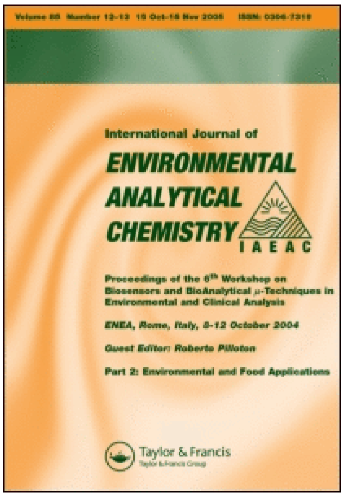

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A New Sequential Extraction Procedure for the Speciation of Particulate Trace Elements in River Sediments

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A NEW SEQUENTIAL EXTRACTION PROCEDURE FOR THE SPECIATION OF PARTICULATE TRACE ELEMENTS IN RIVER SEDIMENTS

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In order to study the bioavailable fraction of river sediments, an analytical procedure involving sequential chemical extraction (soluble with water, really exchangeable, bound to carbonates, manganese oxides, amorphous iron oxides, crystalline iron oxides and to organic matter) has been developed for the speciation of: Si, Ca, Fe, K, Mn, Al, Co, Rb, Sr, Y, Sb, Cs, Pb, U, Th and the lanthanides. Experimental results obtained on replicate samples of river bottom sediments demonstrate that the relative standard deviation of the sequential extraction procedure is very low. The selectivity, the efficiency and the purity of the various reagents toward specific geochemical phases were evaluated and optimized on each individual extraction.

Keywords: Sequential extraction; speciation; river sediments; bioavailability

INTRODUCTION

The determination of total trace elements content in aquatic systems either in suspended load or bottom sediments is not sufficient, because it is the chemical form of the element that determine its mobility, bioavailability and so its toxicity. Adsorbed elements onto solid particles, which own some surface permanently charged or hydroxyl groups, are in their potentially available form because they may be dissolved due to changes in the physico-chemical properties of the aquatic environment such as salinity, pH, redox potential, and concentration of chelators[1–11], as discussed below.

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Salinity increase

The competition between major cations for adsorption sites increases with increasing salinity. That is why many estuaries act as a source of dissolved metals.

Lowering of pH

The acidification of an aquatic system which results from acid precipitation, long-term use of biomass by man, or die-back of trees[12], causes some competitions, for adsorption sites, between H^+ and adsorbed cations. Moreover, a decrease of pH can induce some dissolution of oxides and carbonates and thus dissolution of adsorbed elements.

Redox changes

The oxidising conditions favour the dissolution of organic matter and reducing conditions that of the dissolution of oxides. Consequently, changes of redox potential may release trace elements which were adsorbed on oxides or organic matter. Moreover, in an oxidising environment and with some biological organisms, organic carbon can behave as a strong reducing agent and undergo the following sequential reactions[7, 13–15].

$$Respiration : \ {}^1\!/_4 CH_2O + {}^1\!/_4 O_2 \leftrightarrow {}^1\!/_4 H_2O + {}^1\!/_4 CO_2. \qquad (I)$$

Denitrification :

$${}^1\!/_4 CH_2O + 1/5NO_3^- + 1/5H \leftrightarrow {}^1\!/_4 CO_2 + 1/10N_2 + 7/20H_2O \qquad (II)$$

Nitrate reduction :

$${}^1\!/_4 CH_2O + 1/8NO_3^- + {}^1\!/_4 H^+ \leftrightarrow {}^1\!/_4 CO_2 + 1/8NH_4^+ + 1/8H_2O \qquad (III)$$

Manganese oxide dissolution :

$${}^1\!/_4 CH_2O + {}^1\!/_2 MnO_{2(s)} + H^+ \leftrightarrow {}^1\!/_4 CO_2 + {}^1\!/_2 Mn^{2+}(aq) + 1/8H_2O \qquad (IV)$$

Alcoholic fermentation :

$${}^3\!/_4 CH_2O + {}^1\!/_4 H_2O \leftrightarrow {}^1\!/_4 CO_2 + {}^1\!/_2 CH_3OH \qquad (V)$$

Iron oxide dissolution :

$${}^1\!/_4 CH_2O + FeOOH_{(s)} + 2H^+ \leftrightarrow CO_2 + 7/4H_2O + Fe^{2+}(aq) \qquad (VI)$$

Concentration of chelators

Natural chelators (Cl^- or OH^-) or strong synthetic chelators (such as nitrilotriacetic acid NTA; which is used in some countries as a substitute for detergent polyphosphates) may have significant effects on adsorbed elements. Indeed chelators will form complexes with aqueous cations such as the activities of these aqueous cations will decrease, and adsorbed cations will be released in order to keep a chemical equilibrium between aqueous cations and aqueous complexes.

Sequential extraction is probably the most useful procedure for solid speciation of particulate elements in order to determine the origin, fate, biological and physicochemical availability, and transport of the sorbed elements. The major problems linked to sequential extraction procedures are the lack of selectivity and efficiency of each step of the procedure[9, 16–18]. As the specificity of reagents and of the experimental conditions are extensively discussed, it is necessary to study their impact on natural and synthetic samples in order to be able to chose the best reagent and the best experimental conditions. For this reason, it was decided to develop a new sequential extraction procedure to improve selectivity and efficiency of each step.

Another experimental problem linked to sequential extraction often discussed is the readsorption problem. Indeed trace elements redistribution among different phases during extraction could occur[9, 17–23]. However, other studies[24–25] show that previous articles have overestimated the importance of the opportunity for an element liberated by one extractant to be reassociated with remaining undissolved sediment components before the recovery of the extract. Thus, readsorption phenomena occur, but these reactions are not sufficient to devaluate the speciation results obtained on natural samples[26].

EXPERIMENTAL

Samples

The purity of the samples was checked by X-ray diffraction and electronic microscopy; the chemical compositions were obtained by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

TOT clay minerals

Three smectites (montmorillonite, Clarsol and Colclay) characterised by a deficit of octahedral cations[27] (and sometimes some tetrahedral isomorphic substitutions); one muscovite characterised by tetrahedral isomorphic substitutions[27]

($Si^{4+} \rightarrow Al^{3+}$); one stevensite characterised by octahedral isomorphic substitutions[27] ($Al^{3+} \rightarrow Mg^{2+}$); one saponite characterised by tetrahedral isomorphic substitutions and octahedral isomorphic substitutions[27].

Carbonates

Natural calcite, synthetic calcite (Prolabo) and natural dolomite.

Natural and synthetic oxides

1: synthetic manganese oxide (pyrolusite) from Koch Light Laboratories; 2: synthetic (hematite) iron oxide from Schering A.G. Berlin; 3: natural iron oxide (goethite) from Atlantis II, carrot 1032 VIII 1–6; 4: natural iron oxide (hematite + goethite) from Atlantis II, carrot 1032 XI 75–80); 5: synthetic iron oxide (hematite) from Merck.

River sediment samples

Suspended matter and superficial bank river sediments from Argentina (Chico, Coyle, Colorado and Deseado), Brazil (Piracicaba), France (Ill and Garonne) and Morocco (Sebou) were collected, then dried at 40°C in a stove and stored at 4°C in polypropylene bottles. The use of air dried material for sediments raises the question of preservation of the material. In the case of anoxic sediments this problem is particularly acute[9, 28–29] and Kersten and Forstner[29] have illustrated the major changes in the ralative proportions of the different fractions of heavy metals extracted from a sediment in a sequential extraction scheme following different pretreatment procedures. However, in the case of suspended matter and of superficial bank sediments collected in oxic conditions, the use of air-dried sediments presents here no problem. Moreover, unless they were dried, a microbiological activity would have continued and changes in speciation could occur (reduction reactions and pH evolution[30]). It is why air-dried is the most commonly used conservation method even for river sediments[3, 30–37]. Such materials are then easy to store, homogenise and subsample using procedures well established to the measurement of total element contents.

Instrumentation

The leachates were analysed in the laboratory of water geochemistry following different methods[38–40]. Sodium, potassium and calcium were determined by Flame Atomic Absorption Spectrometry (AAS) with a Perkin Elmer 430 Spectrometer. The silica content has been measured by colorimetry with a Technicon

Autoanalyser II. Iron, manganese and aluminium have been determined by ICP-AES, using an ARL 3500 Spectrometer. The other trace elements have been determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) Fisons VG-Plasma Quad.

Reagents

All reagents were Prolabo analytical grade or Ultrapur quality and presented no pollution problems. However, it is wise to prepare some blanks (no sample) for each extraction in order to determine the cleanness of the different manipulations.

Clean laboratory

To avoid contamination the leachates and the residues were handled with of Teflon or polypropylene materials. The watertight containers used for experiments were previously boiled in 10 % (v/v) chlorhydric acid during at least 2 hours and rinsed with double deionized water.

Leaching procedure, with seven-steps, for trace elements speciation

The leaching procedure (see Table I) was performed in a watertight container to prevent evaporation, with continuous agitation to increase the interaction surface between the reagent and the sediment. The indicated quantities refer to 1g sediment (dry weight at 100°C) of the original sample used for the initial extraction. After each reaction, the residue was filtered and washed with 20 ml of distilled water. At each step of the procedure, the leachate volume was measured in order to prevent the loss of distilled water in the filtration apparatus. Then, the leachate was stored in a polypropylene bottle at 4°C until chemical analyses. Whereas the residue (dried at 40°C in order to prevent any dilution of the following reagent) undergoes the following extraction step. The percentage of each element in the various fractions was calculated on the basis of the total sample concentration of element which was determined by digesting the sample by either a tri-acid attack or an alkaline-melting attack.

TABLE I Protocol summary of the new 7-step sequential extraction procedure

fraction	*reagent*	*reaction time*	*temperature*	*leachate density*
1. dissolved with water	10 ml water	30 min.	20°C	1.000
2. really exchangeable	10 ml of 1 M nitrate magnesium	2 hours	20°C	1.085
3. bound to carbonates	10 ml 1 M sodium acetate, pH=4.50 (HOAc)	5 hours	20°C	1.027
4.a. bound to manganese oxides	10 ml 0.1 M hydroxylammonium chloride	30 min.	20°C	1.002
4.b. bound to amorphous iron oxides	10 ml {0.2 M ammonium oxalate – 0.2 M oxalate acid}	4 hours in the dark	20°C	1.018
4.c. bound to crystalline iron oxides.	10 ml {0.2 M ammonium oxalate – 0.2 M oxalate acid – 0.1 M ascorbic acid}	30 min.	80°C	1.024
5. bound to organic matter	1) 3 ml 0,02M HNO_3 and 8 ml of 35% H_2O_2	1) 5 hours	85 °C	1.057
	2) 5 ml 3.2M ammonium acetate (20% (v/v) HNO_3)	2) 30 min.	85°C	1.057

RESULTS AND DISCUSSION

Preliminary study

A method of separating the extract from the residue had to be chosen between centrifugation or filtration. Thanks to an electronic microscope study we have checked that there were always some suspended particles in the leachate when using centrifugation. This fact could not be accepted for this kind of study. Moreover, a precipitation in the bottom of the centrifugation tubes decrease the interaction surface between the reagent and the surface sediment. Thus, the leachate and the residue were separated by filtration. The dissolved phase is defined as the solution that passes through a 0.45 µm pore size filter. This convention is widely accepted in spite of the fact that a part of the colloidal load (whose size varies from several orders of magnitudes between 1 nm and 10 µm) can pass through the membrane filter[15]. Moreover, the composition and the fabric of the membrane filter have an important influence on the amount of the elements which passes through the filter[41]. Thus, the results are only comparable when filters of the same pore size and of the same material have been used. To be in agreement with most of the scientists, we have filtered the samples with 0.45 μm pore size Millipore filters made of polyvinilidene fluoride (CHR-FF-)n. This kind of filters is known for the purity of the leachates and for its compatibility with several strong acids (HF, concentrate HCl and concentrate HOAc, but not concentrate HNO_3 or HF).

Fraction 1: elements dissolved with water

This fraction is negligible, except if the sample is composed of evaporitic salts[42–43].

Fraction 2: really exchangeable

The aim of this step is to leach cations that are adsorbed onto solid materials due to permanent structural charges (phyllosilicates, phyllomanganates and sometimes organic matter).

Choice of the reagent and experimental conditions

As the ion exchange capacity does not depend on pH, a neutral salt was chosen to leach these cations. The anions currently used are acetates[7, 29,30, 37, 44–47], chlorides[33, 48–51] and nitrates[26, 52]. Nitrates are preferred to avoid selectivity problems with CH_3COO^- and Cl^- which allows the transfer in solution of metals that are not necessarily bound with these active sites[11, 18, 26, 43, 52–54]. A divalent cation, had to be chosen. According to Roger[22] mangnesium is preferred.

Although the pH currently used is 7, the pH of the proposed solution is 5. This pH presents the advantage to minimise readsorption problems which occur especially on neutral surfaces.

Selectivity

In order to study the selectivity of this step, we have applied this procedure to different samples: a natural clay mineral (smectite), natural and synthetic calcites, natural dolomite and iron and manganese oxides. The low concentrations of Si, Al, Ca and Mn measured in the leachates (see Table II) implied that nitrate magnesium treatment did not affect silicates, carbonates, or oxides. Thus all the leachable elements of natural samples are adsorbed elements due to the permanent structural charge only. In spite of the low pH (=5), this extraction is selective.

TABLE II Effect of the leaching with 1 M $Mg(NO_3)_2$ for really exchangeable cations on a synthetic calcite (Prolabo), a natural calcite, a natural dolomite, a synthetic iron oxide (Merck), a synthetic manganese oxide (Koch-Light Laboratories) and a smectite

	weight	*% M*
synthetic calcite.	1 g	0.35 % Ca
synthetic calcite	0.5 g	0.95 % Ca
natural calcite	1 g	0.35 % Ca
natural calcite	0.5 g	1.05 % Ca
natural calcite	0.1 g	2.55 % Ca
natural dolomite	1 g	0.49 % Ca
natural dolomite	0.5 g	1.21 % Ca
natural dolomite	0.1 g	2.27% Ca
MnO_2	1 g	0.01 % Mn
Fe_2O_3	1 g	0.001% Fe
smectite (Clarsol)	0.5 g	0.03 % Al; 0.07 % Si

with M: Ca, Mn, Fe, Al or Si.

Efficiency

In order to study the efficiency of this step, the six pure clay minerals were leached with $Mg(NO_3)_2$. The percentages of interlayer cations (Ca^{2+}, Na^+, K^+) found in leachates were different according to the sample (see Figure 1). This difference can be explained by the fact that the exchangeable cations in the interlayer space must be connected with the distribution of charge on the silicate sheet which they neutralise. When an exchangeable interlayer cation neutralises a deficit in the T-layer or when an exchangeable cation enters a vacancy in the lattice, it cannot really be leached by a neutral salt. Thus, the outer-sphere complexes in the interlayer space are totally leached. Whereas the inner-sphere complexes in the interlayer space and the adsorbed cations which have penetrated in the lattice are not leached. Moreover, we must keep in mind that the non-hydrated K^+ ions prefer to form some inner-sphere complexes when it is possible (when they are some substitutions in the T-layer). On the contrary, the hydrated ions, such as Ca^{2+} or Na^+, form outer sphere complexes in the interlayer space or penetrate the lattice when it is possible (when there are some substitutions or some vacancies in the O-layer).

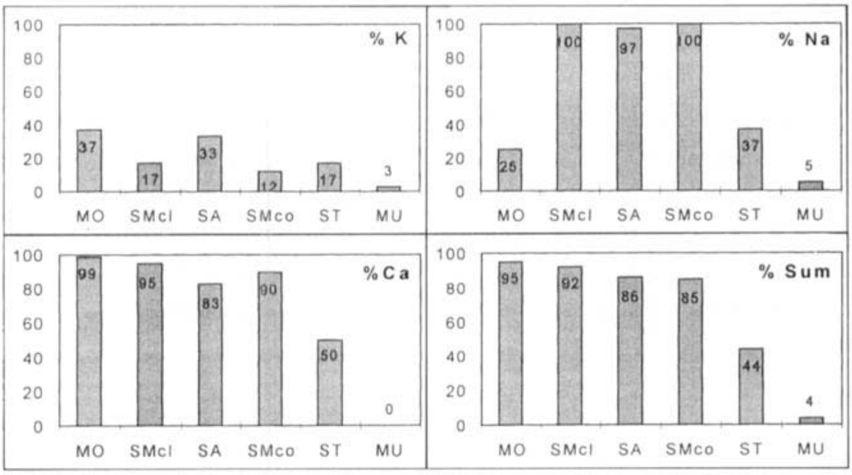

FIGURE 1 Effect of the leaching with 1M $Mg(NO_3)_2$ solution on the really exchangeable cations for seven TOT clay minerals (one montmorillonite (MO), two smectites (clarsol, SM_{cl} and Colclay, SM_{co}), one saponite (SA), one stevensite (ST) and one muscovite (MU)). The results are expressed as the percentage of each cation leached with regard to the total cation concentration in each clay. Sum is the sum (in meq) of Ca, K and Na

Thus, when Ca^{2+} or Na^+ ions are not leached by this magnesium treatment, it can be said that the ion is inside the lattice (on the condition that the stoichiometry of the O-layer is respected). It is the case for the muscovite, where the sodium ions are supposed to be inside the lattice. When a K^+ ion is not leached, it can be said that the ion has lost his hydratation sphere and has formed an inner-sphere complex (on the condition that the amount of T-layer substitution is lower than that of non-leached K^+). It is the case for the muscovite, where the K^+ ions are supposed to have formed an inner-sphere complex. So thanks to these hypothesis and these results it can be known if the cations are present inside the lattice or in the interlayer space (inner or outer sphere complexes).

Conclusion

This second step of the sequential extraction procedure is really selective, and the totality of the elements released in leachates are adsorbed elements due to permanent structural charges. The totality of the outer-sphere complexes in the interlayer space are leached, which is not true for the inner-sphere complexes.

Fraction 3: bound to carbonate

Choice of the reagent and experimental conditions

The reagent usually used to dissolve the carbonates is a mixture of sodium acetate and acetic acid[7, 26, 29, 33, 37, 49, 55]. The percentage of dissolved carbonates is greatly influenced by the pH of 1M NaOAc-HOAc solution (see Table III) and by the amount of carbonates which are present in the sample (see Table IV). The pH=5 commonly used[33] is lowered to 4.50, because experimental tests prove that the sodium acetate solution pH=5 is no efficient to dissolve carbonates (Table III).

TABLE III pH influence on the dissolution percentage of calcite and dolomite for the carbonate fraction

	pH=5.0	*pH=4.5*	*pH=4.0*
1 g natural calcite	12%	77%	100%
1 g natural dolomite	13%	46%	48%

TABLE IV Efficiency of carbonate dissolution with 1 M NaOAc at pH=4.50 according to the initial weight of material

	weight	*% leached Ca; pH = 4.5*
natural calcite	1.0 g	77 %
	0.5 g	100 %
synthetic calcite (Prolabo)	0.5 g	100%
natural dolomite	1.0 g	46 %
	0.5 g	64 %
	0.1 g	73 %

Efficiency

1M NaOAc-HOAc, pH = 4.50 solution is efficient to dissolve carbonates, but we must keep in mind that the studied lg-sample must contain less than 50% of carbonates.

Selectivity

In order to study the selectivity of this step, we have applied this procedure to different samples: an iron oxide, a manganese oxide and a clay mineral (smectite). The low percentages of Fe, Mn, Si and Al measured in the leachates (see Table V) indicate that manganese and iron oxides and silicates are not attacked by the sodium acetate solution, pH=4.50.

TABLE V Effect of the carbonate leaching on an iron oxide, a manganese oxide and a smectite

	weight	*% leached*
MnO_2 (Koch Light Laboratories)	1 g	0.04 % Mn
Fe_2O_3 (Merck)	1 g	0.00002 % Fe
smectite: Clarsol	1 g	0.4 % Si 0,1 % Al

Conclusion

This step of our sequential extraction procedure is really selective and efficient. Indeed, natural river suspended matter and bottom sediment contain less than 50% of carbonates, and thus the totality of calcium carbonates and the majority of carbonates are dissolved during this third step.

Fraction 4: bound to iron and manganese oxides

Under oxidising conditions, hydrous oxides of iron and manganese in sediments are excellent scavengers of metals[3, 18, 35, 42, 47, 56–58]. Their adsorption capacity depends on physico-chemical parameters of the aqueous phase such as pH and ionic strength.

Choice of the reagents

The reductants commonly used to reduce oxides are the sodium dithionite[59–60] (equation X), the acidic hydroxylammonium[29, 30, 33, 37, 42, 49, 61] (equation XI) and the ammonium oxalate[52] (equation XII).

$$S_2O_4^{2-} + 4\,OH^- \qquad 2\,SO_3^{2-} + 2\,H_2O + 2\,e^-,\ E(v) = -1.12^{(62)} \qquad \text{eq X}$$

$$2\,NH_3OH^+ \qquad N_{2(g)} + 2\,H_2O + 4\,H^+ + 2\,e^-,\ E(v) = -1.87^{(62)} \qquad \text{eq XI}$$

$$H_2C_2O_4 + 2\,H_2O \qquad 2\,H_2CO_3 + 2\,H^+ + 2\,e^-,\ E(v) = -0.386^{(62)} \qquad \text{eq XII}$$

The use of sodium dithionite is avoided because this reagent attack clay minerals too[63]. The acidic hydroxylammonium is the perfect reagent to reduce Mn^{4+} to Mn^{2+}[30, 33, 52, 61]. However, in soft experimental conditions (no heat, low concentrations) this reagent is no efficient to reduce iron oxides[64] and in hard experimental conditions this reagent attack clay minerals. It is why another reagent is preferred to reduce iron oxides. Iron oxides can be dissolved by three different types of reactions[65]. If these reactions are considered together, the dissolution of iron oxides is better and faster :

Dissolution by acid: Protons are adsorbed onto the surface of the oxides and facilitate the detaching of iron(III) from the lattice :

$$\mathrm{Fe(III)-OH+H^+ \leftrightarrow Fe(III)-OH_2^+ \leftrightarrow new\ surface\ site+Fe(III)_{aq}}. \quad \text{(XIII)}$$

Detaching of iron(II) is also promoted by specifically adsorbed chelate ligands.

$$\mathrm{Fe(III)-OH+HL^- \leftrightarrow Fe(III)-L^- + H_2O \leftrightarrow new\ surface\ site+Fe(III)_{aq}}. \quad \text{(XIV)}$$

Reduction: If iron(III) onto oxide surface is reduced by an adsorbed reducing agent, iron (II) is released to the solution much faster than iron(III) because bonds between the reduced iron and O^{2-} ions of the crystalline lattice are weakened.

$$\mathrm{Fe(III)-OH+HR \leftrightarrow Fe(III)-R^- + H_2O \leftrightarrow Fe(II)-OH_2+R\,Fe(II)_{aq}}. \quad \text{(XV)}$$

So according to Schuman[52] the amorphous iron oxides were first attacked with 0.2M oxalic acid (acid dissolution) and 0.2M ammonium oxalate (which is a chelate ligand), and then the crystalline iron oxides have been attacked, at 80°C, with 0.2M oxalic acid, 0.2M ammonium oxalate and 0.1M ascorbic acid (strong reductant). Furthermore an experimental test has proved to us that because of the temperature the experiment must be done in a watertight container.

Selectivity

In order to verify the selectivity of these three steps, these procedures were applied to a clay mineral. The low levels of Si and Al found in leachates (see Table VI) show that these three treatments do not affect silicates.

TABLE VI Effect of the oxide leaching procedure on a smectite (Clarsol)

	Si	*Al*
mmoles in 1g sample	4.617	1.58
% leached during manganese oxides leaching	0. 13	0.00
% leached during amorphous iron oxides leaching	0.17	0.67
% leached during crystalline iron oxides leaching	0.23	1.02

Efficiency

The results of the leachates of the five natural and synthetic oxides (see Tables VII and VIII) prove that these three steps (4.a, 4.b and 4.c) are efficient. However, a saturation problem may appear (this problem is recognisable by a brown leachate instead of an colourless or a yellow one) and can be solved by the use of twice or more reagent quantity.

TABLE VII % Mn leached during the oxide leaching procedure on a manganese oxide. For the composition of oxide 1, see text

	manganese oxide leaching	*amorphous iron oxide leaching*	*crystalline iron oxide leaching*	*total oxide leaching*
oxide 1	61	11	12	84

TABLE VIII % Fe leached during the oxide leaching procedure on four iron oxides. For the composition of oxides 2 to 5, see text

	4.a manganese oxide leaching	*4.b amorphous iron oxide leaching*	*4.c crystalline iron oxide leaching*	*total oxide leaching*
oxide 2	0	1	78	79
oxide 3	0	46	50	97
oxide 4	0	2	94	96
oxide 5	0	0	73	73

Fraction 5: bound to organic matter

Choice of the reagent

Two oxidants are commonly used to oxidize organic matter hydrogen peroxide[7, 29, 30, 33, 66] (equation XVI) and sodium hypoclorite[26, 52] (equation XVII). The hydrogen peroxide solution attack carbonates[67] and oxides[52, 68]. However, as the aim of this study was to develop a new sequential extraction procedure and not a parallel extraction procedure, hydrogen peroxide was chosen.

$$H_2O_2 + 2\,H^+ + 2\,e^- \Leftrightarrow H_2O \quad E(v) = 1.77^{[62]} \qquad \text{eq XVI}$$

$$ClO^- + H_2O + 2\,e^- \Leftrightarrow Cl^- + 2\,OH^-,\ E(v) = 1.40\,(pH = 8.5)^{[18]} \qquad \text{eq XVII}$$

Efficiency

In order to study the efficiency of this step, some dead leaves were collected, dried, and crushed to obtain 0.5 to 2 cm pieces. After the oxidation of the organic matter, no pieces of leaves were visible, but after the filtration a white paste covered the filter. By comparison between the initial weight and the residual weight we have determined that 76% of leaves were dissolved. A second test of efficiency has been realized on a soil humus sample and gave a similar percentage (78%). In river suspended matter or in bottom sediments, the organic matter is partially decomposed and thus easier to oxidise. Moreover, chemical bonds between metals and organic compounds are the first bonds to be broken[69]. Thus, this last step can be considered as efficient.

Selectivity

We have applied this procedure to a clay mineral. The low percentages of Si and Al measured in leachates (see Table IX) involve that silicates are not attacked by this treatment. However, sulphurs must be solubilised by this hydrogen peroxide solution[33].

TABLE IX Effect of the organic matter dissolution procedure on a smectite

	Si	*Al*
mmoles total / g sample.	4.617	1.58
% leachate	0.9%	0.4%

Repeatability of this extraction procedure

Four identical samples (bottom sediments from the Garonne river) have been leached by this sequential extraction procedure. The means and standard deviations for the four replicate analyses of the four identical samples are presented in Table X.There were no statistically significant differences between data from the four leachates. The repeatability (which is equal to twice the standard deviation[70]) of this new sequential extraction procedure is below 6% for all the tested elements.

TABLE X Mean and standard deviation of the percentage of leached cations during each step of the sequential extraction procedure on a Garonne river bottom sediments

	fraction 1		*fraction 2*		*fraction 3*		*fraction4.a*		*fraction4.b*		*fraction 4c*		*fraction 5*		*sum*	
	mean	*deviation*	*mean*	*deviation*	*mean*	*deviation*	*mean*	*deviation*	*mean*	*deviation*	*mean*	*deviation*	*mean*	*deviation*	*mean*	*deviation*
Si	0.0	0.0	0.0	0.0	0. 1	0.0	0.0	0.0	0.1	0.0	0.5	0.1	0.2	0. 1	0.8	0.2
Ca	0.7	0.1	8.0	1.0	74.0	4.0	6.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	88.0	3.0
Fe	0.0	0.0	0.0	0.0	1.3	0.2	0.1	0.0	11.0	1.0	35.0	2.0	5.0	1.0	50.0	3.0
K	0.2	0.0	0.3	0.0	0.3	0.1	0.2	0.0	0.2	0.0	0.9	0.1	0.5	0.1	2.3	0.3
Mn	0.0	0.0	2.4	0.3	34.0	4.0	9.0	3.0	9.6	1.3	7.7	0.8	2.3	0.4	64.0	3.0
Al	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	1.2	0.1	4.1	0.4	1.3	0.2	6.2	0.9
Co	0. 1	0.0	0.4	0.2	10.7	2.8	2.5	0.9	19.0	1.4	32.6	2.2	7.8	1.9	73.0	2.5
Rb	0.1	0.0	0.3	0.0	0.2	0.0	0.2	0.0	0.6	0.1	2.5	0.3	1.3	0.2	5.3	0.4
Sr	0.6	0. 1	10.1	1.2	25.0	1.3	2.6	0.5	0.2	0.1	0.7	0.1	0.9	0.1	40.1	2.0
Y	0.0	0.0	0.1	0.0	7.6	0.8	0.1	0.0	2.1	0.9	1.2	0.2	0.3	0.2	11.4	1.1
Sb	0.3	0.0	3.6	0.2	2.7	0.3	0.8	0.1	8.1	0.5	21.9	1.2	3.3	0.6	41.0	1.0
Cs	0.1	0.0	0.2	0.1	0.2	0.0	0.1	0.0	1.0	0.2	4.5	0.5	2.9	0.3	9.0	0.6
La	0.0	0.0	0.2	0.0	7.8	0.8	0.1	0.0	0.7	0.3	0.7	0.1	0.4	0.3	9.9	0.7
Ce	0.0	0.0	0.0	0.0	7.8	0.8	0.1	0.0	0.8	0.4	0.7	0.1	0.6	0.3	10.1	0.9
Pr	0.0	0.0	0.2	0.0	8.6	1.0	0.1	0.0	0.8	0.4	0.7	0.1	0.3	0.2	10.7	0.9
Nd	0.0	0.0	0.1	0.0	9.5	1.1	0.1	0.0	0.8	0.4	0.7	0.1	0.3	0.2	11.4	1.0

	fraction 1		*fraction 2*		*fraction 3*		*fraction4.a*		*fraction4.b*		*fraction 4c*		*fraction 5*		*sum*	
	mean	*deviation*	*mean*	*deviation*	*mean*	*deviation*	*mean*	*deviation*	*mean*	*deviation*	*mean*	*deviation*	*mean*	*deviation*	*mean*	*deviation*
Sm	0.0	0.0	0.3	0.1	11.3	1.2	0.1	0.0	1.0	0.5	0.8	0.2	0.5	0.3	14.1	1.2
Eu	0.1	0.0	1.9	0.4	15.6	1.5	0.3	0.0	1.7	0.8	1.5	0.2	0.7	0.2	21.7	1.5
Gd	0.0	0.0	0.5	0.1	14.0	1.5	0.2	0.0	1.5	0.8	1.2	0.3	0.5	0.3	17.9	1.4
Tb	0.1	0.0	1.6	0.3	12.1	1.2	0.2	0.0	2.3	1.1	1.4	0.3	0.5	0.2	18.2	1.5
Dy	0.0	0.0	0.3	0.0	8.7	1.0	0.1	0.0	2.2	1.0	1.4	0.2	0.4	0.2	12.9	1.3
Ho	0.0	0.0	0.9	0.3	8.0	0.9	0.1	0.0	2.3	0.9	1.4	0.2	0.4	0.1	13.2	1.2
Er	0.0	0.0	0.4	0.1	7.5	0.7	0.1	0.0	2.3	0.8	1.5	0.3	0.3	0.2	12.2	1.1
Tm	0.1	0.0	1.8	0.4	6.1	0.6	0.1	0.1	2.3	0.6	1.5	0.3	0.5	0.2	12.3	1.0
Yb	0.0	0.0	0.4	0.1	5.6	0.6	0.1	0.0	2.1	0.7	1.7	0.3	0.4	0.1	10.2	0.9
Lu	0.1	0.0	2.0	0.4	6.1	0.6	0.1	0.1	2.3	0.5	1.8	0.2	0.7	0.1	13.0	0.9
Pb	0.1	0.0	0.1	0.0	19.4	1.6	0.3	0.1	2.7	0.7	9.3	1.2	4.3	0.8	36.2	0.7
Th	0.1	0.0	0.2	0.1	3.2	0.3	0.0	0.0	21.5	2.0	16.5	2.4	2.9	0.5	44.2	1.1
U	0.1	0.0	0.9	0.3	5.7	0.5	0.1	0.0	4.7	0.4	6.4	0.5	2.8	0.3	20.6	0.9

Some applications

Predictably, the intensity of the leachate varies according to the different samples, for example, the Argentine samples, which are poor in carbonate and organic fractions, are less leachable than the other ones. Nevertheless, whatever the origin of the sample, the elements which belong to a same chemical family have a similar leachate profile[71]. For example, the alkalines (Rb, Cs), silicium and aluminium stay linked to the residual fraction. On the contrary, metals (Fe, Mn, Co and Pb) are highly bioavailable; 30 to 60% and 50 to 100% of the cobalt are available in Argentinean, Brazilian, French and Moroccan samples, respectively. On the other hand, until 78% of lead are bioavailable in French river suspended matters. Metals are mainly controlled by iron and manganese oxide fraction, but they are sometimes present in the carbonate or organic fractions too. The alkaline earth elements (Sr and Ca) are highly bioavailable (between 40 to 90%, 40 to 65% and 65 to 100% of the total Sr is bioavailable, respectively, in Brazilian, French and Moroccan river sediments) and they are mainly associated with the exchangeable and carbonate fractions. The actinides (U and Th) present often two kinds of profiles : Th is mainly associated to the oxides whereas U is linked at the same time to the oxides and to the carbonates. Nevertheless, for a given sample, uranium and thorium have the same bioavalability, which is very different from a sediment to an other (between 7 to 82%). The rare earth elements (REE) are mainly linked to the carbonates, organic matter and iron oxides.

CONCLUSION

The aim of this new sequential extraction procedure is to leachate the total bioavailable fraction of a river sediment (which includes : soluble with water, really exchangeable fraction, carbonate fraction, oxide and organic matter fractions). The efficiency and the selectivity of each step is improved compared with the commonly used sequential extraction procedures. If we want to compare this new sequential extraction procedure with the commonly used Tessier's procedure[33], we may notice five main differences :

- magnetic agitation is applied to increase the surface interaction between the reagent and the sediment.
- filtration process is preferred to centrifugation to avoid precipitation problems on the bottom of centrifugation tubes.
- in fraction 2 (really exchangeable cations), magnesium nitrate replaces magnesium chloride to avoid complexation problems and pH is lowered to prevent readsorption problems.

- in fraction 3 (bound to carbonates), the pH is lower in order to improve the efficiency of this step.
- in fraction 4 (bound to oxides) the procedure is completely modified to optimise the dissolution of the oxides.

The improvement of the technique was found to be satisfactory, with a good repeatability, no pollution problems, a good efficiency and a good selectivity for each step. The fractionation scheme presented may be used to study the behaviour of particulate trace elements during their fluvial transport and to determine their speciation and their toxicity. This method could be a useful tool for a better understanding of trace elements biogeochemistry in river suspended matter and bottom sediment chemistry and for the development of improved soil extraction techniques.

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