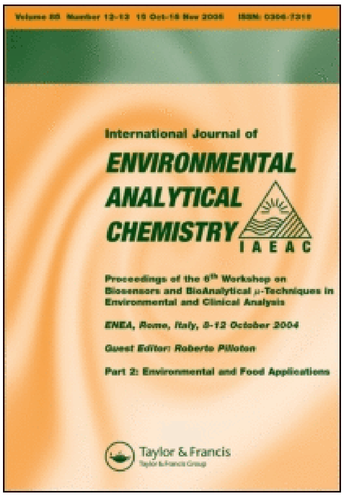

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COMPARISON OF TWO SEQUENTIAL EXTRACTION PROCEDURES FOR TRACE METAL PARTITIONING IN SEDIMENTS

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Two sequential extraction schemes (a modified Tessier procedure with five steps and a three steps protocol designed by BCR) are applied to four sediment samples with different heavy metal contents. The results obtained for Cd, Cr, Cu, Ni, Pb and Zn partitioning show that the metal distribution obtained with both procedures are significantly different. With the second procedure amounts of all the heavy metals are extracted with the oxidizing reagent (third fraction) whereas with the first one the non residual metals are distributed among the second, third and fourth fractions (acetic acid-acetate buffer (pH=5), reducing and oxidizing reagents respectively). The residual fraction obtained applying the three steps procedure is in general higher than that obtained using the five steps procedure, except for cadmium.

KEY WORDS: Sediments, trace metal partitioning, sequential extraction methods, cadmium, chromium, copper, nickel, lead, zinc.

INTRODUCTION

In studies of heavy metal pollution in sediments, the use of sequential extraction schemes to determine metal partitioning has experienced increased attention during recent years, because it has been recognized that the chemical form of the metal in the sediment determines its behaviour in the environment.[1-5] All the schemes described in the literature deal with the distribution of the heavy metals among the different phases of a sediment: sorbed metals, carbonates, reducible and oxidizable substrates, extractable organics, sulfides and residual minerals. Among the proposed schemes that proposed by Tessier *et al.*[6] is the most widely used, but those proposed by Salomons and Förstner,[7] Towner,[8] Meguellati *et al.*[9] or Lum and Edgar[10] are also applied. Several studies[11-14] pointed out that some changes in the experimental variables, even using the same scheme, can lead to different distributions of heavy metals in the different fractions. In a study performed by Ure *et al.*[15] it was concluded that the crucial need in sequential extraction studies is to establish a standard procedure.

To harmonize criteria the Community Bureau of Reference (BCR) has organized a project concerned with improving the quality on the determination of extractable contents of trace metals in soils and sediments using sequential extraction schemes. As a result of this project a protocol to be used by the participants in an intercomparison study was designed.

This paper compares the results obtained when using two different schemes. Firstly, one proposed by Tessier *et al.*, slightly modified for heavily polluted sediments,[13,14] which implies five fractions: pH=7 exchangeable metal, acetic acid-acetate buffer extractable, acidic hydroxilammine extractable and acidic hydrogen peroxide extractable and residual metals, and secondly the protocol designed by the BCR which implies only three fractions: acetic acid extractable, acidic hydroxylamine extractable and acidic hydrogen peroxide extractable metals. These procedures were applied to four sediment samples with different heavy metal contents. The results obtained are compared and the distribution of the metals in the different fractions is discussed.

EXPERIMENTAL

Sampling

Samples T5, B4 and B5 were collected in Besos river basin (Spain) at three different sampling points, and were pretreated as described previously.[16] Sample (BCR-S7) was obtained from BCR.

Instrumentation

An atomic absorption spectrophotometer, Perkin Elmer Model 4000, with double beam, background corrector and hollow cathode lamps was used, coupled with a graphite furnace, Perkin Elmer HGA 500. Injection was carried out using the Perkin Elmer AS-40 autosampler. An atomic absorption spectrophotometer, Perkin Elmer Model 1100 B, with single beam, background corrector and hollow cathode lamps was used for air-acetylene flame measurements.

Reagents

All reagents were Merck analytical grade or Suprapur quality. Stock solutions contain 1 $g.l^{-1}$ of metal, acidified with nitric acid. All standards and reagent solutions were stored in polyethylene bottles. Double deonized water (Culligan Ultrapure GS 18.3 $Mohm.cm^{-1}$ resistivity) was used.

Clean laboratory

Sample treatment was performed in a clean laboratory with a Class-100 air work bench. All glassware and plasticware used in the experiments was previously soaked in a 10% (v/v) nitric acid solution for at least 24 hours and then rinsed five times with double deionized water before use.

Speciation procedures

Procedure A): A modified Tessier procedure[13,14] was applied. Extractions were carried out in 50 ml PTFE tubes, stoppered with PTFE screw caps. Determination of metal content in each fraction was carried out by atomic absorption spectroscopy.

Procedure B): Three step procedure. The sequential extraction procedure defined in the BCR intercomparison exercise and used in this study is given below:

Step 1. Extract 1 g of dry sediment by shaking overnight (16 h) with 40 ml of acetic acid 0.11 $mol.l^{-1}$, at 20°C.

Step 2. The above residue is then extracted overnight (16 hours) with 40 ml of hydroxylammonium hydrochloride 0.1 $mol.l^{-1}$ (pH=2 with nitric acid). Prepare this reagent on the same day as the extraction is to be carried out because it is not stable for long periods.

Step 3. Rinse the residue from step 2 with distilled water and transfer by means of borosilicate glass rod into a 50 ml glass beaker. Rinse the residue with 10 ml of 30% hydrogen peroxide (8.8 $mol.l^{-1}$) adjusted to pH=2–3 with nitric acid. Cover the beaker with a watch glass and allow to digest, in the cold, for 1 hour. Digest again for 1 hour at 85°C and reduce the volume to a few ml on a steam bath or similar. Add a further aliquot of 10 ml of 30% H_2O_2, and heat the covered beaker to 85°C for 1 hour. Reduce the volume of the liquid to a few ml. Transfer the wet residue to a suitable centrifuge tube by the addition of 50 ml of ammonium acetate 1 $mol.l^{-1}$ adjusted to pH=5 with acetic acid, and extract by shaking overnight. Carry out all extractions by shaking in a horizontal-rotative shaker at about 20°C±2°C. Separate the extracts by centrifugation and decant into high density polyethylene containers which are stoppered, and store at 4 °C until analysis by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

The results obtained for metal partitioning are given in Tables 1 to 4; they are expressed as $mg.kg^{-1}$ of metal extracted in each step. In Table 1 each value is the mean of five independent determinations, and the percentage of relative standard deviation (RSD) is also given. In Tables 2,3 and 4 the results are the mean of two independent determinations, and the percentage of relative standard deviation (RSD) is also given. The total metal extracted obtained as a sum of all the fractions is also given in both cases. In sample T5 Cd and Zn partitioning was not determined.

It can be observed in Figure 1 that the metal partitioning obtained with both procedures are quite different. With procedure B significant amounts of heavy metals are extracted in

Table 1 Cd, Cr, Cu, Ni, Pb and Zn partitioning in BCR sediment (BCR-S7) using both sequential extraction procedures.

Procedure A (modified Tessier).

Step	*Cd* $\bar{x}$	*RSD*(a)	*Cr* $\bar{x}$	*RSD*	*Cu* $\bar{x}$	*RSD*	*Ni* $\bar{x}$	*RSD*	*Pb* $\bar{x}$	*RSD*	*Zn* $\bar{x}$	*RSD*
1	5.55	8.6	nd(b)	-(c)	2.02	5.5	nd	-	nd	-	11.9	8.6
2	4.97	5.8	8.49	3.3	16.6	1.0	14.0	1.0	56.4	0.8	302	3.6
3	1.33	4.5	71.8	2.5	13.1	5.2	18.5	2.7	70.0	2.8	152	3.4
4	nd	-	46.1	4.3	58.5	3.8	7.25	11	21.6	8.5	49.7	4.5
5	1.58	18	79.8	3.7	21.2	4.3	38.1	7.9	32.7	8.6	55.1	4.1
Σ5F	13.4	4.5	206	2.5	111	1.1	77.9	5.1	180	3.0	570	3.0

Procedure B (three steps).

Step	*Cd* $\bar{x}$	*RSD*	*Cr* $\bar{x}$	*RSD*	*Cu* $\bar{x}$	*RSD*	*Ni* $\bar{x}$	*RSD*	*Pb* $\bar{x}$	*RSD*	*Zn* $\bar{x}$	*RSD*
1	3.33	11	2.81	13	3.62	5.2	5.44	13	5.00	3.6	98	13
2	7.36	2.6	4.10	5.6	2.41	10	6.69	2.7	20.7	5.3	174	1.7
3	2.69	5.1	83.4	12	61.8	9.2	27.2	7.4	97.0	6.3	235	5.5
Σ3F	13.4	2.4	90.4	11	67.9	8.7	39.3	4.3	122	4.9	508	2.7

(a): The values of relative standard deviation (RSD) are expressed as a percentage.
(b): non detected
(c): non calculated

the third fraction, mainly related with organic matter and sulphides, whereas with procedure A the non residual metals are distributed among the second, third and fourth fractions, which are related with carbonates, iron-manganese oxides and organic matter-sulphides, respectively. The residual fraction obtained by applying procedure B is in general higher than the one obtained using procedure A, except for cadmium.

Table 2 Cr, Cu, Ni and Pb partitioning in sediment T5 using both sequential extraction procedures.

Procedure A (modified Tessier).

Step	*Cr* $\bar{x}$	*RSD*(a)	*Cu* $\bar{x}$	*RSD*	*Ni* $\bar{x}$	*RSD*	*Pb* $\bar{x}$	*RSD*
1	nd(b)	-(c)	15	23	14	40	nd	-
2	168	8.4	4.0	15	264	1.6	494	1.0
3	2310	15	13	22	696	10	801	3.3
4	217	11	1220	4.2	90	7.9	54	4.0
5	3652	2.5	200	19	567	4.5	284	19
Σ5F	6347	8.5	1450	1.4	1631	2.7	1633	6.1

Procedure B (three steps).

Step	*Cr* $\bar{x}$	*RSD*	*Cu* $\bar{x}$	*RSD*	*Ni* $\bar{x}$	*RSD*	*Pb* $\bar{x}$	*RSD*
1	12.6	19	23.2	4.0	66.1	7.6	47.0	11
2	27.1	7.3	28.8	7.5	112	7.6	213	0.3
3	725	6.5	748	4.3	619	3.2	725	2.1
Σ3F	765	6.8	800	5.0	797	4.8	985	3.3

(a): The values of relative standard deviation (RSD) are expressed as a percentage.
(b): non detected
(c): non calculated

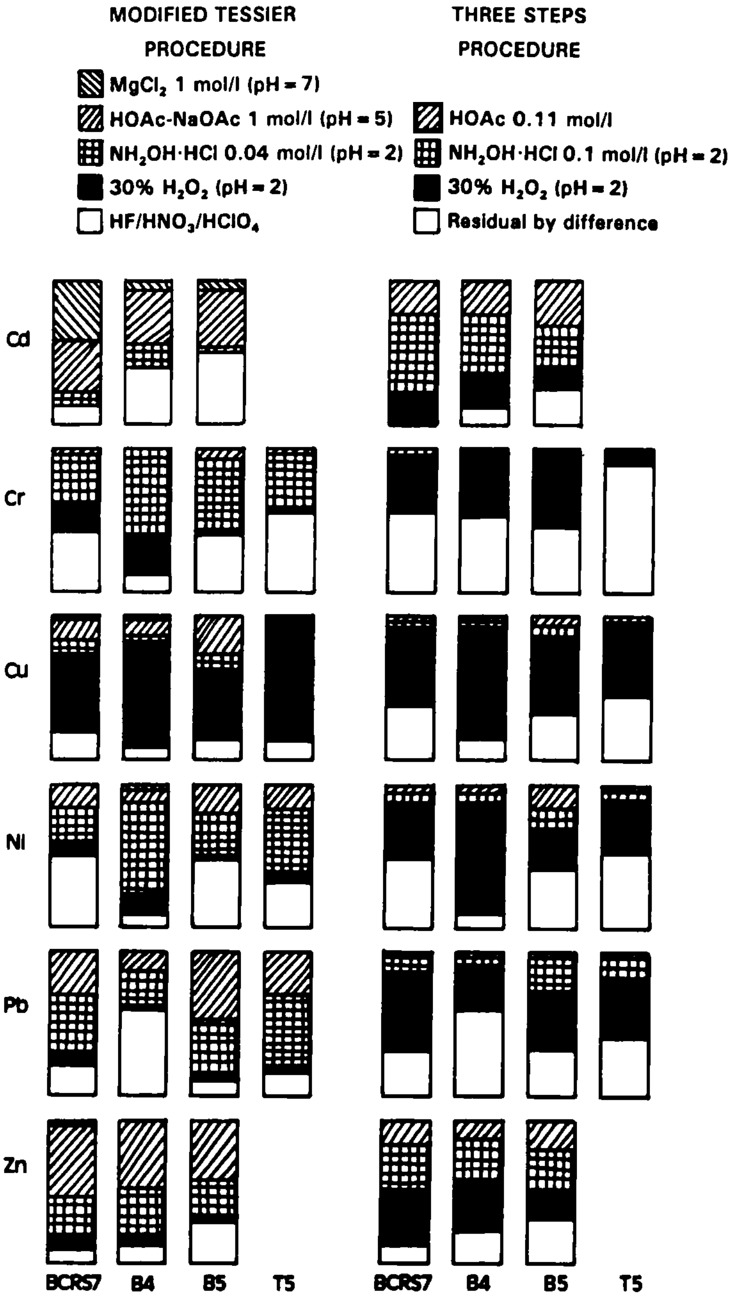

Figure 1 Comparison of metal partitioning in sediment samples using both sequential extraction procedures.

Table 3 Cd, Cr, Cu, Ni, Pb and Zn partitioning in sediment B4 using both sequential extraction procedures.

Procedure A (modified Tessier).

Step	*Cd*		*Cr*		*Cu*		*Ni*		*Pb*		*Zn*	
	$\bar{x}$	*RSD*$^{(a)}$	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*
1	0.286	53	4.87	13	21.8	7.1	12.4	9.1	nd$^{(b)}$	-$^{(c)}$	14.8	9.1
2	1.67	2.1	15.7	18	65.6	1.0	70.8	2.1	44.8	2.5	407	1.6
3	0.776	14	885	5.2	29.8	0.5	481	2.6	73.1	16	297	1.0
4	nd	-	378	0.9	517	3.3	103	0.7	16.4	15	44.7	6.0
5	1.61	4.4	152	5.6	68.1	12	74.3	4.9	162	17	103	4.1
Σ5F	4.34	3.4	1436	3.5	702	3.3	742	1.3	296	4.1	867	0.5

Procedure B (three steps).

Step	*Cd*		*Cr*		*Cu*		*Ni*		*Pb*		*Zn*	
	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*
1	1.04	27	3.76	4.9	28.1	62.4	12	8.79	32	143	21	
2	1.76	8.0	7.26	71	19.0	24	53.0	4.9	11.6	15	246	1.4
3	0.96	7.0	672	6.1	545	0.8	571	1.4	85.4	6.6	296	8.9
Σ3F	3.76	7.0	683	6.8	592	1.3	686	0.3	106	9.6	685	1.1

(a): The values of relative standard deviation (RSD) are expressed as a percentage.

(b): non detected

(c): non calculated

For cadmium using procedure A significant amounts are extracted in the two first fractions whereas no detectable Cd is extracted with the hydrogen peroxide reagent. With procedure B cadmium is mainly solubilized in the second step and significant amounts are extracted with the oxidizing reagent (third step).

For chromium, the distribution patterns obtained by both procedures are completely different. With procedure A chromium is mainly extracted with the reducing reagent, whereas with procedure B is principally extracted with the oxidizing reagent.

Table 4 Cd, Cr, Cu, Ni, Pb and Zn partitioning in sediment B5 using both sequential extraction procedures.

Procedure A (modified Tessier).

Step	*Cd*		*Cr*		*Cu*		*Ni*		*Pb*		*Zn*	
	$\bar{x}$	*RSD*$^{(a)}$	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*
1	0.227	67	nd$^{(b)}$	-$^{(c)}$	2.78	15	0.931	5.0	nd	-	2.82	13
2	1.15	6.1	8.42	3.2	36.5	0.6	10.8	2.6	91.7	0.6	125	1.7
3	nd	-	49.0	0.9	14.1	12	17.3	2.5	74.9	0.2	85.3	3.3
4	nd	-	3.22	23	49.1	4.6	nd	-	6.83	8.4	11.5	3.7
5	1.37	8.8	37.8	2.4	32.4	7.4	29.3	3.9	20.6	8.6	77.4	3.7
Σ5F	2.75	1.5	98.4	0.0	135	1.6	58.3	1.8	194	0.7	302	8.0

Procedure B (three steps).

Step	*Cd*		*Cr*		*Cu*		*Ni*		*Pb*		*Zn*	
	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*
1	0.86	9.9	nd	-	10.1	5.3	9.62	7.1	10.6	8.0	60.5	2.8
2	0.82	0.0	nd	-	8.54	1.2	7.94	0.1	47.1	0.6	81.8	1.4
3	0.35	5.0	53.7	7.0	79.3	1.4	15.7	6.7	78.2	6.3	59.8	4.3
Σ3F	2.03	5.2	53.7	7.0	97.9	2.1	33.3	5.4	136	8.7	202	3.0

(a): The values of relative standard deviation (RSD) are expressed as a percentage.

(b): non detected

(c): non calculated

Table 5 Non residual metal extracted by both procedures: (A) modified Tessier procedure, and (B) three steps procedure in samples T5, B4, B5 and BCR sample.

	T5				*B4*				*B5*				*BCR*			
Elemt.	*A*		*B*		*A*		*B*		*A*		*B*		*A*		*B*	
	$\bar{x}$	*RSD*[a]	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*	$\bar{x}$	*RSD*
Cd	*[b]		*		2.73	8.0	3.76	6.9	1.38	5.9	2.03	5.2	11.9	3.5	13.4	2.3
Cr	2695	8.4	765	6.8	1284	3.2	683	6.8	60.2	1.5	53.7	7.0	126	2.9	90.4	11
Cu	1250	4.6	800	5.0	634	2.4	592	1.3	103	0.1	97.9	2.1	90.2	2.3	67.9	8.7
Ni	1064	7.0	797	4.8	677	2.1	686	0.3	29.0	0.3	33.3	5.4	39.8	3.1	39.3	4.3
Pb	1349	2.3	985	3.3	134	11	106	9.6	173	0.1	136	8.7	148	1.9	122	4.9
Zn	*		*		764	1.0	685	1.1	225	0.3	202	3.0	516	3.2	508	2.7

[a]: The values of relative standard deviation (RSD) are expressed as a percentage.

[b]: non determined.

Copper shows a similar behaviour with both procedures. Significant amounts of this metal are extracted in the fractions related to the organic matter. However, in the most polluted sample (T5) the amount of copper extracted with procedure A is higher than the amount extracted with procedure B.

Nickel and lead show a similar behaviour when only procedure A or procedure B are considered, but show different distribution patterns when both procedures are applied to the same sample. Significant amounts of these metals are extracted in the second and third fractions of procedure A, whereas with procedure B the hydrogen peroxide reagent extracts the higher amount of metal.

For zinc the amounts extracted with procedure A in the second and third fractions are higher than the amount released with the oxidizing reagent. On the contrary, with procedure B the amount of Zn extracted in the third step is similar to the one extracted in previous steps.

From these results we can consider that the two procedures extract metals from the non-residual phases with different efficiency. This fact can be due to the different experimental conditions used to isolate each fraction. In procedure B the extraction of metal bonded to carbonates is performed with acetic acid 0.11 $mol.l^{-1}$, whereas procedure A employs an acetic-acetate buffer 1 $mol.l^{-1}$ (pH=5), with different shaking times. To extract metals related with Fe-Mn oxides both procedures use acidified hydroxylammonium hydrochloride (pH=2) at similar concentrations but the temperatures are completely different: room temperature is used in procedure B, whereas 95 °C is used in procedure A. The extraction time and the shaking system are also different. For extraction of metal bonded to oxidizable phases both procedures use an acidified solution of hydrogen peroxide (pH=2) at 85°C. Taking into account the number of steps, procedure A is longer (five steps) than procedure B (four steps), but in both cases a complete week is necessary for the application of the respective schemes, because the extraction steps are longer in procedure B than in procedure A.

The extracted metal with each procedure is given in Table 5. For procedure B the extracted metal is calculated as the sum of the metal extracted in the three fractions, and for procedure A it is calculated as the sum of the metal extracted in the first four fractions. It can be observed in Table 5 that for the less polluted samples (BCR sample and B5) there is a good agreement between the amounts extracted by both procedures. However, this agreement is not found when the heavy metal content increases, specially in sample T5. On the other hand, the reproducibility of both procedures is similar, taking into account the values of RSD (as percentage) given in the tables. When five replicates were performed, Table 1, the RSD values obtained in the different steps of the procedure A range from 0.8 to 18%, and those obtained with the procedure B range from 1.7 to 13%. The results obtained show that the procedure A was more effective in extraction heavy metals in sediment samples with high content of heavy metals, and the partitioning obtained for the extractable metal is quite different.

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