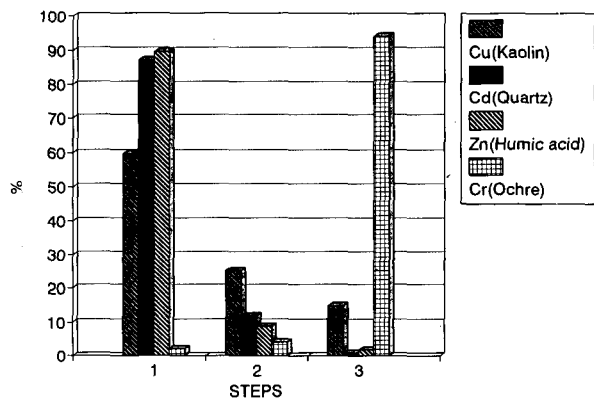
4(d) Model A



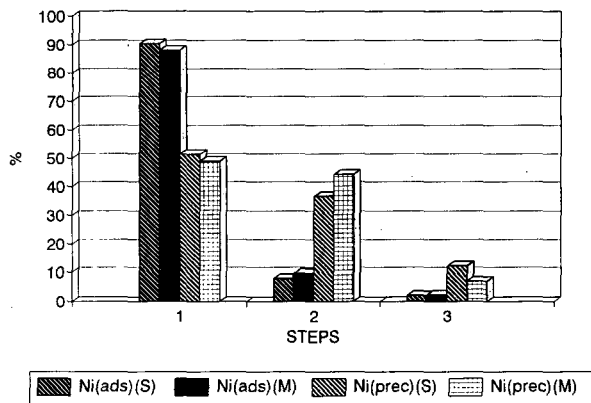
4(b) Model D Single phases



4(e) Model D



4(c) Model B(ads) and C(prec)



4(f) Model E(prec)

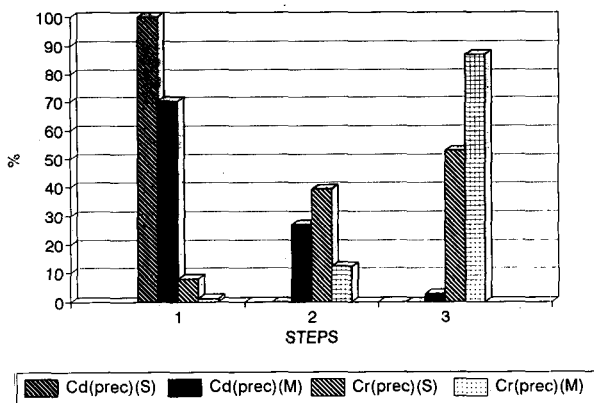


Figure 4

% Recovery in the different extracting steps

(a) Model A single phases

(b) Model D single phases

(c) Model B and C single phases (s) and Model (M)

(d) Model A

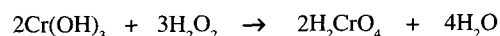
(e) Model D

(f) Model E single phase (s) and Model (M)

TABLE 5
RECOVERY IN SEQUENTIAL EXTRACTIONS OF LOADED SUBSTRATES AND MODELS (mg·l⁻¹ IN 40 ml)

Substrate		Step 1	Step 2	Step 3	Tot	Load	%REC L*	%REC S**
Model A & D								
A:Quartz (S)	Pb	49	0	0	49	48	103	
A:Quartz (M)	Pb	10	27	10	48	48	100	98
A:Ochre (S)	Ni	3.5	0	0	3.5	3.4	103	
A:Ochre (M)	Ni	3.1	0.1	0.2	3.4	3.4	100	97
A:Kaolin (S)	Zn	90	1.0	0.3	92	96	95	
A:Kaolin (M)	Zn	85	9.4	1.0	95	96	99	104
A:Humic (S)	Cu	2.4	6.7	9.3	18	17	110	
A:Humic (M)	Cu	3.0	2.9	4.9	11	17	64	60
D:Quartz (S)	Cd	124	5.7	0.5	130	113	115	
D:Quartz (M)	Cd	124	16	0.8	141	113	123	107
D:Ochre (S)	Cr	0.1	0.3	15	16	15	105	
D:Ochre (M)	Cr	0.2	0.4	19	20	15	131	125
D:Kaolin (S)	Cu	66	1.8	0.2	68	53	128	
D:Kaolin (M)	Cu	32	12	21	65	53	122	97
D:Humic (S)	Zn	15	5	0.2	20	11	178	
D:Humic (M)	Zn	21	2.1	0.2	23	11	209	117
Model B								
B:Calcite (S)	Pb	52	0	0	52	61	85	
B:Calcite (M)	Pb	12	29	13	53	61	87	102
B:Goethite (S)	Ni	90	8.4	2.2	101	89	113	
B:Goethite (M)	Ni	90	9.8	2.3	103	89	114	100
B:Kaolin (S)	Zn				26	28	94	
B:Kaolin (M)	Zn	23	2.7	0.4	26	28	94	100
Model C & E								
E:Calcite (S)	Cd	3.5	0	0	3.5	3.1	114	
E:Calcite (M)	Cd	2.6	1.0	0	3.6	3.1	116	100
E:Goethite (S)	Cr	0.3	1.7	2.3	4.3	6.9	61	
E:Goethite (M)	Cr	0.1	0.5	3.7	4.3	6.9	61	100
C:Goethite (S)	Ni	2.1	1.5	0.5	4.1	6.6	66	
C:Goethite (M)	Ni	2.1	1.9	0.3	4.3	6.2	69	100
*L denotes % recovery relative to total loading **S denotes % recovery relative to sum of amounts obtained in extraction of the single phases								

practically 100% to Step 3. The high charge on the chromium species could lead to the formation of strong surface complexes (or surface precipitation of Cr(OH)₃) with the ochre substrate (primarily iron oxide and aluminium silicate). The adhesion of Cr to the surface is thus so strong that acetic acid used in Step 1 could not remobilise Cr as had been the case for all other elements studied for different substrates. Even in Step 2 where hydroxylamine is supposed to attack iron oxides, Cr is not released. It was, however, observed that ochre does not dissolve in Step 2 to any significant extent. The remobilisation of Cr in Step 3 during the oxidative treatment with H₂O₂ could be explained by the partial oxidation of Cr(III) to chromate by H₂O₂, according to the well-known reaction used for the preparation of chromates:



Model B (adsorption onto synthetic phases): Synthetic calcite dissolved completely in Step 1 (0.11 M acetic acid) and adsorbed lead was quantitatively released. Ni adsorbed onto synthetic goethite was released rather effectively in Step 1 indicating the stability of the Ni-acetate complexes.

Model C and E (co-precipitation with synthetic phases): Model E single phases consisted of Cd co-precipitated with CaCO₃ (calcite) and Cr co-precipitated with goethite. As was to be expected Cd was released quantitatively in Step 1 because the calcite substrate was dissolved completely in acetic acid used in this Step as extractant. Cr behaved in the same way whether it was adsorbed onto ochre in Model D or co-precipitated with goethite in Model E. Although goethite was dissolved to some extent in Step 2 less than 40% of the Cr was released in this step. The remainder

TABLE 6 Pb REDISTRIBUTION AS A FUNCTION OF HUMIC ACID CONTENT ($\text{mg} \cdot \text{l}^{-1}$ IN 40 ml)		
Composition of model	Pb conc. in Step 1	Redistribu- tion (%)
0.1g calcite, 0.75g kaolin 0.00 humic acid	72	4
0.1g calcite, 0.75g kaolin 0.025g humic acid	35	50
0.1g calcite, 0.75g kaolin 0.05g humic acid	21	70

was as before released in the oxidative treatment in Step 3. Figure 4(c) shows that co-precipitated Ni (goethite) reacted a little differently from Ni adsorbed to synthetic goethite in Model B in that the remobilisation of co-precipitated Ni was about evenly distributed between Step 1 and 2. It could be interpreted that the actual speciation of Ni consisted of a surface-adsorbed component as well as a co-precipitated form which would make up an integral part of the goethite structure.

Model sediment extractions

Model A and D: Adsorption onto natural phases

Figure 4(d) presents the extraction results for Model A, which contained adsorbed metals onto the natural phases: quartzite (Pb), ochre (Ni), kaolin (Zn) and humic acid (Cu). If compared to the results for extractions performed on single doped phases shown in Fig. 4(a) it is clear that a significant amount of redistribution might have taken place for Pb. The results do, however, make sense if it is taken into account that quartzite (host for Pb) is not a strong adsorbing surface. Thus when Pb is released from its host phase in the first step, it could subsequently be re-adsorbed onto available sites on other components in the sediment. This would represent the typical redistribution explanation often encountered in the literature. It is, however, difficult to explain why adsorption of Pb should occur in ca. 0.1 M acetic acid medium at ca. pH 2.8, while our pH adsorption curves suggest that only limited adsorption of Pb occurs at pH values below 5. We have therefore investigated the redistribution of lead in more detail by determining the effect which each phase in Model A would have on the amount of Pb finally measured in Step 1. It was found that ochre and kaolin had a negligible effect but that humic acid adsorbed substantial amounts of lead released in Step 1. The test mixture consisted of 0.1 g synthetic calcite with 75 μg Pb co-precipitated, 0.75 g kaolin and different amounts of humic acid. Table 6 summarises the results.

It would seem that Ni and Zn also released in Step 1 are not affected in the same way as Pb by the presence of humic acid. Further investigation is needed to clarify the differences in the interaction of metals and humic acid.

Cu and Zn show the same pattern in single phase and multiphase extraction in this model, probably because Zn is contained in kaolin which is the major phase component and Cu is

complexed to humic acid and is only released to a significant extent in Step 3. In the case of Ni about 90% is effectively remobilised in Step 1.

The pattern shown in Fig. 4(e) observed in Model D where Cu, Cd, Cr and Zn were adsorbed onto the natural substrates, kaolin, quartzite, ochre and humic acid respectively, was similar to that observed in the single phase extraction results shown in Fig. 4(b). In both cases Cr was released quantitatively in Step 3. The most obvious difference, however, is the fact that only slightly more than half of the Cu was released in Step 1 whereas almost 100% was released in the single phase extraction. A possible explanation could be the effect of humic acid which has a particularly strong affinity for Cu species. There could therefore have been some occurrence of redistribution, as was the case for Pb in Model A, of Cu to humic acid during Step 1. This might explain why Cu also appeared in Steps 2 and 3.

Model B: Adsorption onto synthetic phases

Model B contained adsorbed metals onto the synthetic phases goethite (Ni) and calcite (Pb) mixed with kaolin (Zn) and pure humic acid. Again Zn was quantitatively extracted in Step 1 while Ni and Pb practically showed the same pattern as in Model A shown in Fig. 4(d), indicating no essential difference in behaviour between synthetic and natural phases.

Model C and E co-precipitated phases

Model C contained co-precipitated metal in the synthetic phases goethite (Ni) mixed with kaolin (Zn) and clean humic acid. Essentially the same pattern as in Fig. 4(c) was observed for single phase and model extractions.

In Model E (Fig. 4(f)) the response of the extraction procedures to the co-precipitated fractions Cd (calcite) and Cr (goethite) was investigated. Cd was found not to report quantitatively in Step 1 as was the case in single fraction extraction. The difference is, however, not judged to be large enough to draw significant conclusions.

Cr was primarily released in Step 3 as was previously discussed. The partial dissolution of goethite in Step 2 may explain the presence of some Cr in Step 2. It should be pointed out that according to the Tessier interpretation, Cr should have reported quantitatively in Step 2.

Conclusion

Reproducibility

The average precision obtained in the sequential extraction procedure for more than 200 measurements on 5 models and 6 elements was about 3%. This much better than expected precision, considering the fact that naturally occurring sediment phases were used, strengthens the confidence in reliability of the chemical procedures followed and supports the conclusions drawn from the results.

Indications of redistribution

Redistribution phenomena would show up as differences between single phase extractions and model extractions consisting of mixtures of the same phases.

In Model A, the behaviour of Pb, which was primarily adsorbed onto quartzite, seems to indicate that redistribution of Pb might have occurred. This hypothesis was experimentally investigated and the results indicated that humic acid could play a major role in this phenomenon.

In Model D, Cu showed similar behaviour with some indication of redistribution to the major component, kaolin, or humic acid.

Thus only 2 cases of possible redistribution have been demonstrated. Verification in specially designed experiments is, however, necessary to prove this hypothesis conclusively.

Comments on selectivity

Step 1 Acetic acid

Acetic acid seems to be an efficient extractant to release adsorbed metals from a variety of substrates. It also completely dissolves synthetic calcite.

Step 2 Hydroxylamine hydrochloride

Hydroxylamine hydrochloride is included in the protocol to bring reducible species into solution, particularly iron and manganese oxides. Results show that synthetic goethite co-precipitated with Ni is also attacked by acetic acid, releasing about 50% of the Ni in Step 1. This could also indicate that Ni is partially precipitated as a thin easily dissolved layer onto goethite particles (this hypothesis could, however, not be confirmed by SEM or XRD studies). The remainder is then dissolved with hydroxylamine indicating an incorporation of Ni into the goethite structure. In our results the performance of this extractant provides inconclusive evidence of selectivity.

Step 3 Hydrogen peroxide/ammonium acetate

This extractant is designed to attack oxidisable matter, particularly organic matter. The natural humic acid used in this study was easily dissolved in H_2O_2 . The strength of the metal - humic acid bond, however varied considerably from metal to metal. Zn bonded to humic acid is primarily released in Step 1 with acetic acid whereas Cu could only be released in the last step where the humic acid is dissolved completely. A very important function of the oxidation step with H_2O_2 is to convert Cr(III) to chromate, facilitating its release in Step 3. Further investigation should look into the effect of H_2O_2 on other easily oxidised metals such as Mn(II). Manganese oxides are common components in many

sediments. Depending on the oxidation state of Mn it could therefore either respond in Step 2 or 3.

Assessment

Our overall impression is that the reagents are not selective enough to interpret results in terms of a specific origin in a particular phase. The results, however, indicate that the procedure can distinguish between adsorbed metals primarily reporting in Step 1, except those which form part of the calcite fraction or other substrate that dissolves completely in acetic acid, and co-precipitated or incorporated metals. It should also be kept in mind that trivalent Cr is not released until Step 3, even if adsorbed.

Elements reporting in Step 3 are not necessarily associated with the organic phase as was seen in the case of Cr. Metals associated with the organic phase can be measured in the earlier steps depending on the strength of the metal humic acid complexation constant. Weak complexes will report in Step 1, strong complexes in Step 3.

In conclusion it can be stated that, judging from percentage recovery data, the BCR protocol can distinguish effectively between anthropogenically introduced metals and inert metals or metals integrally contained in the natural mineral fraction. It would therefore seem unnecessary to include the final HF treatment step to dissolve the mineral fraction if the primary aim is to establish the level of pollution or bioavailable content of sediments.

References

- ALLISON, JD, BROWN, DS and NOVO-GRADAC, KJ (1991) MINTEQA2. A Geochemical Assessment Model for Environmental Systems. EPA/600/3-91/021.
- BELZILE, N, LECOMTE, P and TESSIER, A (1989) Testing readsorption of trace elements during partial chemical extractions of bottom sediments. *Environ. Sci. Technol.* **23** 1015-1020.
- BENJAMIN, MM and LECKIE, JO (19??) Amorphous iron oxyhydroxid. *J. Coll. Interface Science* **79** 209-224.
- CAMPBELL, PGC and TESSIER, A (1987) Current status of metal speciation studies. In: Patterson, JW and Passino, R (eds.) *Metal Speciation, Separation, and Recovery*. Lewis Publishers, Chelsea, Michigan, USA. 201-241.
- GUY, RD, CHAKRABARTI, CL and McBAIN, DC (1987) An evaluation of extraction techniques for the fractionation of copper and lead in model sediments. *Water Res.* **12** 21-24.
- HÅKANSSON, K, KARLSSON, S and ALLARD, B (1989) Effects of pH on the accumulation and redistribution of metals in a polluted stream bed sediment. *The Sci. of the Total Environ.* **87/88** 43-57.
- KERSTEN, M and FÖRSTNER, U (1986) Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. *Water Sci. Tech.* **18** 121-130.
- KHEBOIAN, C and BAUER, CF (1987) Accuracy of selective extraction procedures for metal speciation in model sediments. *Anal. Chem.* **59** 1417-1432.
- KIM, ND and FERGUSON, JE (1991) Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soils. *The Sci. of the Total Environ.* **105** 191-209.
- LÓPEZ-SÁNCHEZ, JF, RUBIO, R and RAURET, G (1993) Comparison of two sequential extraction procedures for trace metal partitioning in sediments. *Int. J. Environ. Anal. Chem.* **51** 113-121.
- LUM, KR and EDGAR, DG (1983) Determination of the chemical forms of cadmium and silver in sediments by Zeeman effect flame atomic-absorption spectrometry. *Analyst* **108** 918-924.
- MARTIN, JM, NIREL, P and THOMAS, AJ (1987) Sequential extraction techniques: Promises and problems. *Mar. Chem.* **22** 313-341.
- MEGUELLATI, N, ROBBE, D, MARCHANDISE, P and ASTRUC, M (1983) A new chemical extraction procedure in the fractionation of heavy metals in sediments - interpretation. *Heavy Metals in the*

- Environment, Int. Conf.* **2** 1090-1093.
- NIREL, PMV and MOREL, FMM (1990) Pitfalls of sequential extractions. *Water Res.* **24** 1055-1056.
- RAPIN, F, TESSIER, A, CAMPBELL, PCG and CARIGNAN, R (1986) Potential artefacts in determination of metal partitioning in sediments by a sequential extraction procedure. *Environ. Sci. Technol.* **20** 836-840.
- RAURET, G, RUBIO, R and LOPEZ-SANCHEZ, JF (1989) Optimization of Tessier procedure for metal solid speciation in river sediments. *Int. J. Environ. Anal. Chem.* **36** 69-83.
- RENDELL, PS and BATLEY, GE (1980) Adsorption as a control of metal concentrations in sediment extracts. *Environ. Sci. Technol.* **14** 314-319.
- SALOMONS, W and FÖRSTNER, U (1980) Trace-metal analysis of polluted sediments. Part 2. Evaluation of environmental impact. *Environ. Technol. Letters* **1** 506-517.
- SLAVEK, J, WOLD, J and PICKERING, WF (1982) Selective extraction of metal ions associated with humic acids. *Talanta* **29** 743-749.
- TESSIER, A, CAMPBELL, PCG and BISSON, M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51** 844-851.
- TOWNER, JV (1985) Studies of chemical extraction techniques used for elucidating the partitioning of trace metals in sediments. PhD Thesis, Liverpool University.
- URE, AM, QUEVAUVILLER, PH, MUNTAU, H and GRIEPINK, B (1993) Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *Int. J. Environ. Anal. Chem.* **51** 135-151.
- WRAY, JL and DANIELS, F (1957) Precipitation of calcite and aragonite. *J. Amer. Chem. Soc. Phys. & Inorg. Chem.* **79** 2031-2034.
- XIAO-QUAN, S and CHEN BIN (1993) Evaluation of sequential extraction for speciation of trace metals in model soil containing natural minerals and humic acids. *Anal. Chem.* **65** 802-807.
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