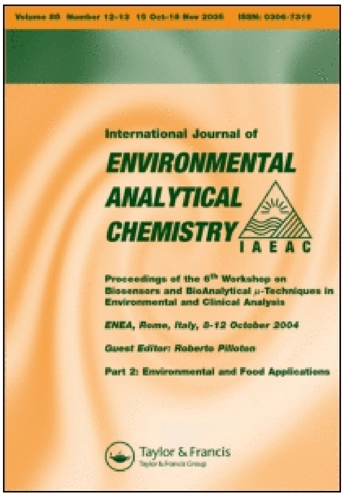

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SPECIFIC PROCEDURE FOR METAL SOLID SPECIATION IN HEAVILY POLLUTED RIVER SEDIMENTS*

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Sequential extraction schemes are used in determining the partitioning of trace metals in sediments. Among them the most widely used is that proposed by Tessier *et al.*[5] A modified Tessier procedure, with successive extractions until completeness is attained, using pH control for extraction of metal solubilized by acetic acid–acetate buffer, control of extracted iron and manganese for metal extracted by hydroxylamine hydrochloride and control of redox potential (Eh) of extractant solution for metal solubilized by hydrogen peroxide, is proposed for copper, lead, chromium and nickel speciation. The results obtained with the initial Tessier procedure and those obtained with the modified procedure are compared with a heavily polluted sediment sample, and the resulting metal distributions are discussed.

KEY WORDS: Heavy metals, solid metal speciation, river sediments, distribution, sample handling, partitioning, AAS.

INTRODUCTION

To assess the environmental impact of polluted sediments the determination of total trace metal content is not sufficient, because it is the chemical form of the metal in the sediment that determines its behaviour in the environment and its mobilization capacity. The methods for determining the partitioning of trace metals in sediments are based on sequential extraction procedures. In the literature several sequential extraction schemes are described,[1–5] among them the most widely used is that proposed by Tessier *et al.*[5] which includes five fractions: exchangeable metal (Fraction 1), metal extracted by acetic acid–acetate buffer (Fraction 2), metal extracted by hydroxylamine (Fraction 3), metal extracted by hydrogen peroxide in nitric acid (Fraction 4) and residual metal (Fraction 5). Independently of the scheme used to obtain different fractions, the speciation shows some problems mainly related to possible changes in the chemical species during sampling and pre-treatment of samples[6] or related to the limited selectivity of the reagents which release several metal species in each extraction step.[7] In a study of heavily polluted sediments from a Mediterranean river (Tenes river) in Catalonia[8] a new problem has been encountered: The partitioning patterns found

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in the sediment following the Tessier scheme for the studied metals, Pb and Cu, were unusual. In spite of the fact that copper was mainly associated to organic matter and lead was mainly associated to iron and manganese oxides, important contents of copper and lead were found in the residual fraction from the Tessier scheme for the most heavily polluted sample. From data given by Turekian[9] it should be expected 40–50 $\mathrm{mg\,Kg^{-1}}$ of Cu and 20–30 $\mathrm{mg\,Kg^{-1}}$ of Pb approximately in the residual fraction, data which are often adopted as criteria to evaluate the background level in polluted sediments.[3,10] A similar distribution has been found in Subae river in Brazil,[11] using a simplified scheme and different grain size ($<2\,\mu$m), and in Rhine river, using a more elaborated method which includes six fractions;[10] however, in both studies the levels of metal content are not completely comparable and they do not reach as high values in the residual fraction as those found in Tenes river.

The high values found in residual fraction are due probably to an incomplete metal solubilization in previous fractions. Förstner has noted[12] that extractions are influenced by the duration of the experiment, the temperature, and by the ratio of solid matter to volume of extractant. Pfeiffer *et al.*[13] have demonstrated that the chemical system may overload if the content of metal is too high. To avoid this problem and to attain a completeness in the metal solubilized in each fraction, for heavily polluted samples, we have carried out successive extractions in each one of the steps proposed by Tessier *et al.*, controlling the parameters involved in the solubilization of metal extracted by the acetic acid–acetate buffer ($\mathrm{pH}=5.0$), by hydroxylamine hydrochloride and by hydrogen peroxide. An improved Tessier procedure can be developed from the information obtained in these studies for trace metal solid speciation in heavily polluted river sediments.

EXPERIMENTAL

Sample

The sample was collected in the River Tenes and treated as described earlier.[8] In spite of the fact that drying sediment samples prior to their extraction can introduce changes in the partitioning, the sample has been dried in order to obtain a stable sample with a reproducible behaviour.

Instrumentation

An atomic absorption spectrophotometer, Perkin Elmer Model 4000, with double beam and background corrector and hollow cathode lamps were used. Air acetylene flame and graphite furnace (Perkin Elmer HGA 500) were used. Manual injection was carried out using an Eppendorf 20 μl pippete. pH measurements were performed with a Hach Model 19000 digital pH meter equipped with a calomel-glass combined electrode. An Orion SA 720, potentiometer, with a Radiometer

Model P101 platinum electrode and double junction Ag/AgCl Orion 900200 reference electrode were used for Eh measurements.

Reagents

All reagents were Merck analytical grade or Suprapur quality. Stock solutions containing 1.000 g.L^{-1} of metal, acidified with nitric acid, were used. All standards and reagent solutions were stored in polyethylene bottles. Standard Zobell solution[14] for redox electrode calibration and double deionized water (Culligan Ultrapure GS 18.3 Mohm.cm resistivity) were used.

Clean Laboratory

Sample treatment was performed in a clean laboratory with a Class-100 air work bench.[15] All glassware and plasticware used for experiments were previously soaked in 10% (v/v) nitric acid during at least 24 hours and rinsed with double deionized water.

Proposed Procedure for Metal Speciation

The studied procedure is based on Tessier scheme. For Fractions 2, 3 and 4, successive extractions with the pertinent reagent were performed under control of pH, of extracted iron and manganese and of redox potential (Eh), respectively. It was assumed that the extraction is accomplished when:

For Fraction 2: the pH of the solution resulting from an extraction step differs from that of the extractant solution in less than 0.1 units.

For Fraction 3: the amounts of Fe and Mn extracted in one step reach a constant minimum.

For Fraction 4: the Eh of the solution resulting from an extraction step differs from that of the extractant solution in less than 25 mV.

In Figure 1 a scheme of the proposed procedure is represented.

Copper, lead, chromium and nickel contents are determined in the solution from each fraction after each extraction step by Flame AAS or Graphite Furnace AAS, depending on concentration level, in the usual conditions. Standard addition technique was used for calibration to avoid matrix interferences.

RESULTS AND DISCUSSION

a) Preliminary Study

In a preliminary study successive extractions on the same sample under the

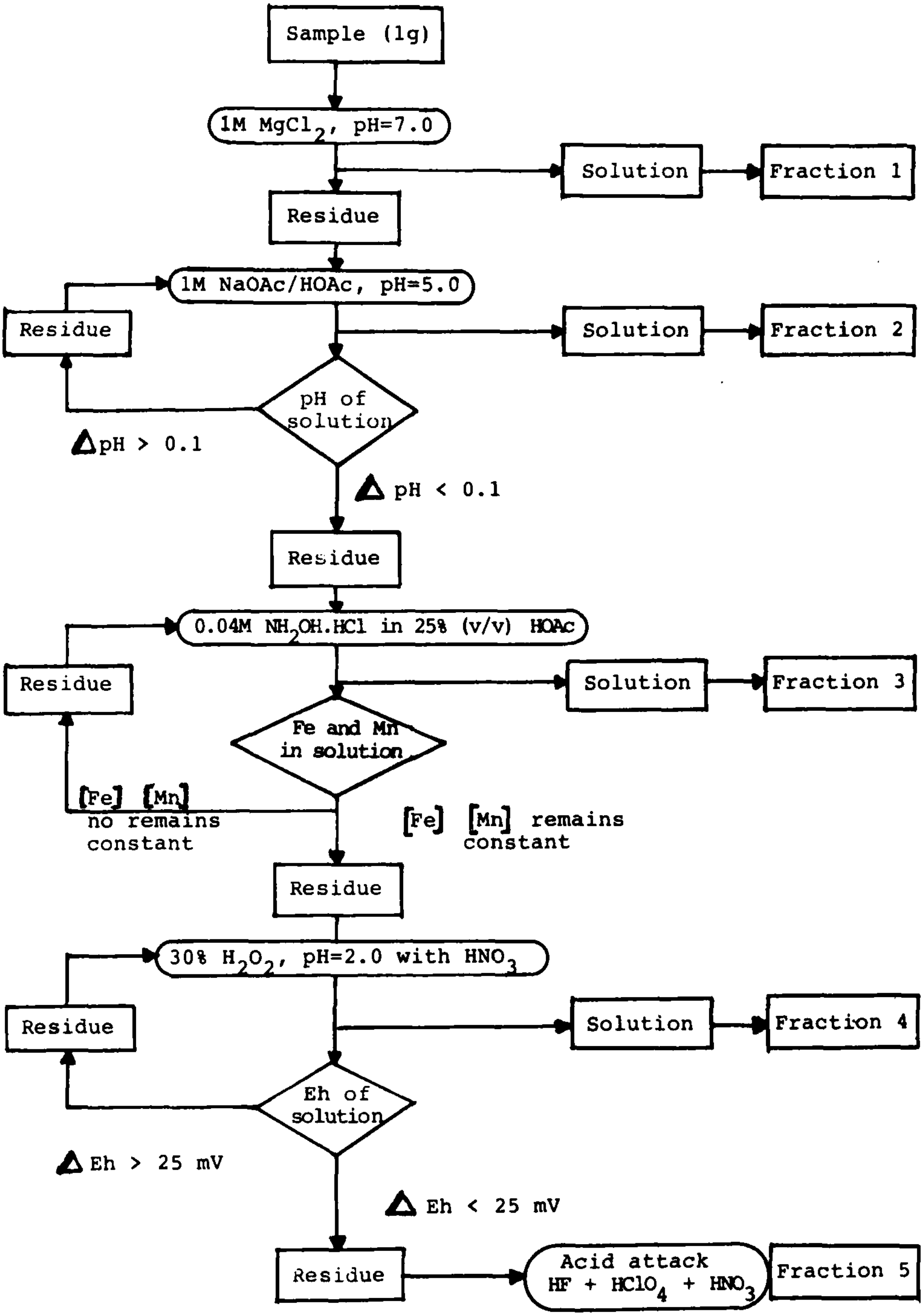

Figure 1 Schematic representation of the proposed procedure.

Table 1 Preliminary successive extraction study

Fraction number	*Extraction number*	*Copper*[a] $(mg.Kg^{-1})$	*Lead*[a] $(mg.Kg^{-1})$	$\sum$*ext*[b] *Cu* $(mg.Kg^{-1})$	$\sum$*ext*[b] *Pb* $(mg.Kg^{-1})$
1	1	2.9	ND[c]		
	2	0.9	ND		
	3	1.2	ND		
	4	0.9	ND		
	5	1.1	ND	7.0	ND
2	1	1.7	66		
	2	1.8	115		
	3	2.4	81		
	4	3.1	67		
	5	11	61		
	6	14	59	34	449
3	1	4.8	546		
	2	12	230		
	3	15	132	32	908
4	1	1398	94		
	2	68	37		
	3	12	47	1469	178
5	(Residual metal)	13	21	13	21
Total metal				1555	1556

[a] Average value from three independent determinations.
[b] $\sum$ext = total metal extracted in a fraction.
[c] ND = non-detected.

conditions described by Tessier *et al.* were carried out. The results obtained for Cu and Pb are shown in Table 1. The number of successive extractions performed on each sample for each fraction were: five for exchangeable metal, six for metal extracted by acetic acid–acetate buffer, three for metal extracted by hydroxylamine hydrochloride and three for metal extracted by hydrogen peroxide. The residual metal obtained by acid digestion and the total amount of metal obtained as a sum of the five fractions are also shown.

Only copper is released in Fraction 1, in very low amounts; one extraction is enough to determine the exchangeable metal.

The mobilization of copper in Fraction 2 is low too. The increase observed after the second extraction suggests a mobilization of copper from subsequent fractions. On the other hand, lead is solubilized in a large extent and the equilibrium is only attained at the third extraction.

In Fraction 3 the mobilization of lead is very important and clearly higher than that of copper. This is a decisive step for lead. The results obtained show that one extraction is not enough to extract all the lead leached by hydroxylamine hydrochloride in 25% acetic acid; this fact may be attributed to an insufficient volume of extractant solution. A constant ratio between the extracted and non-extracted lead in each successive extraction is also observed.

The decisive step for copper mobilization is, as the results show, the fourth fraction, metal extracted by hydrogen peroxide in nitric acid (pH = 2). In this step the copper is mainly released in the first extraction.

The experimental results obtained in this preliminary study show a great change in metal distribution in the different fractions when successive extraction steps are used (Table 1) instead of only one equilibrium extraction (see Table 4, first column). Furthermore, the values for the metal content in the residual fraction from the successive extraction procedure are closer to those which can be expected in the background level. The question arises as to the number of extractions that must be done in order to mobilize the total amount of metal belonging to each fraction according to Tessier scheme. From a consideration of the meaning of each fraction (Fraction 2, the amount of metal released when the sample is treated with a solution of known pH; Fraction 3, the amount released when iron–manganese oxides are dissolved; and Fraction 4 the amount released when organic matter is oxidized) it can be concluded that a good criterion to establish the minimum number of successive extractions is the measurement, for each fraction, of a particular parameter which will show that the extraction is completed. With this purpose the successive extraction procedure here described was performed under control of pH in Fraction 2, of the amount of iron and manganese released in Fraction 3 and of the redox potential in Fraction 4.

b) Successive Extractions Under Controlled Conditions

This study was carried out in two series of experiments. In the first one, copper and lead were analyzed and in the second one chromium and nickel were also determined. In Tables 2 and 3 the results obtained for copper and lead and for chromium and nickel, respectively, under the described controls are given. Only one extraction was carried out for Fraction 1.

In Fraction 2 the successive extractions were carried out until pH variation was less than 0.1 pH units, since it can be considered that at this point the release of metal takes place actually at pH 5.

In Fraction 3 four successive extractions were carried out, and the iron and manganese contents in the solution were measured. In Figure 2 the amount of iron and manganese solubilized in each step is shown, and in Figure 3 the amounts of copper, lead, chromium and nickel released at each extraction step are shown. It can be observed that lead is mainly released in this fraction, and that a good correlation exists between lead, chromium and nickel release and iron and manganese solubilization. Copper is released to a slight extent in this fraction, but an increase of solubilized metal is observed from the second extraction on. This fact cannot be related to metal associated to iron and manganese oxides because these have been completely solubilized at the end of three extractions.

In Fraction 4 four successive extractions were carried out under Eh control, as an indicator parameter for oxidant consumed to destroy organic matter. In Figure 4 the Eh of the solutions and copper, lead, chromium and nickel released in each extraction are shown. Eh variation after the first extraction is sharp, suggesting a strong oxidation of organic matter and consequently an important release of trace

Table 2 Copper and lead successive extraction study under controlled conditions

Fraction	Extraction	Cu		Pb		pH		Δ pH		Fe		Mn		Eh		Δ Eh	
		$\bar{x}^a$	s^b	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
1	1	3.2	0.7	ND[c]													
2	1	1.3	0.12	56	5.1	5.76	0.04	0.66	0.04								
2	2	1.5	0.40	100	4.6	5.53	0.02	0.37	0.02								
2	3	1.9	0.69	104	6.1	5.15	0.01	0.05	0.01								
3	1	5.3	0.59	557	31					9914	188	227	8.2				
3	2	3.2	1.0	247	10					4513	75	63	3.0				
3	3	9.3	1.9	219	24					2105	131	20	1.7				
3	4	13	0.58	138	12					1518	56	16	2.0				
4	1	1368	49	65.5	3.9									535	63	109	63
4	2	93.0	8.6	30.0	2.7									619	0.03	13	0.03
4	3	12.9	0.21	17.7	3.9									608	2	19	1.6
4	4	6.01	0.66	11.9	2.7									602	1	21	0.59
5	1	36	2.5	49	11												

[a] Mean value of three independent determinations.

[b] Standard deviation.

[c] Non-detected.

Table 3 Chromium and nickel successive extraction study under controlled conditions

Fraction	*Extraction*	*Cr*		*Ni*		*pH*		*ΔpH*		*Fe*		*Mn*		*Eh*		*ΔEh*	
		$\bar{x}$[a]	s[b]	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
1	1	ND[c]		5.20	0.57												
2	1	35.3	3.29	66.6	7.39	5.72	0.02	0.55	0.02								
2	2	99.7	13.2	130	11.6	5.40	0.05	0.34	0.05								
2	3	61.9	5.45	87.4	15.2	5.18	0.03	0.05	0.03								
3	1	2072	67.0	466	7.30					14030	591	233	10.7				
3	2	329	50.5	113	10.7					4060	443	58.5	5.07				
3	3	72.3	9.93	29.9	1.38					1610	132	20.1	1.35				
3	4	52.0	6.83	13.4	2.20					1190	135	15.7	1.98				
4	1	99.4	2.08	29.0	2.57									569	45	71	45
4	2	40.9	1.52	5.36	0.30									639	10	18	10
4	3	20.7	0.59	8.27	1.72									628	1	28	1
4	4	19.4	3.32	7.88	2.01									626	1	21	1
5	1	2820	189	606	58.2												

[a] Mean value of four independent determinations.

[b] Standard deviation.

[c] Non-detected.

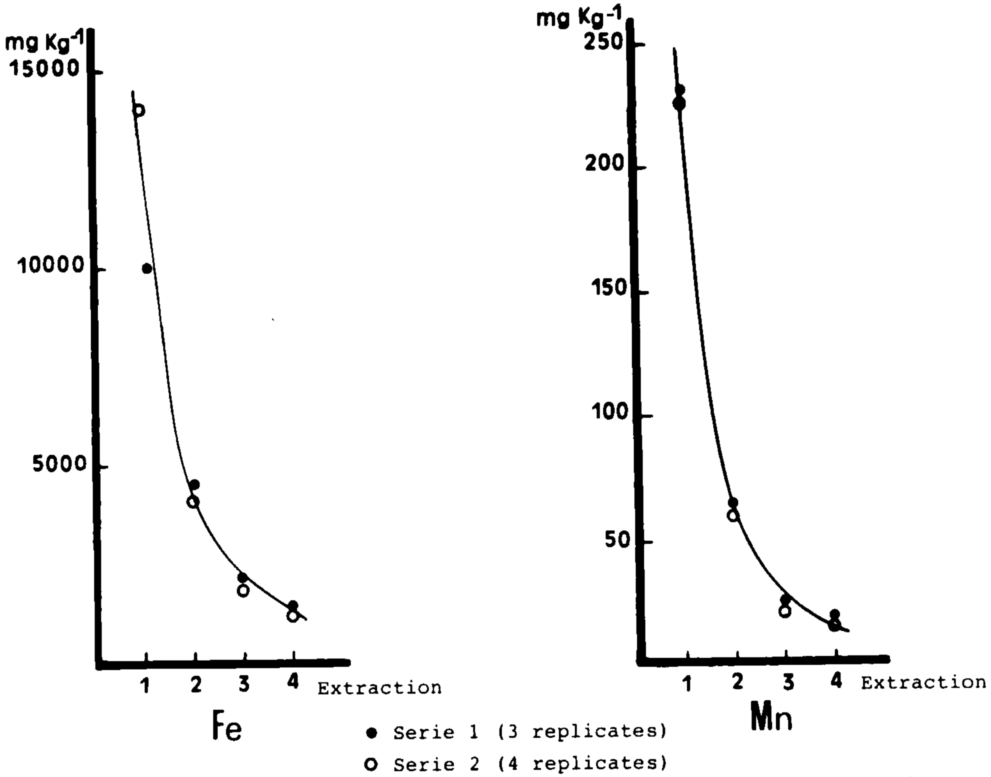

Figure 2 Iron and manganese released by hydroxylamine hycrochloride in repetitive extractions.

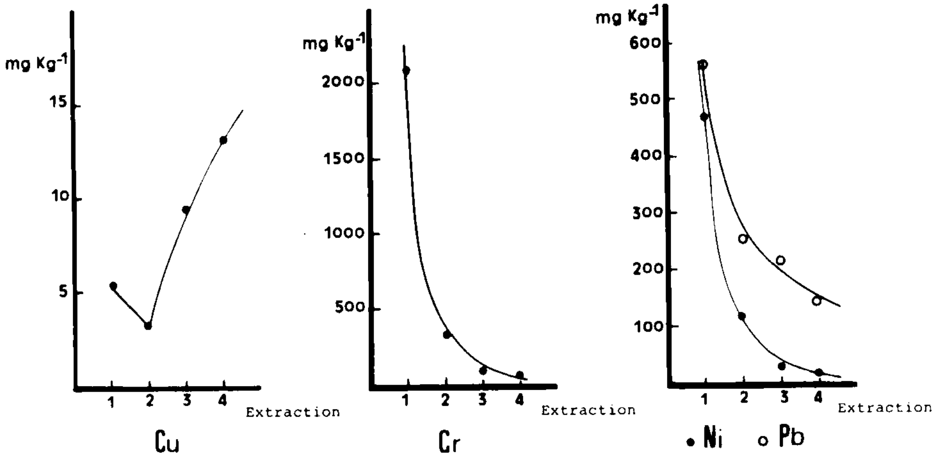

Figure 3 Copper, lead, chromium and nickel released by hydroxylamine hydrochloride in repetitive extractions.

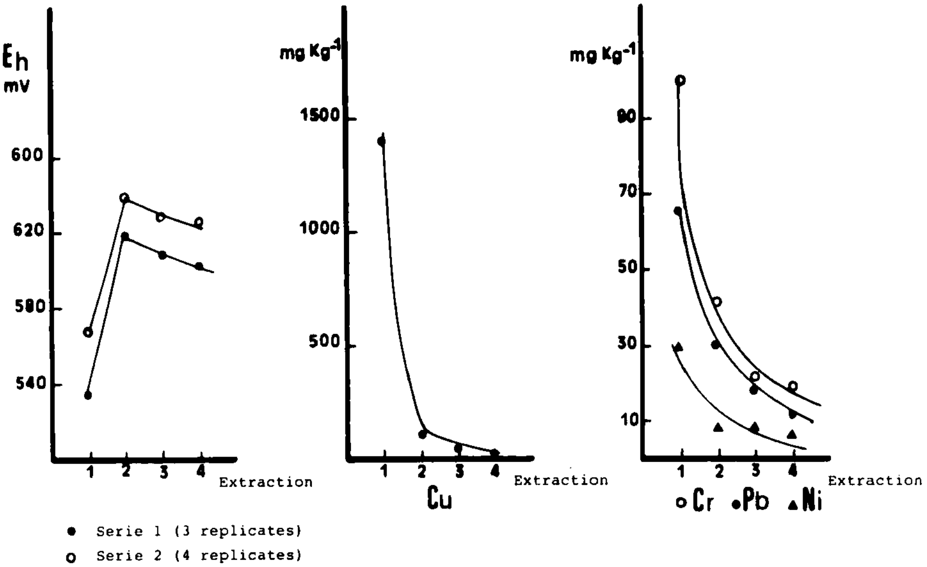

Figure 4 Eh variation and metal released by hydrogen peroxide in repetitive extractions.

metals associated to it. In successive extractions, Eh variations are small, showing that no organic matter remains in solution and only a very small amount of metal is solubilized, as it is shown in the figure. In this case the copper is released mainly in the first extraction.

Successive extractions with monitoring of mandatory parameters (pH, Fe and Mn concentrations, and Eh) in metal release allow the determination of the number of extractions required to assure a proper distribution of metals in each fraction.

In Table 4 the distributions of Cu, Pb, Cr and Ni for the heavily polluted river sediment sample as obtained with Tessier procedure are given. In Figure 5 the metal percent in each fraction is plotted; Figure 5a shows the values obtained using the proposed multiple successive extraction procedure and Figure 5b those obtained using Tessier procedure. An absolutely different pattern for copper and lead and a similar behaviour for chromium and nickel can be observed. It can be concluded that, dealing with heavily polluted samples, the multiple successive extraction procedure yields for copper and lead a more reliable distribution pattern, in which the residual metal is in a good agreement with what is to be expected according to Turekian.[9] For chromium and nickel the differences in the pattern distribution are not important in spite of the very high contents of these metals.

Acknowledgements

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Table 4 Copper, lead, chromium and nickel partitioning obtained with Tessier procedure

Cu	*a*	*b*	*c*	*d*	$\bar{x}$	*s*	%
F1	3	3	5	–	4	1.2	0.2
F2	1	1	2	–	1	0.6	0.1
F3	3	2	3	–	3	0.6	0.2
F4	1030	1050	1200	–	1070	93	61
F5	732	785	530	–	682	135	38
$\sum$F	1770	1840	1740	–	1780	51	–
Pb	*a*	*b*	*c*	*d*	$\bar{x}$	*s*	%
F1	–	–	–	–	–	–	–
F2	45	39	–	–	42	4.2	3
F3	501	517	–	–	509	11	32
F4	129	109	–	–	119	14	8
F5	912	908	–	–	910	2.8	57
$\sum$F	1587	1573	–	–	1580	35	–
Cr	*a*	*b*	*c*	*d*	$\bar{x}$	*s*	%
F1	–	–	–	–	–	–	–
F2	25.4	27.6	24.4	24.2	25.4	1.56	0.4
F3	2400	2500	2390	2320	2400	74.1	39.3
F4	415	348	362	347	368	32.1	6.0
F5	3190	3470	3280	3280	3310	117	54.2
$\sum$F	6030	6346	6056	5981	6103	–	–
Ni	*a*	*b*	*c*	*d*	$\bar{x}$	*s*	%
F1	6.29	5.12	5.25	4.16	5.21	0.87	0.3
F2	66.6	65.2	59.1	60.2	62.8	3.68	4.0
F3	518	497	427	480	481	38.9	30.6
F4	207	211	231	244	223	17.4	14.2
F5	742	828	750	859	795	57.8	50.6
$\sum$F	1540	1610	1470	1647	1570	–	–

Columns *a*, *b*, *c* and *d* are the results obtained in replicate samples; $\bar{x}$ is the mean value; *s* is the standard deviation; % is the metal percent in each fraction.

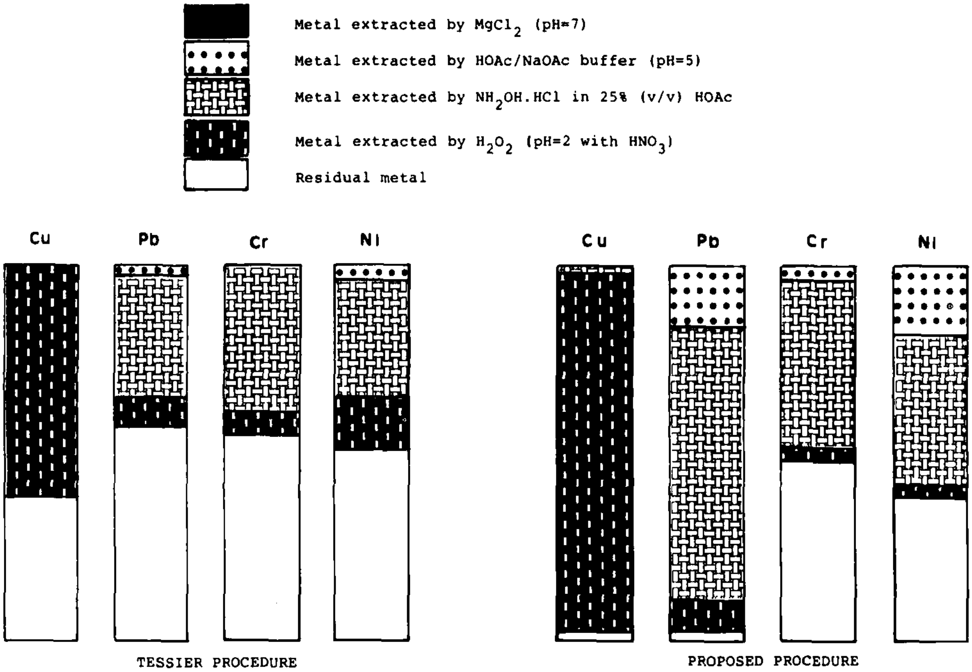

Figure 5 Metal partitioning using both proposed and original procedures. Metal released by each reagent is expressed as a percent value of total metal in sediment.

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