

Comparison of three sequential extraction protocols for the fractionation of potentially toxic metals in coastal sediments

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Abstract In the determination of the best sequential extraction procedures (SEP) for the speciation of metals in sediment samples from the Lagos lagoon system, three sequential extraction procedures were compared for the fractionation of Cd, Cr, Cu, Pb, and Zn. The SEP compared included a modified Tessier's procedure carried out in five steps, while the two other procedures were the three-step original Community Bureau of Reference (BCR) and the modified BCR techniques (four steps). Quantification of the metal concentration was achieved with a flame atomic absorption spectrophotometer. The results obtained by the three methods were compared, and the modified BCR and Tessier SEP were found to extract more Cu, Cr, Pb, and Zn in the reducible phase and therefore a decrease in the oxidizable phase than the original BCR SEP. The most mobile elements were found to be Cd, Pb, and Zn. These are of environmental concern, as these potentially toxic metals could be easily released into the aquatic environment with consequent inges-

tion by aquatic organisms, thereby entering the food chain. The mass balance (percent recovery) was found to be between 85% and 115% in most cases. Prior to the comparison, the analytical performance of the laboratory was tested using a secondary reference material, GLAURM, using the three-step modified BCR procedure. The results showed high reliability of the analytical performance of the laboratory for all the metals considered.

Keywords Speciation · Potentially toxic metals · Sediments · Lagos lagoon · Sequential extraction

Introduction

Environmental pollution from potentially toxic metals (PTMs) is of concern because they exhibit behavior consistent with those of persistent toxic chemicals. Unlike many organic contaminants that lose toxicity with biodegradation, metals cannot be degraded and their toxic effects can therefore be long lasting (Clark 1992). Although their concentration in biota can increase through bioaccumulation, some heavy metals are known to have toxic effects even at very low concentrations (Davey et al. 1973).

The total concentration of potentially toxic elements in the environment does not provide information about the distribution, mobility, and

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potential bioavailability of elements. Consequently, the knowledge of the strength of bonds between the metals and the sediments is necessary to evaluate the availability and the capacity of mobilization of the PTMs in the sediments. To acquire this information, operationally defined speciation is necessary. This can be carried out by sequential extraction (SE; Mester et al. 1998; Filgueiras et al. 2002). The main goal of the studies on operational speciation is to convert the metals bound in the solid phases into soluble forms with the extractants used at each step (Tokalioglu et al. 2000). Sequential extraction schemes provide information on the potential bioavailability and mobility of sediment-bound metals (Stone and Marsalek 1996) and heavy metal bioavailability (Kennedy et al. 1997). Different sequential extraction schemes have been proposed, and most of these include a number of steps between 3 and 8. One of the first and most applied sequential extraction procedure proposed is a five-step procedure published by Tessier et al. (1979). Several other procedures followed the Tessier procedure, and there is now a wide variety of sequential extraction procedures available based on different sequence of extractants and different operational conditions.

The lack of uniformity of the extraction schemes and also of reference materials hindered the comparison of the schemes and the validation of the procedures. Consequently, the Community Bureau of Reference (BCR, now Standards, Measurements and Testing Programme) organized a series of intercomparisons on extractable trace metal determination and a workshop on sequential extraction techniques in sediments and soils to discuss results of intercomparisons and establish a common procedural scheme. This project led to the optimization of a three-step procedure and also to the production of a reference material (BCR 601; Quevauviller et al. 1993, 1997).

The original BCR procedure has been used with good reproducibility within laboratories. The use of a sediment standard reference material showed excellent reproducibility, except for analytes that were close to detection limits (Mester et al. 1998; Svete et al. 2001). The original BCR procedure was tested on sewage sludge (Perez-Cid et al. 1996), river sediments (Svete et al. 2001),

car park dust (Tokalioglu et al. 2003), street dust (Stone and Marsalek 1996), soil (Ho and Evans 1997), and compost (Greenway and Song 2002).

The BCR (original) scheme was tested in a first interlaboratory trial on BCR 601 on the extraction of Cd, Cr, Cu, Ni, Pb, and Zn, and the results showed that while promising, improvements were necessary due to the fact that only 60% of the extractable metals were certifiable (Ure et al. 1993). The remaining metals could not be certified due to the high variability between the results obtained by the different laboratories, and this was attributed to small variations in the pH of the hydroxylamine hydrochloride. It was also reported by Davidson et al. (1999) that when three analysts prepared their own reagent and performed sequential extraction independently and on a different day, results showed significant inter-analyst variability.

The BCR scheme was therefore improved with respect to the second step by the addition of a fixed amount of nitric acid; the concentration of hydroxyl ammonium chloride was increased from 0.1 to 0.5 M, and a reference material (BCR701) was certified. The modified protocol also recommended the inclusion of an additional step, a residual extraction stage (step 4) to allow comparison with pseudo-total digestion results for validation purposes (Pueyo et al. 2001). The original and modified BCR sequential extractions have been compared (Rauret et al. 1999; Mossop and Davidson 2003; Brunori et al. 2004; Joksic et al. 2005). Mossop and Davidson (2003) observed that increasing the concentration of hydroxylamine hydrochloride in step 2 had little effect on Fe, but the influence of the extractant pH was more important. This was also the case for copper and lead, while it was observed that the zinc partitioning was relatively unaffected by the changes in the sequential extraction scheme.

The purpose of this study was to compare the results of three sequential extraction protocols (a slightly modified five-step Tessier, the original BCR, and the modified BCR protocols) for the fractionation of some potentially toxic metals in sediments from the Lagos lagoon system. The investigation of the sediments of the Lagos lagoon system is based on the importance of this water body to the lives of people in Lagos State

in Southwest Nigeria and also because there has been no previous comparison of the efficiency of these three SE protocols in coastal sediments.

Experimental

Instrumentation

Analyses were carried out on a flame atomic absorption spectrophotometer fitted with a hollow cathode lamp (Perkin-Elmer AA Analyst 200) using an air–acetylene flame. Sequential extractions were performed using 50-ml polytetrafluoroethylene centrifuge tubes, an IKA HS 260 basic reciprocating shaker, and an R-8C laboratory centrifuge.

Reagents

Stock standard solutions of Cd, Cr, Cu, Pb, and Zn (1,000 µg/ml) were obtained from VWR International (BDH). The working standard solutions for the calibration of the FAAS were prepared daily, and distilled water was used for all dilutions. All the glasswares used were soaked in 5% HNO₃ overnight and rinsed properly with glass-distilled water before use. For quality control, a reference material, GLAURM, an urban soil secondary material prepared by participants in the EU URBSOIL project (Davidson et al. 2006) was used to check the analytical performance of the laboratory as well as that of the analyst.

Sampling and sample preparation

Surface sediments (0–5 cm) were collected from the Lagos Lagoon system (Nigeria) by means of a stainless steel grab sampler into polyethylene containers and taken to the laboratory. Once in the laboratory, the sediment samples were air dried, homogenized in a mortar, sieved to pass through a 2-mm stainless steel sieve (Endecott test sieve), and stored in polyethylene containers.

Aqua regia digestion

Pseudo-total metal concentration was determined by digesting with aqua regia (3 HCl:1 HNO₃) on a

hot plate. One gram of the sediment was digested with 20-ml aqua regia for 2 h. After cooling, the digest was filtered into a 100-ml flask (using a Whatman filter paper, 11 cm) and stored in plastic bottles at a temperature of 4°C prior to the analyses. The metals were determined by FAAS under optimal conditions.

Sequential extraction protocols

Tessier et al. (1979) protocol (slightly modified)

1. Step 1 (exchangeable phase). One gram of sediment was extracted at room temperature with a sodium acetate solution (1 M, pH 8.2) for 1 h with continuous agitation.
2. Step 2 (bound to carbonates). The residue from step 1 was leached at room temperature with 8 ml of 1-M NaOAc (adjusted to pH 5.0 with acetic acid) for 5 h with continuous agitation.
3. Step 3 (bound to Fe–Mn oxides). The residue from step 2 was extracted with 20 ml of 0.04-M NH₂OH·HCl in 25% (v/v) HOAc at 96 ± 3°C for 5 h with occasional agitation.
4. Step 4 (bound to organic matter). To the residue from step 3 was added 3 ml of 0.02-M HNO₃ and 5 ml of 30% H₂O₂ adjusted to pH 2 with HNO₃. The mixture was heated to 85 ± 2°C for 3 h with intermittent agitation. A second 3-ml aliquot of 30% H₂O₂ was then added, and the mixture was heated again to 85 ± 2°C for 3 h with intermittent agitation. After cooling, 5 ml of 3.2-M NH₄OAc in 20% (v/v) HNO₃ was added, and the sample was diluted to 20 ml and agitated continuously for 30 min.
5. Step 5 (residual). In order to calculate the mass balance, this step was modified by using aqua regia instead of HF-HClO₄ as recommended by Tessier. The residue from step 4 was digested with aqua regia for 2 h on a hot plate.

Original BCR protocol

1. Step 1 (exchangeable and acid soluble fraction). One gram of air-dried sediment was ex-

tracted with 40 ml of 0.11-mol^{-1} CH_3COOH for 16 h at $22^\circ\text{C} \pm 5^\circ\text{C}$ (overnight).

2. Step 2 (reducible fraction). The residue from step 1 was extracted with 40 ml of freshly prepared 0.1-mol^{-1} hydroxylamine hydrochloride at pH 2.0 for 16 h at $22^\circ\text{C} \pm 5^\circ\text{C}$ (overnight).
3. Step 3 (oxidizable fraction). Ten milliliters of 8.8-mol^{-1} hydrogen peroxide was added carefully in aliquots (to avoid losses due to possible violent reactions) to the residue from step 2 and digested at room temperature for 1 h with occasional manual shaking. The digestion was continued for 1 h at $85^\circ\text{C} \pm 2^\circ\text{C}$ with occasional agitation for the first 30 min in a water bath and then reduced to a volume of <3 ml. Ten milliliters of hydrogen peroxide was further added to the digest and concentrated to about 1 ml. Fifty milliliters of 1.0-mol^{-1} ammonium acetate was then added, extracted, and washed as in previous steps.

As an internal check on the procedure, the residue from step 3 was digested in aqua regia, and the total amount of metal extracted (i.e., sum of step 1 + step 2 + step 3 + residue) was compared with that obtained by the aqua regia digestion of a separate 1-g sample of the sediment.

Modified BCR protocol

This was carried out according to the method of Rauret et al. (1999):

1. Step 1 (exchangeable and acid soluble fraction). Forty milliliters of 0.11-mol^{-1} CH_3COOH was added to 1 g of air-dried sediment in a 50-ml centrifuge tube, stoppered, and extracted by shaking with a mechanical, end-over-end shaker at a speed of 23 rpm for 16 h at $22^\circ\text{C} \pm 5^\circ\text{C}$ (overnight). The extract was separated from the solid residue by centrifugation at 3,000 rpm for 20 min, and the supernatant liquid was decanted into a polyethylene container. The extract was stored in a refrigerator at about 4°C prior to the analysis. The residue was washed by adding 20 ml of distilled water, shaken for 15 min on the end-over-end shaker and centrifuged for 20 min at 3,000 rpm. The

supernatant was carefully discarded without discarding any of the solid residues.

2. Step 2 (reducible fraction). Forty milliliters of freshly prepared 0.5-mol^{-1} hydroxylamine hydrochloride was added to the residue from step 1 in the centrifuge tube and extracted, and the residue was washed as in step 1, shaken for 15 min on the end-over-end shaker and centrifuged for 20 min at 3,000 rpm. The supernatant was carefully discarded without discarding any of the solid residues.
3. Step 3 (oxidizable fraction). Ten milliliters of 8.8-mol^{-1} hydrogen peroxide was added carefully in aliquots (to avoid losses due to possible violent reactions) to the residue from step 2 and digested at room temperature for 1 h with occasional manual shaking. The digestion was continued for 1 h at $85^\circ\text{C} \pm 2^\circ\text{C}$ with occasional agitation for the first 30 min in a water bath and then reduced to a volume of <3 ml. Ten milliliters of hydrogen peroxide was further added to the digest and concentrated to about 1 ml. Fifty milliliters of 1.0-mol^{-1} ammonium acetate was then added, extracted, and washed as in the previous steps.

As an internal check on the procedure, the residue from step 3 was digested with aqua regia, and the total amount of metal extracted (i.e., the sum of step 1 + step 2 + step 3 + residue) was compared with that obtained by the aqua regia digestion of a separate 1-g sample of the sediment.

Results and discussion

Physico-chemical properties of sediments

The results of the physico-chemical properties of the sediments used for the comparison of the sequential extraction techniques are shown in Table 1. The sediments used had varying concentrations of potentially toxic metals and were all found to be acidic. In order to assess the quality of the data obtained, a secondary reference material prepared by participants in the EU URBSOIL project for use as internal quality control samples was used and the physico-chemical properties were determined. The result of the GLAURM

Table 1 Result of the physico-chemical properties of the sediment and the reference material (GLAURM)

	pH (CaCl ₂)	% Organic matter	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	CEC (meq/100 g)
A	3.1	5.1	4.8 ± 0.4	102 ± 3	54.4 ± 2.3	43.5 ± 3.7	157 ± 3	4.2
B	3.9	10.2	21.3 ± 0.6	<22	139 ± 3.0	119 ± 8	777 ± 17	14.6
C	5.9	6.6	<0.9	140 ± 3	106 ± 2	202 ± 5	641 ± 25	8.2
D	4.4	1.6	<0.9	112 ± 8	33.8 ± 2.6	44.2 ± 1.9	112 ± 12	3.4
GLAURM								
Target value	4.2	11.7	<0.74	43.2 ± 3.0	111 ± 5	387 ± 25	177 ± 11	*
Found value (n = 4)	4.2	11.2	<0.9	39.2 ± 4.2	107 ± 7	375 ± 19	181 ± 14	*

*not determined

showed that a good agreement was found to exist between the target and found values, and the values found were also within two standard deviations in all the cases. This indicated a good analytical performance of the laboratory and the method.

Evaluation of the analytical performance of the laboratory on the modified BCR protocol

Sequential extraction was performed on the secondary reference material (GLAURM) using the modified BCR protocol. The results obtained are represented in Fig. 1.

The result of fractionation of the GLAURM was also compared to the target values (Fig. 1). There was no significant difference between the values of the sums of steps 1 to 4, whereas higher concentrations were found in step 3 for all the

metals. This could be due to the slightly different extraction procedures used. Generally, a good recovery was found for all the metals in all the steps (80%–116%), except for Cr in all the steps and Zn in step 4, showing a good analytical performance of the laboratory.

Comparison of the three sequential extraction schemes

Figure 2 shows the fractionation pattern of Cd, Cr, Cu, Pb, and Zn in the sediments using the three different SE schemes.

From the graphs, for all the metals analyzed and in all the samples used, there was no significant difference in the sum of the concentrations found in each step of the original BCR and the modified BCR. This is probably due to the similarity in the SES schemes of the two methods.

Comparison between the sequential extraction procedures showed that the Tessier and the modified BCR scheme extracted more Pb, Zn, Cu, and Cr in the reducible phase and, consequently, a decrease in the oxidizable phase (Fig. 2). This might be due to the increase in the concentration of the NH₂OH.HCl and the decrease in the pH for the modified BCR that probably prevented readsorption. Readsorption occurs when the metals that had originally been extracted (using hydroxylamine hydrochloride in this case), moves from the solution and adheres to the surface of the sediment matrix. The higher the concentration of the hydroxyl amine hydrochloride present, the more the amount of ions available to break the Fe and Mn oxide bonds. The increase in concentration therefore provided a more effective attack on the more refractory crystalline oxyhydroxides.

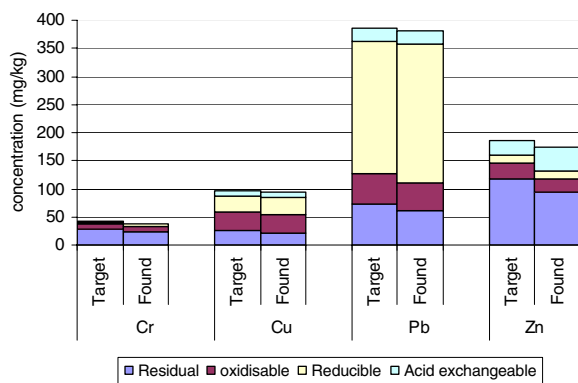


Fig. 1 Fractionation pattern of Cr, Cu, Pb, and Zn in GLAURM, with respect to the target fractionation pattern (n = 4)

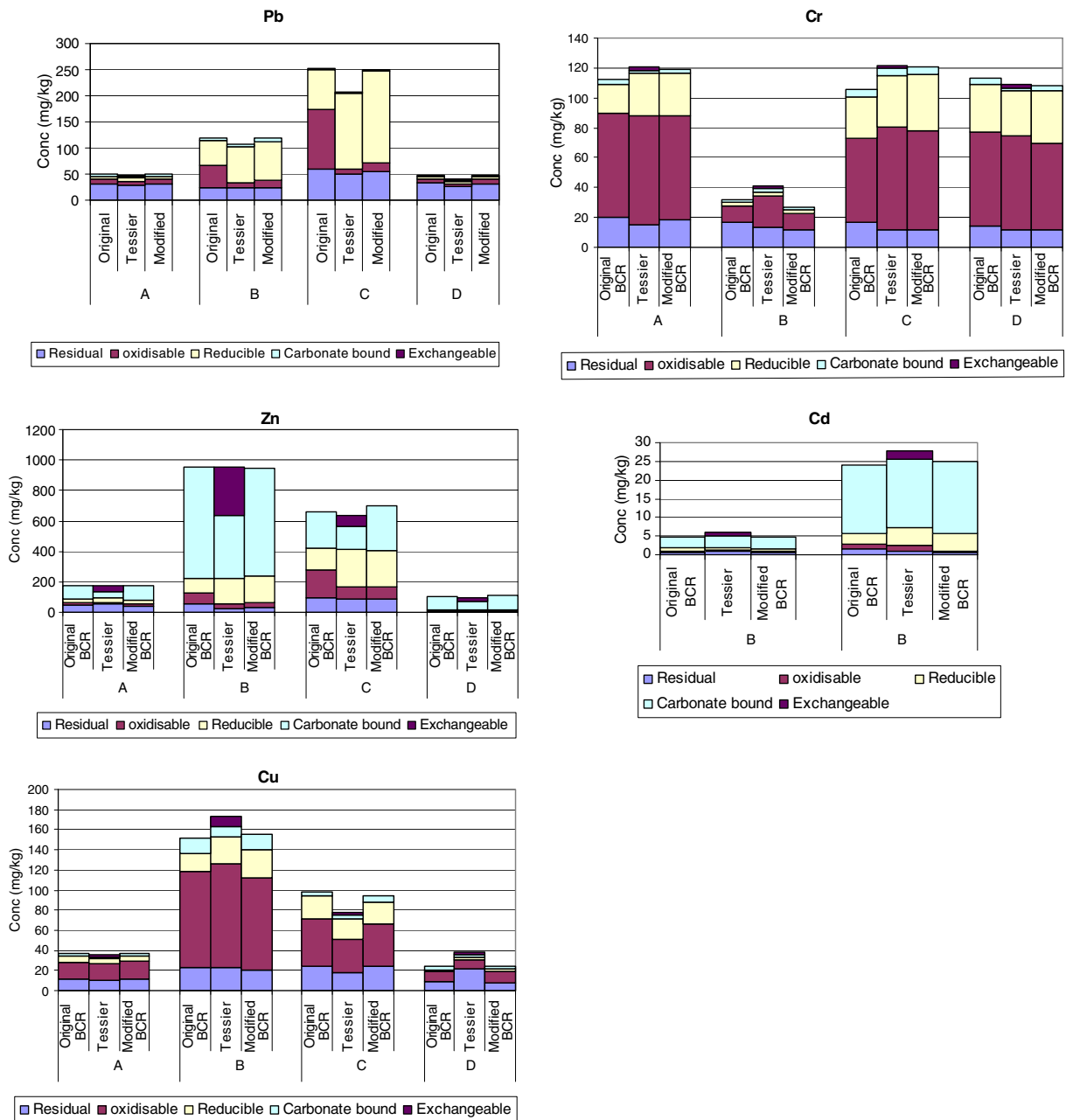


Fig. 2 Fractionation pattern of Cd, Cr, Cu, Pb, and Zn using the three different SE schemes

Furthermore, the decrease in pH probably made the metals more soluble in the extracting solution, preventing re-adsorption. The same trend was observed by Mossop and Davidson (2003) in their comparison of the original and modified BCR sequential extraction procedures for the fraction-

ation of copper, iron, lead, manganese, and zinc in soils and sediments from the UK. In the case of the Tessier method, the increase in the amount of Pb, Zn, Cu, and Cr extracted could be as a result of the acetic acid used in lowering of pH. Compared to the nitric acid used in both BCR protocols (orig-

inal and modified), acetate ions have complexing properties (higher stability constant with metals) that prevent readsorption. This also showed that the modified procedure affords a better attack on the iron-based components of the reducible matrix for a range of soils/sediments.

A small difference in the sum of the concentrations found in each step was observed between the BCR methods and the Tessier method. The BCR methods (both original and the modified) removed more Pb compared to the Tessier method. This might be due to differences in the extraction conditions between the schemes. Tessier’s method was observed to remove more chromium than the BCR methods. This could be because step 1 of the BCR methods (exchangeable and carbonate-bound phase) uses 0.1-M acetic acid, while step 2 of the Tessier method (carbonate bound) uses 1-M sodium acetate adjusted to pH 5 with acetic acid. The reagent in Tessier’s method closely resembles the acetic acid used in step 1 of the BCR methods, but with 10 times its concentration, which means that there are more of the anions present in the solution to bind with the cation. Furthermore, since the chromium ion is a hard acceptor, it has a higher affinity for the acetate ion that is also a hard donor because it uses the oxygen donor atom. Also, sodium acetate has a higher ionization constant compared to the acetic acid, and this makes the acetate ion in the sodium acetate more readily available for complexation. The higher ionization constant is because sodium is a better leaving group than hydrogen ion due to its bigger size. This explains why Tessier’s method in step 2 is much more efficient in extracting chromium.

In the case of zinc, no significant difference was observed both in the sums of the steps and the distribution of the metals along the steps [except for the original BCR (step3) for sample C].

Elemental recoveries

For a further validation of the result, recoveries were calculated. According to Tokalioglu et al. (2003), an important consideration in the reliability of a sequential extraction data is the percentage recovery relative to a single digestion using a

mixture of strong mineral acids, i.e., aqua regia at the digestion of the residual phase of the sequential extraction protocol employed. The recovery (mass balance) was calculated by summing up the concentration of each of the metals in the different fractions and then comparing with the concentration of the pseudo-total metals.

Recovery

$$= \frac{[\sum \text{sequential extraction procedure}]}{\text{single digestion with strong acids}} \times 100$$

The mass balance (average percentage recoveries obtained from the three different SES) is shown in Table 2. This was between 85%–115% in most cases, with the exception of Cd in the Tessier method which has a recovery of 130%.

Conclusions

This research has compared the results of fractionation of potentially toxic metals in sediments using the three-stage original BCR protocol, the modified BCR protocol, and the five-stage Tessier SE protocol (modified).

Generally, and according to Mester et al. (1998), the differences between the sequential extraction schemes could be explained by the variability of the analytical methods, the different extraction conditions of the three SES schemes, and difference in the complexing ability of the metals with the different complexing agents. It was also observed that the measured concentration of metals in the different fractions of the SE protocols depend strongly on the extractant as well as the sequence in which the reactants are applied.

It can therefore be concluded that if the aim of the experiment is to determine the concentration

Table 2 The average percentage recoveries obtained from the three different SES

Metal	Original BCR	Tessier method	Modified BCR
Cd	107 ± 7	130 ± 2	106 ± 15
Cr	98 ± 16	110 ± 22	98 ± 14
Cu	85 ± 19	94 ± 29	86 ± 19
Pb	111 ± 10	98 ± 9	110 ± 10
Zn	99 ± 9	97 ± 13	103 ± 9

of the fraction of the metal characterized by the highest mobility and bioavailability, the three-step procedure, applied on samples for which the total concentration is high enough, is therefore recommended for speciation instead of the long and more tedious procedures. However, on the contrary, the five-step protocol gives more information about the fraction of metals bound to different phases of the sample.

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