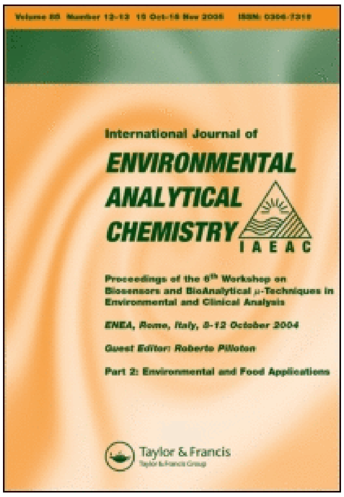

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OPTIMIZATION OF TESSIER PROCEDURE FOR METAL SOLID SPECIATION IN RIVER SEDIMENTS*

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Optimization of Tessier procedure for trace metal partitioning in sediments is studied. Firstly simplex optimization method is applied and the results indicate that the volume of extractant solution/weight of sediment ratio (V/m) is the main variable. Optimization of V/m ratio for second, third and fourth fractions of Tessier scheme is studied on two different river sediments. The optimum values of V/m ratio obtained are applied for copper, lead, chromium and nickel partitioning. The results obtained are compared with those obtained using Tessier procedure. Some conclusions about the behaviour of each fraction are presented.

KEY WORDS: Sample handling, river sediments, speciation, copper, lead, chromium, nickel, successive extraction, partitioning, AAS.

INTRODUCTION

In 1986 a study of copper and lead partitioning in sediments of a Mediterranean river using the Tessier scheme[1] was carried out in our department.[2] In this work high values of metal content were found in the residual fraction. This fact was attributed to an incomplete metal solubilization in previous fractions. To attain a complete solubilization of the metal compounds in each fraction, a repeated successive extraction in each one of the steps was proposed.[3] This procedure, which implies also the control of pH, of Fe and Mn released in solution and of Eh in the different fractions, was applied for partitioning studies of Cu, Pb, Cr and Ni in the sediments previously studied by Rauret *et al.*[2] Three successive extractions for the metal solubilized at $pH = 5$ (fraction 2) and four for the metal extracted by hydroxylamine hydrochloride (fraction 3) and hydrogen peroxide (fraction 4) were required to keep under control the parameters involved in the solubilization of the metal extracted in each fraction. The distribution pattern obtained using this modified procedure was more reliable and the residual metal was in better agreement than what is to be expected according to Turekian.[4] Nevertheless this procedure is tedious and time consuming, so it would be suitable to find working conditions that assure the same results as those obtained by repeated successive

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extractions but using only one extraction for each fraction. With this aim a systematic optimization of the experimental conditions are studied in two sediments of different composition and degree of heavy metals pollution. Firstly simplex optimization is applied, but once observed that only one variable plays an important role in the solubilization of metal in each fraction, this method is abandoned and only the main variable is studied systematically. From the results obtained new working conditions are proposed and some conclusions about the behaviour of each fraction are presented.

EXPERIMENTAL

Samples

The oxic sediment samples were collected in the River Tenes and treated as described earlier.[2] Two samples were chosen. Their chemical composition expressed as % were:

Sample 2: SiO_2, 42.48; Al_2O_3, 11.97; Fe_2O_3, 4.45; MgO, 3.10; CaO, 11.04; Na_2O, 0.98; K_2O, 3.50 and MnO, 0.06.

Sample 5: SiO_2, 30.31; Al_2O_3, 8.46; Fe_2O_3, 10.11; MgO, 2.44; CaO, 16.88; Na_2O, 0.89; K_2O, 1.78 and MnO, 0.16.

Their content of Cu, Pb, Cr and Ni was 130, 123, 117 and 44 mg/Kg respectively for sample 2 and 1780, 1580, 6130 and 1570 mg/Kg respectively for sample 5.

Instrumentation

An atomic absorption spectrophotometer, Perkin Elmer Model 4000, with double beam and background corrector and hollow cathode lamps, and an air acetylene flame and graphite furnace (Perkin Elmer HGA 500) were used. Manual injection was carried out using an Eppendorf 20 μL pipette. 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 contained 1 g/L of metal, acidified with nitric acid. All standards and reagent solutions were stored in polyethylene bottles. Standard Zöbell solution[5] for redox electrode calibration and double deionized water (Culligan Ultrapure GS 18.3 Mohm/cm resistivity) were used.

Table 1 Results obtained by simplex optimization method in the extraction of second fraction of sediment sample 5

Exp.	*V/m*	*t*	*(V/m)'*	*t'*	*Pb*	*Fe*	*Mn*	100*Pb/Fe*
1	8.00	5.00	0.000	0.000	82	9 320	130	0.879
2	38.90	10.18	0.966	0.259	456	16 300	286	2.798
3	16.29	24.32	0.259	0.966	351	15 600	249	2.250
4	39.79	24.55	0.993	0.966	484	16 500	272	2.933
5	39.93	10.87	0.998	0.293	448	15 200	241	2.947
6	40.02	5.02	1.000	0.001	457	16 200	241	2.821
7	40.12	19.90	1.000	0.745	497	16 200	255	3.068
8	39.89	24.78	0.997	0.989	513	17 100	275	3.000

V/m ratio in mL/g. *t* is the time in hours. (V/m)' and *t'* are the normalized variables. Metal concentrations are expressed in mg/Kg.

Clean Laboratory

Sample treatment was performed in a clean laboratory with a Class-100 air work bench.[6] All glassware and plasticware used for experiments were previously soaked in 10% (v/v) nitric acid for at least 24 hours and rinsed with double deionized water.

RESULTS AND DISCUSSION

Simplex Optimization Method

Simplex optimization method has been widely applied to establish analytical conditions either for the treatment of the samples[7] or for the measurement process.[8,9] In this work simplex optimization method has been applied to find the best conditions to solubilize the amount of heavy metal belonging to second fraction in Tessier scheme. As variables the ratio between the volume of extractant solution and the sediment weight and the time of extraction were chosen. As a function the ratio between the lead and the iron extracted was used. The range of application of the variables moved between the values proposed by Tessier and five times more.

In Table 1 the results found are given. It can be observed that the ratio volume of extractant/weight of sample reaches quickly the highest value while the effect of extraction time is scarcely important. From these results it was concluded that only one variable plays an important role in metal solubilization so further work was performed optimizing only the ratio volume of extractant solution/weight of sediment (V/m).

Effect of the volume of extractant solution

The efficiency in the metal solubilized after each extraction with increasing volumes of solution was measured in each step for the two sediments studied. The first fraction (metal extracted with $MgCl_2$, 1 M at pH 7.0) was disregarded because of the amounts of metals released in this step were negligible in relation to the total metal content.

The second fraction (metal solubilized by acetic acid-acetate buffer, pH = 5) was studied in the range included between the ratio V/m proposed by Tessier until ten times more. The Fe, Mn, Cu and Pb releases in each experiment have been determined and the pH measured. In Figures 1 and 2 the values for these parameters for each V/m ratio are represented for the two sediments. As it could be expected, the sample with a higher carbonate content (sediment 5) shows sharper pH changes. To obtain a pH variation (versus a blank sample) of less than 0.1 pH units the V/m ratio must be 50 mL/g for both sediments. This ratio is substantially higher than proposed by Tessier (V/m = 8 mL/g). For both sediments the lead released in optimal conditions (V/m = 50 mL/g) is a third of the total lead content in the sediments. This amount of lead is about eight times higher than the amount released with the Tessier procedure for the heavily polluted sediment and two and a half times higher than for the less polluted one.

Another aspect to be taken into account in this step is the amount of iron and manganese solubilized in this fraction. For the less polluted and less carbonated sediment the amount of iron solubilized is negligible (only 0.4% of total content), whereas the amount of manganese solubilized is noticeable (20%). A different behaviour is observed for the more carbonated sample (sediment 5) in which iron is solubilized to an important extent (15%) as well as manganese (11%).

The third fraction (metal extracted by hydroxylamine hydrochloride at pH = 2) was studied in the range between V/m proposed by Tessier until five times more. The iron, manganese, copper and lead were measured. In Figures 3 and 4 the variation of these parameters versus the ratio V/m are represented for both sediments studied. It can be observed that in both cases the solubilization of Fe and Mn reaches a maximum when V/m ratios are small, whereas the solubilization of Pb takes place when V/m values are high. It must be pointed out that the amount of Fe released in this fraction is clearly higher than that released in fraction 2 for the less polluted, less carbonated sediment, as it could be expected, whereas for the other sediment the Fe solubilized in this fraction is of about the same order of magnitude. From these results a ratio V/m of 50 mL/g is proposed to solubilize the heavy metals in this fraction. This value is twice that proposed by Tessier.

The fourth fraction, metal extracted by hydrogen peroxide, was studied in the range extended to ten times the V/m ratio proposed by Tessier. In this fraction iron, manganese, copper and lead were determined and the Eh measured after extraction. As can be observed in Figures 5 and 6 higher Eh changes are done for the most polluted sample, and from this one a ratio V/m = 50 mL/g must be used to obtain an Eh variation (versus a blank sample) lower than 25 mV. For the less polluted sample the Eh variation is obtained with small V/m ratios. The lead released in solution in each extraction has a similar behaviour to the Eh variation, whereas the copper solubilized is independent of the Eh change.

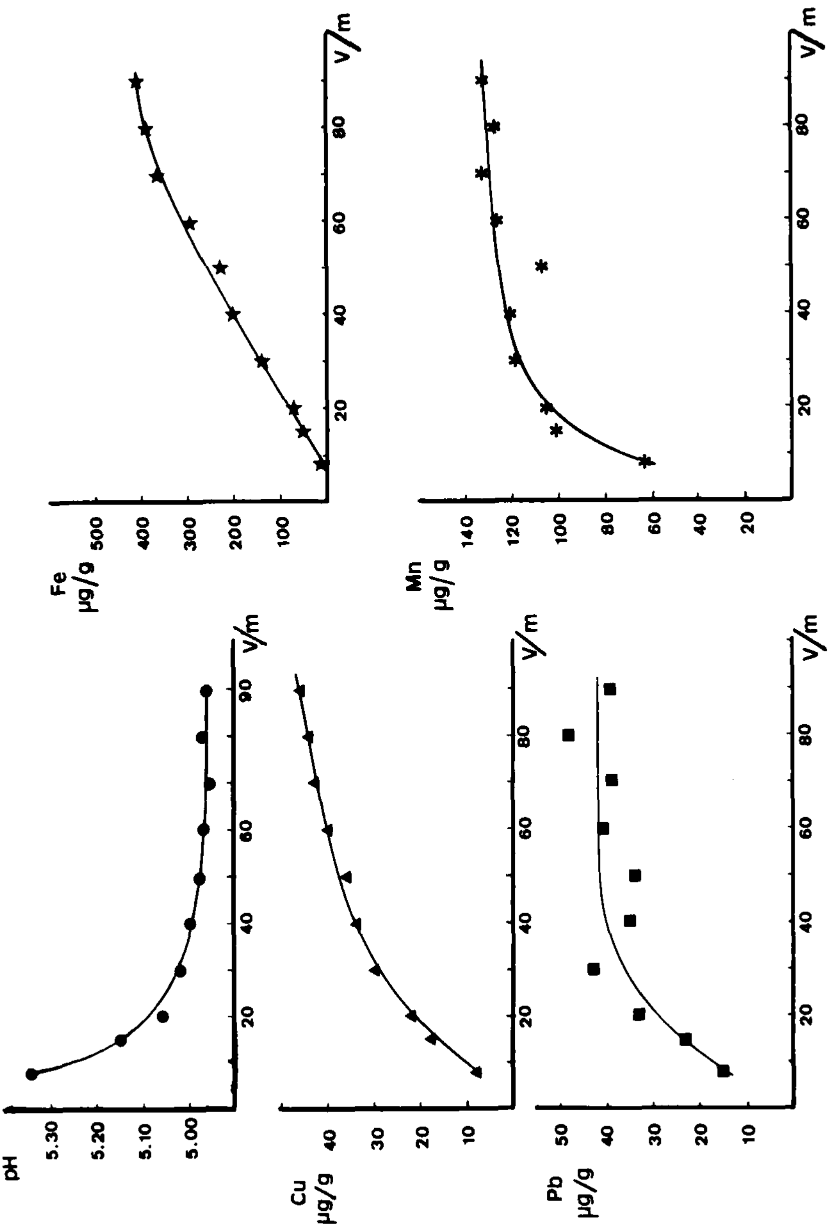

Figure 1 Variation of pH, Cu, Pb, Fe and Mn extracted in second fraction versus V/m ratio (mL/g) in sediment sample 2.

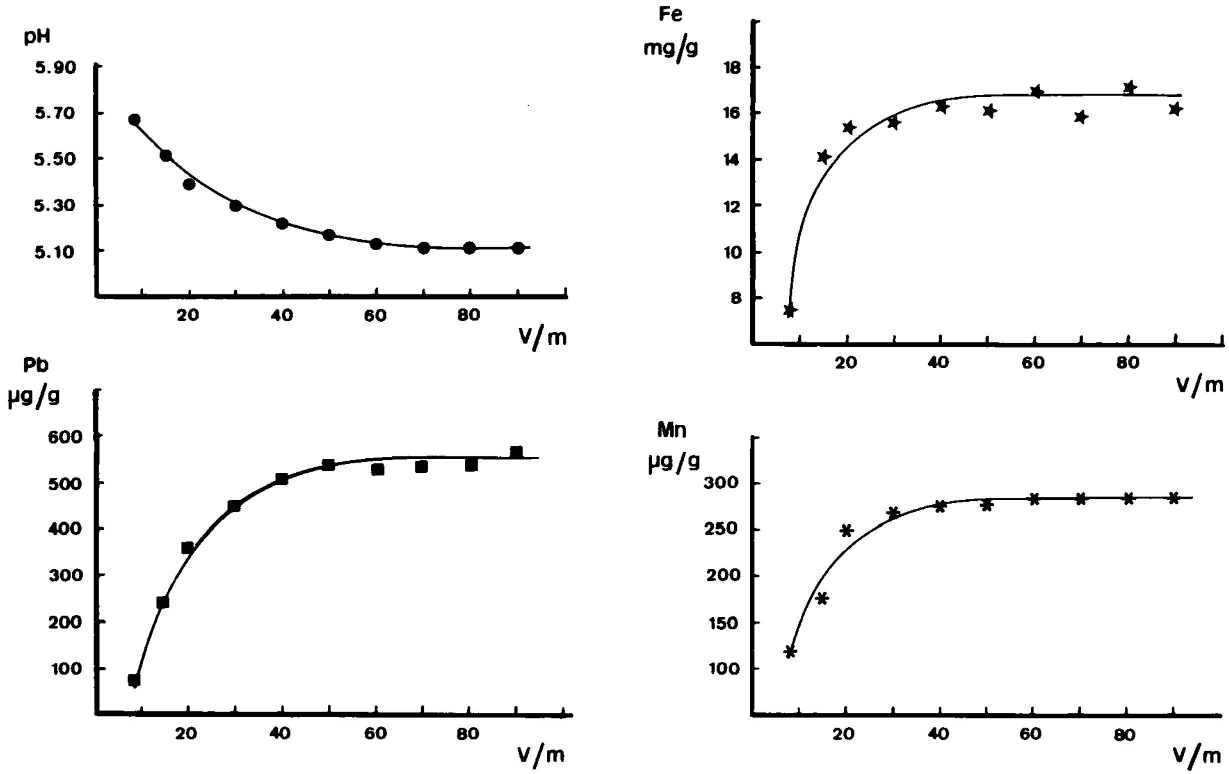

Figure 2 Variation of pH, Pb, Fe and Mn extracted in second fraction versus V/m ratio (mL/g) in sediment sample 5.

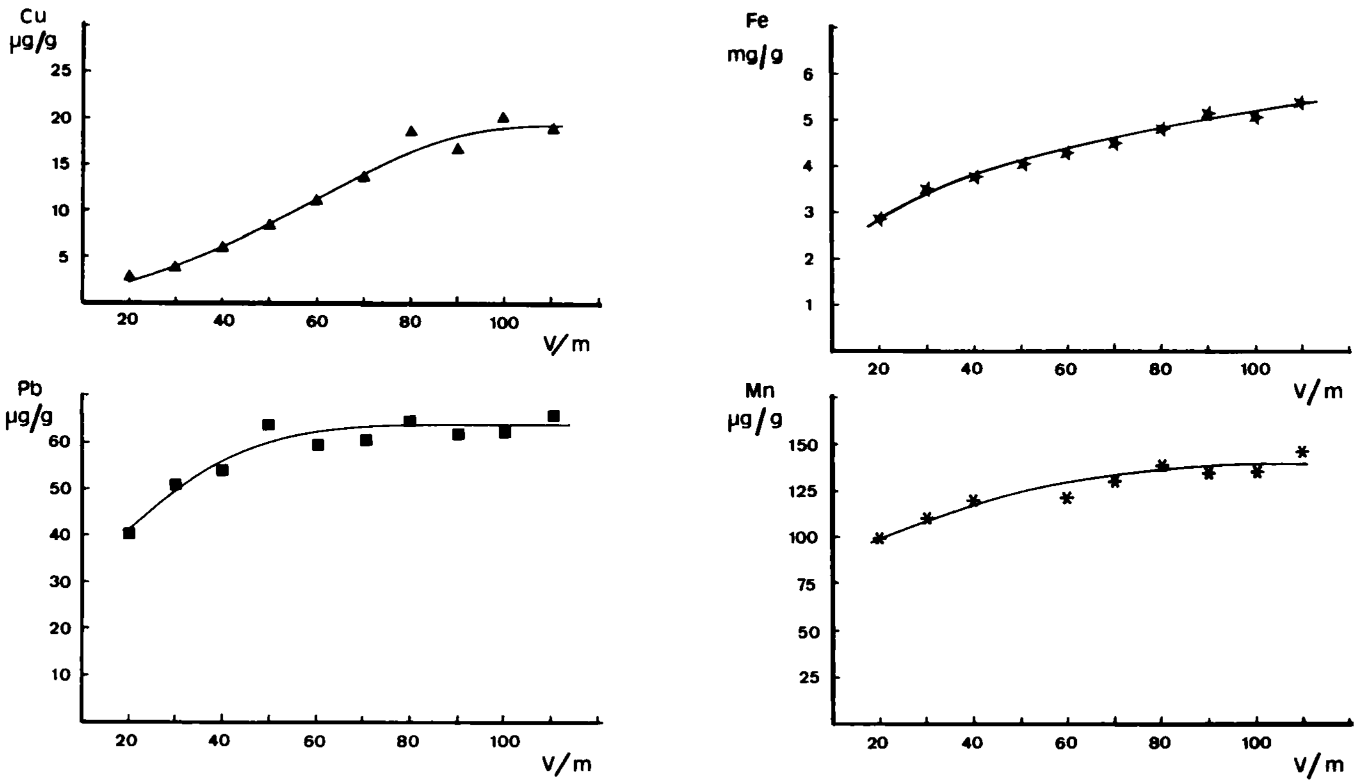

Figure 3 Variation of Cu, Pb, Fe and Mn extracted in third fraction versus V/m ratio (mL/g) in sediment sample 2.

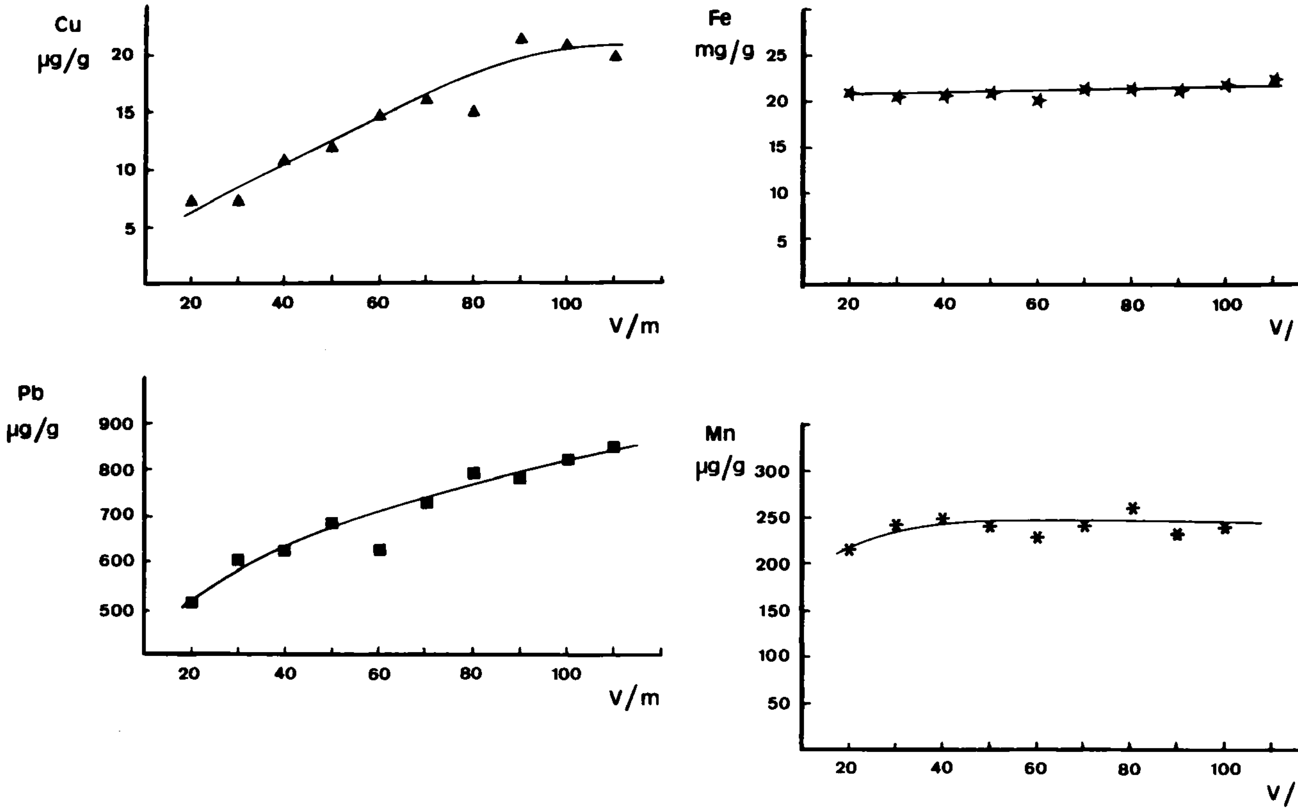

Figure 4 Variation of Cu, Pb, Fe and Mn extracted in third fraction versus V/m ratio (mL/g) in sediment sample 5.

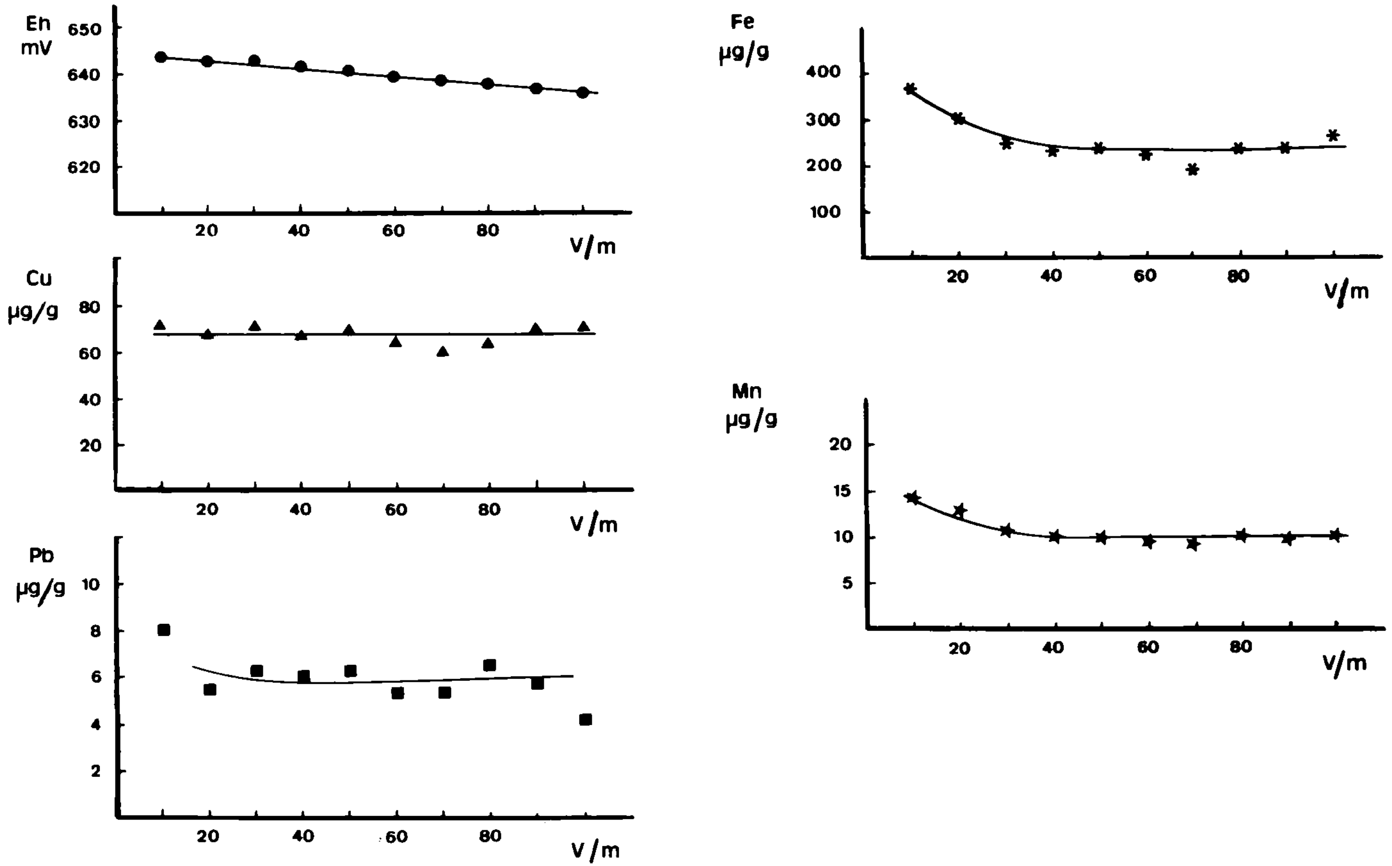

Figure 5 Variation of Eh, Cu, Pb, Fe and Mn extracted in fourth fraction versus V/m ratio (mL/g) in sediment sample 2.

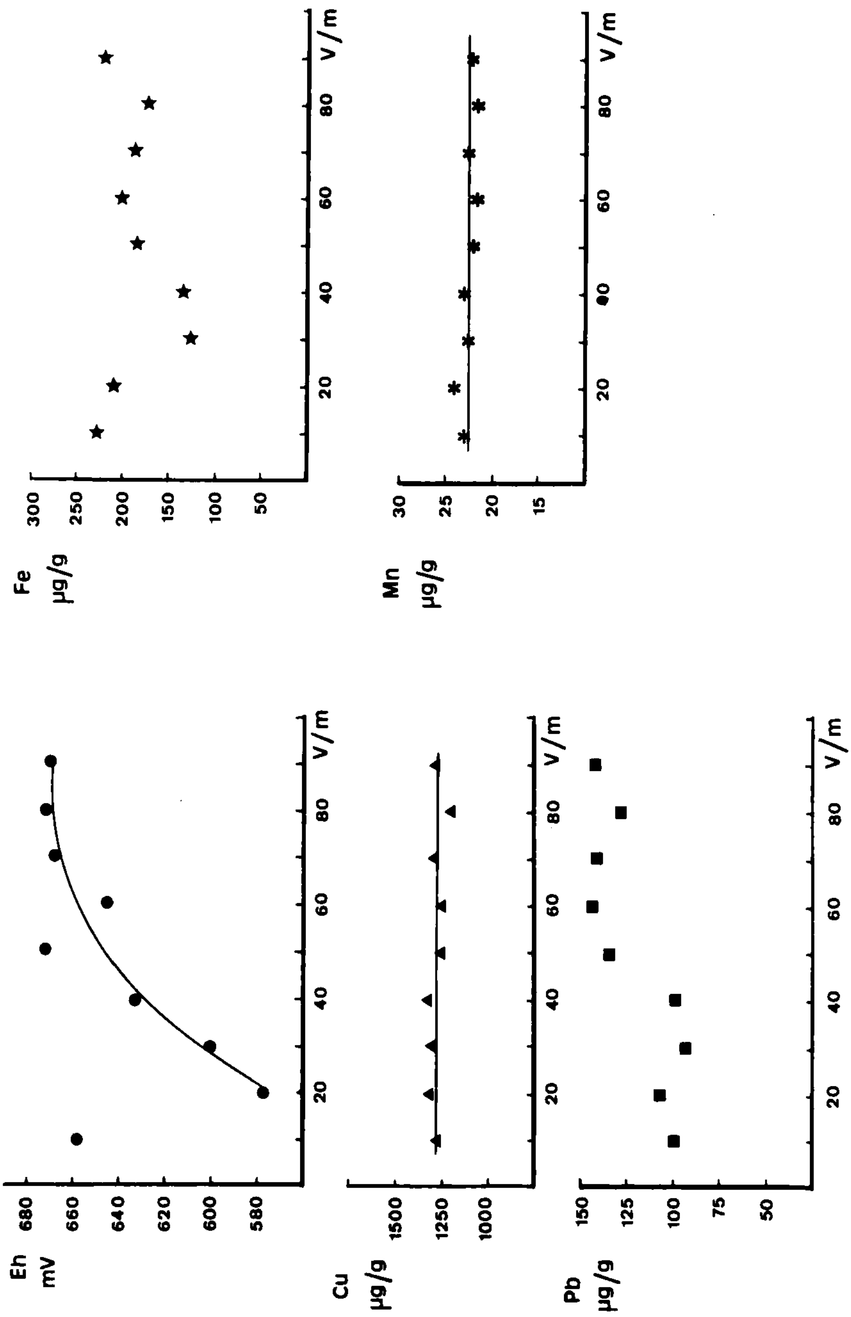

Figure 6 Variation of Eh, Cu, Pb, Fe and Mn extracted in fourth fraction versus V/m (mL/g) in sediment sample 5.

Table 2 Results obtained in copper, lead, chromium and nickel partitioning in sediment sample 2

Fraction	*A*		*B*	
	mg/Kg	%	*mg/Kg*	%
Cu				
1	5	3.8	10	7.0
2	8	6.2	34	23.9
3	3	2.3	6	4.2
4	89	68.5	59	41.5
5	25	19.2	33	23.2
Total	130		142	
Pb				
1	ND		ND	
2	5	4.0	32	20.8
3	50	40.3	64	41.6
4	4	3.2	11	7.1
5	65	52.4	47	30.5
Total	124		154	
Cr				
1	ND		ND	
2	4	3.4	15	12.4
3	23	19.7	29	23.9
4	18	15.4	15	12.4
5	72	61.5	62	51.2
Total	117		121	
Ni				
1	ND		ND	
2	4	9.1	17	35.4
3	11	25.0	11	22.9
4	3	6.8	2	4.2
5	26	59.1	18	37.5
Total	44		48	

The metal concentration values are the mean of three independent determinations. ND is not detected. A: results obtained with Tessier procedure. B: results obtained with V/m ratio optimized procedure.

Partitioning of Cu, Pb, Cr, and Ni in the sediments

Once the ratio V/m is optimized in order to keep the parameters involved in the solubilization of heavy metals in each step constant, the procedure is applied to Cu, Pb, Cr and Ni partitioning in the sediment samples. In Table 2 the results obtained are given together with those obtained applying Tessier procedure. For the most polluted sediment (sediment 5) the results found when repeated successive extractions were applied (Table 3) are also given. In Figures 7 and 8 the percentages of total metal belonging to each fraction using the different procedures for both sediments are represented in a bar diagram. If the pattern obtained with the optimized V/m ratio procedure is compared with that obtained with Tessier's

Table 3 Results obtained in copper, lead, chromium and nickel partitioning in sediment sample 5

Fraction	*A*		*B*		*C*	
	mg/Kg	%	*mg/Kg*	%	*mg/Kg*	%
Cu						
1	4	0.2	3	0.2	15	1.0
2	1	0.1	5	0.3	4	0.3
3	3	0.2	29	2.0	13	0.9
4	1090	61.2	1368	95.0	1220	84.1
5	682	38.3	36	2.5	200	13.8
Total	1780		1441		1450	
Pb						
1	ND		ND		ND	
2	42	2.7	260	16.3	494	30.3
3	509	32.2	1161	72.8	801	49.1
4	119	7.5	125	7.8	54	3.3
5	910	57.6	49	3.1	284	17.4
Total	1580		1595		1633	
Cr						
1	ND		ND		ND	
2	24	0.4	197	3.4	168	2.6
3	2400	39.2	2525	44.1	2310	36.4
4	368	6.0	180	3.1	217	3.4
5	3310	54.0	2820	49.3	3652	57.5
Total	6130		5722		6347	
Ni						
1	5	0.3	5	0.3	14	0.9
2	63	4.0	284	18.0	264	16.2
3	481	30.6	622	39.7	696	42.6
4	223	14.2	50	3.2	90	5.5
5	795	50.6	606	38.7	567	34.8
Total	1570		1567		1631	

The metal concentrations values are the mean of three independent determinations. ND is non detected. A, B and C are, respectively, Tessier procedure, multiple extraction procedure and V/m ratio optimized procedure.

one it can be observed that for sediment 2 for all the metals studied there is an increase of metal released in the second fraction at the expense of a decrease of the metal solubilized in the fourth fraction, mainly for copper, and in fraction 5.

For the most polluted sample (sediment 5) the pattern obtained with the optimized V/m ratio procedure is intermediate between that obtained with Tessier procedure and with repeated successive extraction procedure. Compared with the former, an increase in the metal release in fraction 2 is observed for Pb, Cr and Ni at the expense of a decrease of the metal in fraction 4, and in residual fraction.

For copper the main difference noticed is in the distribution of this metal between the fourth and the residual fraction. When the pattern obtained with optimized V/m ratio procedure is compared with that obtained by repeated successive extraction procedure an increase of the metal remaining in the residual fraction is

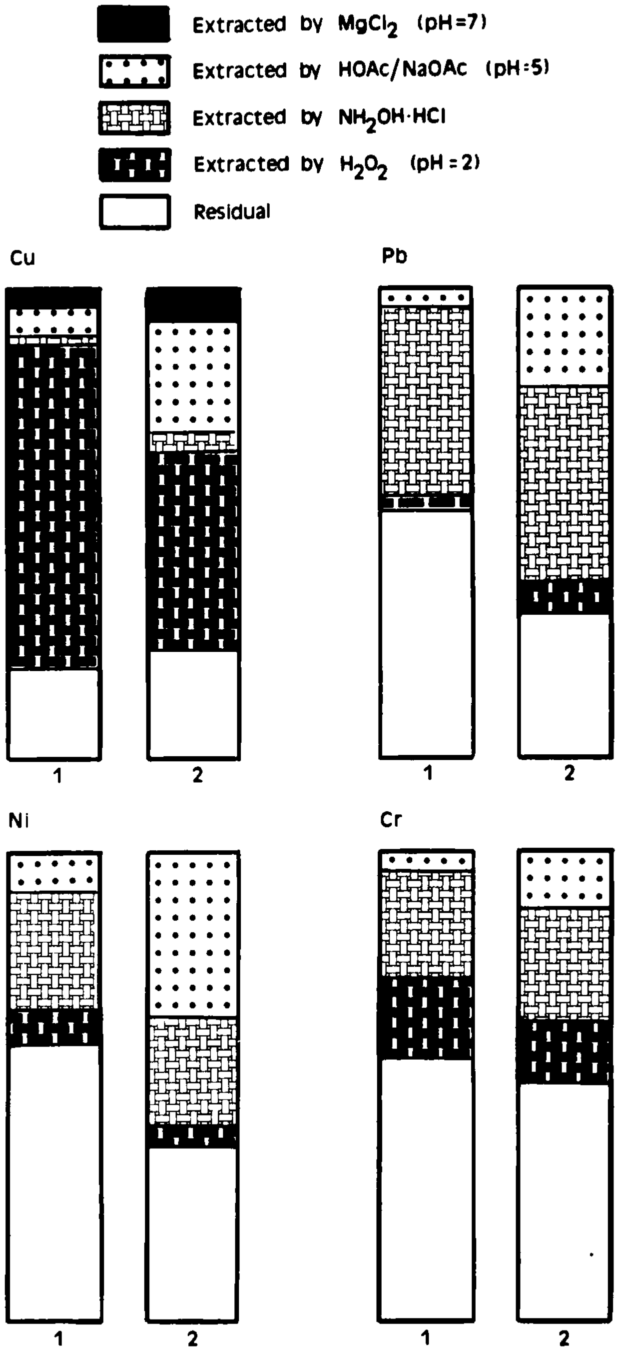

Figure 7 Percentages of total metal bound to each fraction in sediment sample 2 obtained using Tessier procedure[1] and optimized V/m ratio procedure.[2]

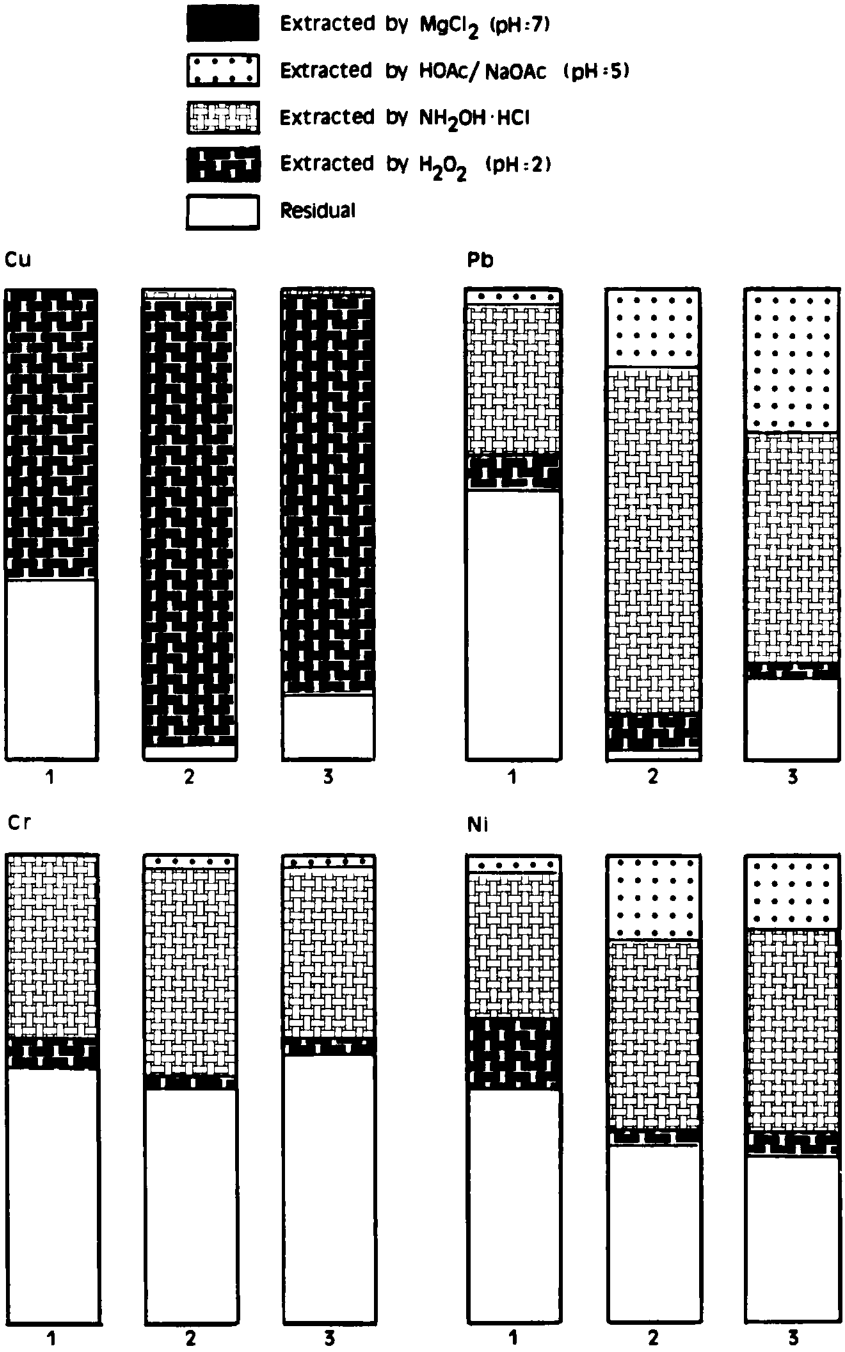

Figure 8 Percentages of total metal bound to each fraction in sediment sample 5 obtained using Tessier procedure,[1] repetitive successive extraction[2] and optimized V/m ratio procedure.[3]

seen. For copper a decrease in the metal belonging to the fourth fraction is observed and for lead redistribution of the metal between the second and the third fraction is found. A different behaviour is observed for chromium and nickel, whose patterns are quite similar to those obtained by repeated successive extraction procedure.

CONCLUSIONS

From the results obtained it can be concluded that the partitioning of heavy metals in sediments using Tessier scheme is dependent either on the experimental procedure followed or on the sediment composition. This dependence is more obvious for heavily polluted sediments and for Pb and Cu more than for Cr and Ni.

It is also observed that there is an important solubilization of iron and manganese in fraction 2, especially for the more carbonated sample (sediment 5). This fact let us to consider that the amount of metal released in fractions 2 and 3 are not clearly defined. This behaviour has also been observed by other authors.[10, 11]

On the other hand and taking into account that the residual fraction is considered equivalent to the base line, a metal content in this fraction, according to the expected values, can show if the procedure used gives an efficient metal solubilization.

From the procedures studied the values of the metal remaining in the residual fraction decrease as follows: Tessier procedure, optimized V/m ratio procedure, repeated successive extraction procedure. With the last method the values of metal in the residual fraction are more in agreement with the values found in the literature for the base line.

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