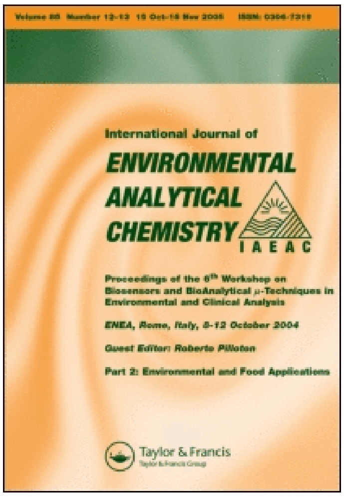

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Comparison between Total Determination and Extractable Heavy Metals from River Sediments using Conventional and Microwave Accelerated Leaching Tests

Benita Pérez-Cid[a]; Cristina Boia[b]
[a] Departamento de Quimica Analitica y Alimentaria, Facultad de Ciencias (Química), Universidad de Vigo, Vigo, Spain [b] Departamento de Ambiente e Ordenamento, Universidade de Aveiro, Aveiro, Portugal

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COMPARISON BETWEEN TOTAL DETERMINATION AND EXTRACTABLE HEAVY METALS FROM RIVER SEDIMENTS USING CONVENTIONAL AND MICROWAVE ACCELERATED LEACHING TESTS

BENITA PÉREZ-CID[a,]* and CRISTINA BOIA[b]

[a]*Departamento de Química Analítica y Alimentaria, Facultad de Ciencias (Química), Universidad de Vigo, Lagoas-Marcosende s/n. 36200 Vigo, Spain;* [b]*Departamento de Ambiente e Ordenamento, Universidade de Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal*

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In the present study the concentration of heavy metals (Cu, Cr, Ni, Pb and Zn) in sediments collected from different sampling stations of the Leça river (Portugal) was determined, using Flame Atomic Absorption Spectrometry. In order to estimate the potential mobility of metals in these samples, the results of the total digestion were compared with those obtained by single extractions using EDTA and acetic acid as extractant solutions; in all samples studied, Cu and Zn were found to be the most mobile elements; Ni and Pb showed a smaller mobility in presence of either acidic medium and complexing ligands; Cr was found the least mobilizable element, given that the low extractability obtained with the two extractants tested in this work. In the single extraction tests, microwave energy was also employed to replace the conventional treatment and only in the case of the EDTA the results obtained were similar to those of the conventional procedure (recoveries between 90.16 and 98.76%); the precision (RSD, $n = 3$) of the proposed microwave procedure for EDTA extractions was comparable to those of the conventional method with values always lower than 8% for all metals.

Keywords: Heavy metals; River sediment; Single extractions; Total metal determination; Mobility predictions; Microwave energy

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*Corresponding author. Fax: +34-986-812382. E-Mail: benita@uvigo.es

INTRODUCTION

Heavy metals are present in streams as a result of anthropogenic emissions: water drainage and discharge of urban and industrial wastewaters. Sediments have been widely employed as environmental indicators of trace contaminants and play an important role in the metal contamination of natural waters [1,2]. Although the most strongly adsorbed pollutants on the sediment may not be readily available for the aquatic medium, the variation of some chemical characteristics (pH, salinity, redox potential and organic chelators) of the overlaying water may provoke the release of the metals [3,4]; hence sediments may become important pollution sources under changing environmental conditions. Therefore, to study the potential impact of a contamination event we need to determine not only the total content but also to estimate the mobility of the pollutants [5,6].

Leaching tests, such as sequential extraction methods and single extractions [7–11] are the most common approach for estimating the metal mobility in environmental samples (soils, sediments, sludges, etc.). Numerous extraction techniques are described in the literature, covering a wide range of extractants and experimental conditions, and there is not yet a common agreement on which is the best approach to estimate the available and mobilizable fraction [9]. One of the main objectives of the Community Bureau of Reference (BCR) has been to improve and validate harmonized analytical methods for environmental assessment and provide reference materials for quality control of these methods. Thus, in the last years, a Working Group of various European laboratories has evaluated different single extractants (EDTA, acetic acid, ammonium acetate, etc.) for heavy metal speciation in soil samples, and even reference materials with certified extractable metal contents in EDTA and acetic acid were introduced as a new contribution to quality control in this field [12,13]. These single extraction tests were widely applied to soil samples [8,9,14] and no works were found in the literature focused on sediments. However, in our opinion, the latter application could be useful to estimate the possible mobility of heavy metals from sediment samples under complexing or acidification processes developed in the environment.

According to the above, the main objective of this work was to compare, in river sediments, the results of the total digestion with those obtained using the EDTA and acetic acid reagents, in order to evaluate the mobilizable metals to the aquatic medium. On the other hand, the microwave energy frequently used for acceleration of different chemical processes [15,16] could be introduced to shorten the treatment time in the two employed single extraction procedures. As little or no work appears in the literature in this way, a second objective of the present work was to compare the results obtained using both the conventional and microwave EDTA and acetic acid single extractions for Cu, Cr, Ni, Pb and Zn. The microwave operating parameters were also optimized for all of the metals, in both extractant solutions, in order to obtain the most favourable extraction conditions for all of them. Flame Atomic Absorption Spectrometry was used for metal measurements.

EXPERIMENTAL

Instrumentation

A double-beam Atomic Absorption Spectrophotometer, GBC model 904 AA, was used for metal determinations. Hollow cathode lamps (Cathodeon) were used as radiation source. Resonance lines employed were 324.8, 357.9, 230.0, 217.0 and 213.9 nm for Cu, Cr, Ni, Pb and Zn, respectively. Lamp intensity and slit width were used according to the manufacturer's recommendations. Air–acetylene flow rate was 11–1 L min^{-1} for all the elements, except for Cr where a more reducing flame was required (11–2 L min^{-1}). A domestic microwave oven with power values ranging from 90 to 650 W (Crown, model NW 070) was used as microwave radiation source. A 45 mL capacity Parr reactor (model 4782) was employed for acid digestion of sediment samples. A magnetic shaker (Plabinco model L 34) was used for the extractions. A centrifuge (Heraus Sepatech, model Labofuge Ae) was used for a complete separation of the extracts from the solid phase. A pH-meter (Philips, model PW 9420) was used for pH adjustments in the extracts.

Reagents

All reagents employed were of high quality analytical reagent grade and all of them supplied by Merck. High purity water (Millipore Milli-Q System) was used throughout. The stock solutions of metals (1000 µg/mL) were obtained by dissolving the appropriate salts or the corresponding metals. Concentrated nitric (65%), hydrochloric (35%) and hydrofluoric (48%) acids were employed for the digestion of the samples. Certified reference materials, such as a domestic sludge (SRM 2781) from the National Institute of Standard Technology (NIST), and a river sediment (CRM 320) from the European Commission Joint Research Centre (Institute of Reference Materials and Measurements) were used to test the digestion method. Other soil reference material (CRM 483), also proceeding from the Institute of Reference Materials and Measurements with certified EDTA and acetic acid extractable metal contents was used to validate the microwave accelerated single extraction tests.

The 0.05 mol/L EDTA solution was prepared as an ammonium salt solution by dissolving the appropriated amount of the salt in concentrated ammonia solution; the addition of ammonia solution must be continued until all the EDTA dissolved; the pH was adjusted to 7 ± 0.05 by addition of a few drops of either ammonia or hydrochloric acid. The 0.43 mol/L acetic acid solution was prepared by adequate dilution of glacial acetic acid. Both extractant solutions were stored in stopped polyethylene containers.

Sample collection and pretreatment

The sediment samples were collected from five sampling stations (Cabreira A and B, Goimil A and B and Amoreira) distributed along the Leça river, next to the town of Porto (Portugal). It is important to emphasize that this river is located close to a new municipal solid waste incinerator plant and moreover some domestic, agricultural and even industrial effluents are also discharged directly into the stream. The sediments were collected in polyethylene bottles from the banks of the river and they were dried in the laboratory at 105°C [17,18] in a heater until constant weight. After this, the samples were sieved using a nylon fibre sieve and those with particle size smaller than 90 μm were separated. The sieved samples were homogenized and stored at room temperature in polyethylene bottles in a dessicator.

Microwave digestion

For total metal determination the sediment samples were dissolved using a microwave digestion procedure optimized in a previous work [19]. A portion (0.1 g) sample (< 90 μm) was placed into the PTFE vessel of the Parr reactor and 4 mL of nitric acid (65%), 1 mL of hydrochloric acid (35%) and 2 mL of hydrofluoric acid (48%) were added. The vessel was closed and then it was heated in a microwave oven for 2 min at 540 W of power. Once the sample was digested, the reactor was allowed to cool in an ice bath before it was opened. The resultant solution was heated to dryness and dissolved with 1 mL of hydrochloric acid, in order to eliminate the unreacted hydrofluoric

TABLE I Analytical results obtained in the certified reference materials after microwave digestion

	Certified values (mg/Kg)	*Found values*[a] *(mg/Kg)*	*Recovery (%)*
Domestic sludge (SRM 2781)			
Cu	627.4 ± 13.5	637.1 ± 9.45	101.5
Cr	202.0 ± 9.0	198.5 ± 5.03	98.27
Ni	80.20 ± 2.3	80.51 ± 5.14	100.4
Pb	202.1 ± 6.5	206.4 ± 9.88	102.1
Zn	1273.0 ± 53	1272.4 ± 23.2	99.95
River sediment (CRM 320)			
Cu	44.10 ± 1.0	43.25 ± 3.05	98.07
Cr	138.0 ± 7.0	138.9 ± 3.90	100.6
Ni	75.20 ± 1.4	74.98 ± 4.04	99.71
Pb	42.30 ± 1.6	42.78 ± 3.30	101.1
Zn	142.0 ± 3.0	142.6 ± 4.10	100.4

[a]Concentrations are expressed as mean value of three determinations ± standard deviation.

acid. Finally, it was quantitatively transferred into a 10 mL volumetric flask and made up to volume with ultrapure water. The solution was decanted and stored at 4°C in stopped polyethylene bottles until it was analyzed.

In order to check the microwave digestion method, a domestic sludge (SRM 2781) and a river sediment (CRM 320) reference materials with certified contents of all the metals studied were employed. Three replicates of the reference samples were digested and analyzed following the same procedure as the unknown samples. The results obtained for Cu, Cr, Ni, Pb and Zn are shown in Table I and no significant differences were obtained between the experimental and certified values.

Conventional and microwave single extraction procedures

Two single extraction tests were applied, in triplicate, to the sediment samples studied. All the extractions were performed in 50 mL capacity glass tubes also used for centrifugation, in order to avoid possible loss of sample.

The extractions with EDTA were carried out following the established extraction method [20]: approximately 2.5 g of pretreated sediment sample were placed into a centrifuge tube and 25 mL of 0.05 mol/L EDTA solution were added; the mixture was shaken for 1 h at room temperature by means of a magnetic shaker. The acetic acid extracts were obtained using the following extraction conditions [20]: approximately 1 g of pretreated sediment sample was placed into the centrifuge tube and 40 mL of 0.43 mol/L acetic acid were added; the mixture was also shaken for 16 h at room temperature.

In both cases, after shaking, the suspension was centrifuged for 12 min at 2500 rpm. The supernatants were quantitatively transferred to volumetric flasks of 25 and 50 mL for EDTA and acetic acid extracts, respectively. The resultant solutions were decanted in polyethylene bottles and stored at 4°C until analysis. Blank extractions were carried out in parallel for each set of analysis using the same procedure as described above.

The EDTA and acetic acid microwave single extractions were carried out using the same volume of reagents and amount of sample to the conventional procedure, but replacing the magnetic shaking with microwave heating, in order to reduce the operation time. In the microwave procedure, and prior to the heating step, the extraction mixture (extractant/sample) was mixed by means of a magnetic shaker (for 5 s) with the aim to obtain a homogeneous slurry, which was microwaved before the sedimentation process was initiated. The influence of microwave heating time on metal leached by both extractants studied was evaluated by comparing the results obtained using the conventional procedure with those attempted from microwave extractions, for a time between 1 min and 4 min 30 s in the case of the EDTA and between 1 and 7 min in the case of acetic acid, at 90 W of power.

The influence of microwave power could not be evaluated, since power values higher than 90 W caused the solution to boil over the tube.

The recovery was defined as the following ratio: [metal leached using the microwave extraction method/metal leached applying the conventional extraction method] × 100. It should be cleared that the goal of this study was not to enhance the extraction efficiency of the traditional extraction methods but rather to find microwave extraction conditions that yield identical extractable metal contents with shorter treatment times.

RESULTS AND DISCUSSION

Interference effects

Chemical interferences caused by the sediment matrix composition were investigated in the Cabreira A sample by means of a single point standard addition to EDTA and acetic acid extracts [21]; the amount of analyte added was approximately equivalent to that already present in the sample; the recoveries of Cu, Cr, Ni, Pb and Zn standard solutions added to EDTA and acetic acid extracts are shown in Table II. On the other hand, the presence of chemical interferences associated with the extractant agent was established by statistical comparison (*t*-test, $p = 0.95$) of the slopes

TABLE II Interference effects caused by the extractant agent and the matrix composition of the sediment

	Aqueous[a] *slope (AS)*	*Acetic acid*[a] *slope (ACAS)*	*EDTA*[a] *slope (ES)*	*Change*[b] *(%) (AS-ACAS)*	*Change*[b] *(%) (AS-ES)*
Extractant effects					
Cu	0.1007	0.1003	0.1100	−0.40	9.23
Cr	0.07514	0.07443	0.08929	−0.94	18.83
Ni	0.05200	0.05214	0.06014	0.27	15.62
Pb	0.02804	0.03500	0.03431	24.82	22.36
Zn	0.2450	0.2367	0.2359	−3.38	−3.71
Matrix effects					
	Acetic acid recovery (%)	*EDTA recovery (%)*			
Cu	93.94	94.81			
Cr	93.33	99.62			
Ni	94.00	83.91			
Pb	94.20	73.11			
Zn	93.03	85.95			

[a] All slopes are expressed as mL/μg.

[b] The slope change was calculated using the following ratio: [(slope of extractant calibration (ACAS or ES) − slope of aqueous calibration (AS))/slope of aqueous calibration (AS)] × 100.

obtained with aqueous standards and those obtained using standards prepared in the EDTA and acetic acid extractants; these results are also listed in Table II.

According to the reported results in Table II, it is possible to ensure that no significant matrix interference was observed for Cu and Cr in the EDTA extracts and for all the metals studied in the acetic acid extracts (recoveries between 93.03 and 99.62%); however, the recoveries obtained for Ni, Pb and Zn in the EDTA extracts oscillated between 73.11 and 85.95%, and consequently, the influence of the matrix composition was noted. In what concerns the evaluation of chemical interferences associated with the extractant agent, when the percentage of change in slope between the aqueous and extractant standards was lower then 5%, it was considered that no significant differences existed, so calibration with aqueous standards could be carried out; by taking into account the above considerations, Cu, Cr, Ni and Zn could be determined using calibration with aqueous standards in the acetic acid extracts; calibration with standards prepared in the extractant solution can be used for Pb in the acetic acid extracts and for Cu and Cr in the EDTA extracts. According to the study of matrix interferences, calibration using the standard addition method is necessary for Ni, Pb and Zn in the EDTA extracts.

Influence of microwave heating time

The results corresponding to the optimization of microwave heating time in the single extraction procedures are summarized in Fig. 1(a)–(b). This optimization study was also carried out using the Cabreira A sediment sample.

In general and according to these graphics, while in the EDTA extracts the microwave procedure provided similar results to the conventional method at longer heating times, in the acetic acid extracts all metals were poorly leached. In the case of the EDTA (Fig. 1(a)), the extraction efficiency

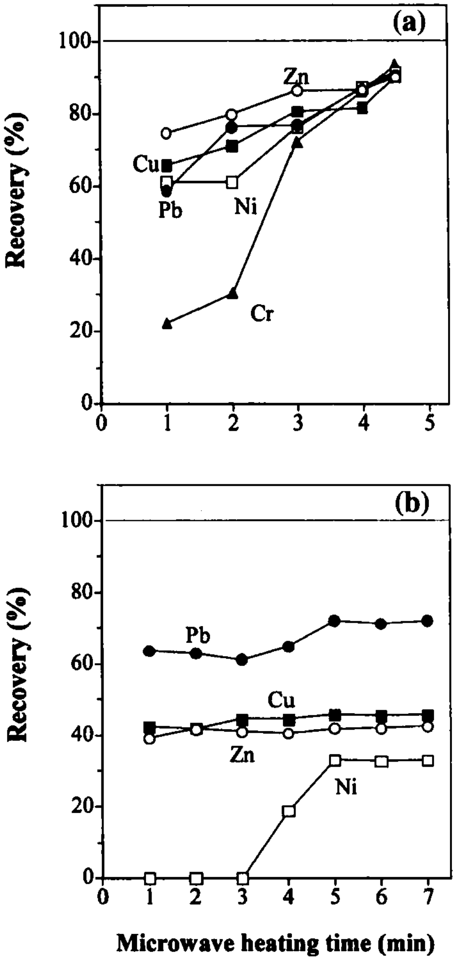

FIGURE 1 Influence of microwave heating time on metal leached by EDTA (a) and acetic acid extracts (b) from river sediments.

of all the metals studied was improved when the microwave heating time was also increased; therefore, the most favourable extraction conditions were achieved using a heating time of 4 min and 30 s at 90 W of power given that longer heating times caused the solution to boil and spill over the tube; the recovery values were always higher than 90% for all metals. The precision of the proposed method (expressed as RSD, $n = 3$) was similar to the conventional procedure with values between 6.1 and 7.5% for Cr, Ni, Pb and also lower than 4.8% for Cu and Zn. In the extracts obtained with acetic acid (Fig. 1(b)), the amount of metals leached was enhanced when the microwave heating time was varied from 1 to 5 min; for heating times higher than 5 min, the extraction efficiency was scarcely modified; in this case, all metals were poorly extracted even using the most favourable microwave extraction conditions ($\geq$ 5 min of treatment); so, the percentages of recovery were around 72% for Pb and lower than 46% for Cu, Ni and Zn; Cr was not extracted at quantifiable level when the accelerated procedure was applied. In this case, a worst precision was achieved when the accelerated procedure was employed, given that the RSD obtained ranged from 8.30 and 9.20% in the case of Ni, Pb and Zn and lower than 6% in the case of Cu. By taking into account the above considerations, the best microwave extraction conditions for metal leached with EDTA and acetic acid solutions were achieved by heating for 4 min 30 s and 5 min, respectively.

Comparison between metal leached using conventional and microwave single extractions

The conventional EDTA and acetic acid single extractions and the microwave accelerated procedures were applied, in triplicate, for metal leaching in all the samples studied. The comparison of these results is displayed in Fig. 2, where all the values are given as mean of three determinations (μg/g).

According to these graphs, the results obtained with the EDTA microwave accelerated procedure were, for all metals, in good agreement with those reported by the conventional extraction method. For all the studied sediments the percentages of recovery obtained, in relation to the conventional procedure, oscillated between 90.16 and 98.76%. This means that the EDTA metal extractions could be estimated using the proposed approach, considerably reducing the operational time. Moreover, the precision of this proposed method (RSD, $n = 3$) was similar to the conventional procedure, with values lower than 5% for Cu and Zn and between 6.59 and 7.85% for Cr, Ni and Pb.

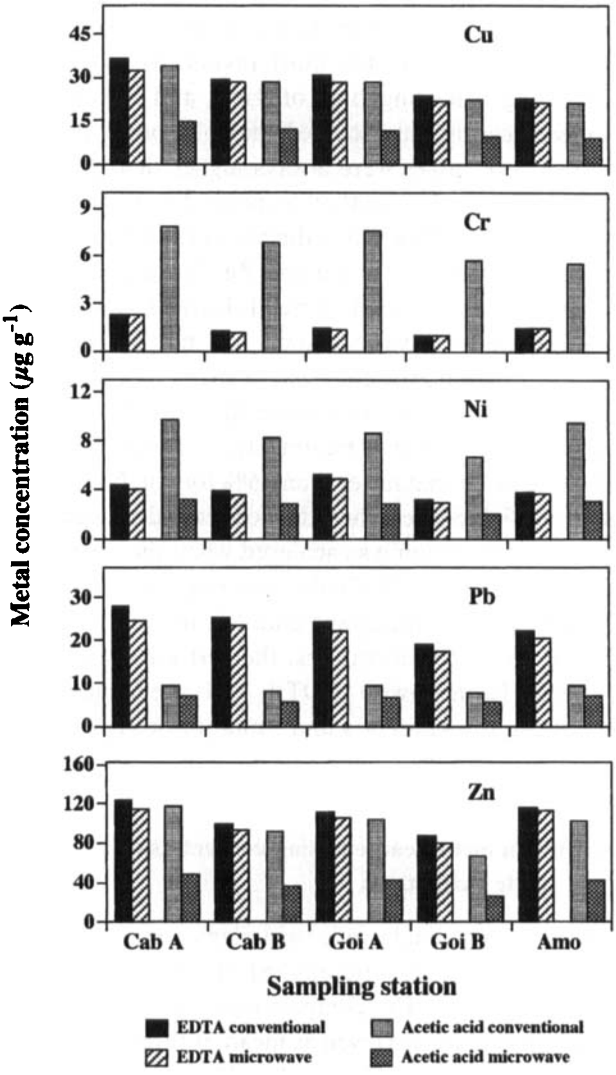

FIGURE 2 Metal leached in sediment samples using the conventional and microwave single extractions. Cab = Cabreira; Goi = Goimil; Amo = Amoreira.

In contrast, in the case of the acetic acid, and according to the previous optimization (Fig. 1(b)), the extraction efficiency of the microwave procedure was considerably lower than that of the conventional method and significant differences were observed between the results obtained by both compared extraction methodologies. The best percentages of recovery correspond to Pb (71–74%) and the worst case corresponds to Cr, which was not leached using the proposed approach. Therefore, the conventional acetic acid extraction method cannot be replaced by the microwave procedure although it would allow a great simplification of the experimental task due to an important reduction of the treatment time.

Despite some differences between the studied sediment samples and the soil reference material (CRM 483), the two optimized microwave EDTA and acetic acid leaching tests were applied, in triplicate, to that certified soil in order to evaluate the extraction efficiency of both accelerated single extraction procedures. The results of this study are shown in Table III. According to these data, quantitative recoveries were obtained for all the elements (95–103%), except for Cr (around 82%), in the EDTA extracts, and a good agreement was found between these results and those previously obtained in river sediments (see Fig. 2), except for the case of Cr. In the acetic acid extracts, no quantitative recoveries were found for any studied elements when the accelerated procedure was used. In relation to sediment samples (Fig. 2), some differences in the extraction efficiency were observed for Cu, Pb and Cr (recoveries lower than 22%) but not for Ni and Zn (recoveries lower than 48%). This different behaviour obtained between the soil and sediment samples could be explained by taking into account the different matrix composition of both samples and other variables such as different particle size, different distribution of metals among the components of the sample, etc., which could affect the efficiency of the extraction.

TABLE III Analytical results obtained in the reference material (CRM 483) after EDTA and acetic acid microwave extractions

	Certified values (mg/Kg)	*Found values*[a] *(mg/Kg)*	*Recovery (%)*
EDTA extractable metals			
Cu	215.0 ± 11.0	210.8 ± 6.2	98.04
Cr	28.6 ± 2.6	23.45 ± 1.4	81.99
Ni	28.7 ± 1.7	29.19 ± 0.73	101.7
Pb	229.0 ± 8.0	217.6 ± 6.1	95.02
Zn	612.0 ± 19.0	630.4 ± 9.2	103.0
Acetic acid extractable metals			
Cu	33.5 ± 1.6	7.35 ± 0.65	21.94
Cr	18.7 ± 1.0	2.82 ± 0.39	15.08
Ni	25.8 ± 1.0	11.78 ± 0.87	45.66
Pb	2.10 ± 0.25	nd	–
Zn	620.0 ± 24	297.6 ± 5.10	48.0

[a] Concentrations are expressed as mean value of three determinations ± standard deviation.
nd = not detected by FAAS.

Comparison between total metals and single extractable contents

The results of the total digestion and those obtained applying the EDTA and acetic acid single extractions (conventional method) are shown in the graphics of Fig. 3. All data are expressed as mean values (µg/g) of three determinations. In relation to the total metal concentration, comparable results were obtained for each element in all the sediments studied. As expected, Zn is the most abundant element in all samples with concentration values between 433 and 492 µg/g, except in the Goimil B sample where a lower value was found (353 µg/g). Pb presents concentrations close to 140 µg/g in all sediments. For Cu and Cr, the total contents ranged from 70 to 130 µg/g, except for Cr in the Goimil A (160 µg/g) sample. Ni presents the lowest concentrations in all samples with values oscillating between 30 and 50 µg/g.

By comparing the total metal contents with the EDTA and acetic acid extractable metals, in the same sediment samples, it is possible to conclude that the most mobilizable metals in all samples were Cu and Zn. The percentages of extraction with respect to the total content oscillated between 26.7–38.9% for Cu and between 18.9–25.4% for Zn, using both employed extraction procedures. On the other hand, Ni and Pb present a lower mobility since they were less leached by both extractants (EDTA/acetic acid). The major extractability of these metals was achieved for Ni using the acetic acid (around 19% of the total content) and for Pb using the EDTA (around 17% of the total content). The least mobilizable metal in the samples studied was Cr, given that it was almost not extracted using EDTA and with acetic acid was only leached around 4–6% of the total content. By taking into account the above results and in agreement with other authors [7–11], the total metal determination does not provide sufficient information to evaluate the mobility and bioavailability of metals in the environment.

The extraction efficiency of the EDTA and acetic acid was compared, a different behaviour was found for the metals studied; whereas Cu and Zn were leached in a similar way by both extractants, Cr and Ni were more released using acetic acid, and Pb was more released when EDTA was employed. Similar results to those obtained in this work were also observed for Pb [9,14] and Cr [9] in soil samples. However, the results obtained for Cu, Ni and Zn in this study do not agree with those reported by other authors [9,12,14]; in these previous works, Cu and Zu were more released using the EDTA and acetic acid, respectively; Ni was extracted in a similar way by both reagents. However, in our opinion, these discrepancies could be attributed to a different metal association with the different components of the samples studied (soils, sediments, etc.).

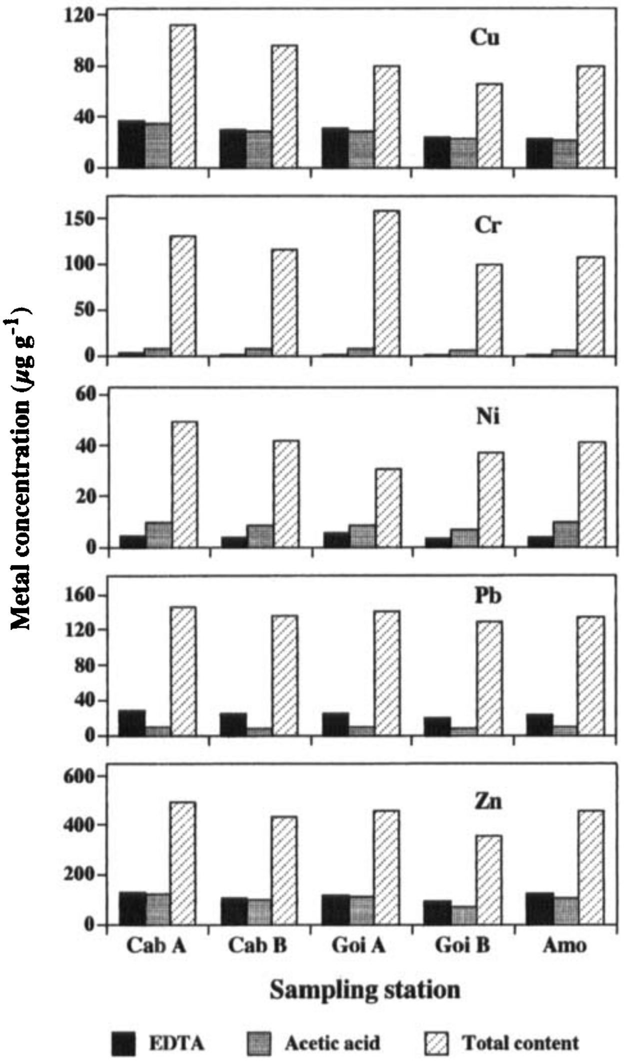

FIGURE 3 Comparison between total determination and extractable metal contents using EDTA and acetic acid extractants. Cab = Cabreira; Goi = Goimil; Amo = Amoreira.

In summary, the results reported in this work allow us to say that, in these particular sediment samples, Cr and Ni would be more mobilized by acidification processes than by increasing the complexing agents in the environment. In contrast, Pb could be more easily liberated in the last conditions, and the environmental availability of Cu and Zn is very similar in both cases.

CONCLUSIONS

On the basis of the results obtained in this work it is possible to conclude that the application of leaching tests, such a single extractions, provides valuable information about the possible mobility and availability of heavy metals under changing environmental conditions. In the samples studied, Cu and Zn are the most mobilizable elements, as shown by the higher desorption obtained with the two extractants tested in this work. Ni and Cr present a major potential mobility in acidic medium, whereas Pb is more released when the concentration of complexing ligands is increased.

On the other hand, the application of microwave energy to replace the conventional treatment in the single extractions provides satisfactory results in the case of the EDTA but not in the acetic acid extractions. According to the reported results, the proposed microwave procedure for EDTA extractions allow us to obtain, for all metals, similar results to the conventional procedure (recoveries between 90.16 and 98.76%), but substantially reducing the treatment time; in fact, the traditional shaking time has been reduced from 1 h to 4 min and 30 s of microwave heating. In contrast, the extraction efficiency of the microwave acetic acid extractions was considerably lower than that of the conventional method. It means that the application of the proposed microwave EDTA extractions provides a promising approach to obtain rapid information about the environmental impact of heavy metals, particularly in presence of complexing ligands. Moreover, the application of the microwave EDTA accelerated procedure to a certified soil sample (CRM 483) also provides satisfactory results for all the studied elements, except for Cr.

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