

Mónica B. Alvarez · Mónica E. Malla
Daniel A. Batistoni

Comparative assessment of two sequential chemical extraction schemes for the fractionation of cadmium, chromium, lead and zinc in surface coastal sediments

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Abstract Two existing sequential chemical extraction schemes, involving respectively five and six leaching steps with solutions of increasing dissolving power, were compared. The methods have been applied to surface sediment samples collected in a marine estuary zone potentially exposed to contamination arising from nearby industrial activities. A certified reference material (MURST-ISS-A1) consisting of an Antarctic bottom sediment for which no information regarding phase dependent concentration is available, was also analyzed. In order to evaluate the partition of metals among different geochemical forms, the concentrations of cadmium, chromium, lead and zinc were measured in the liquid extracts by Zeeman-corrected flame atomic absorption and by inductively coupled plasma-atomic emission spectrometry. The total metal concentrations were determined after strong acid attack, and the adequacy of this total digestion/dissolution technique was verified by its application to the reference material. Comparison of total metal concentrations with the sum of concentrations associated with the individual phases was employed to assess possible analyte losses or contaminations. Precisions for both sequential procedures were comparable, but some inconsistencies in mass balances were found in one of the samples for the distribution of Zn in the soluble/exchangeable fractions and for Cd in the bound to carbonates form. In addition, the six steps procedure produced lower concentration values in the case of elements associated to the residual fraction.

For the five steps method mass balances showed acceptable agreement, with average recoveries in the 87 to 106% range. On the whole, differences in metal distributions were observed, being more marked for the bottom sediment. Significant proportions of the studied elements, with the exception of Cr, were found as easily extractable forms. X-ray diffraction and petrographic observation of the surface sediments allowed qualitative correlation between the leaching results obtained and the presence of defined geochemical phases.

1 Introduction

Evidence of contamination of sediments and soils by potentially toxic elements is usually obtained by estimation of the total amount of those substances present above specific concentration limits. However, because of the different chemical forms in which metals can accumulate, total concentrations are usually not sufficient to obtain information relevant to environmental studies aimed to evaluate the impact of anthropogenic or natural contamination sources. The mechanisms by which metals can be removed (i.e. sediments may act as sources or sinks of contaminants) are highly dependent on the bonding forms under which those metals are associated with the different geochemical phases constituting the sedimentary material.

Interest in the use of partial dissolution techniques originates in geochemical exploration studies aimed to detect anomalous concentrations of elements [1, 2]. The component elements of minerals, when released to the environment by weathering followed by hydromorphic or other transportation processes, may react with specific reaction sites in solids. As a result the elements may remain retained under relatively labile forms via different chemical or physicochemical reaction mechanisms. In environmental sciences selective leaching of sediments with defined chemical extractants (or mixtures) [1] is meant to establish which fractions of an element that, being previously in a labile form, have reached a lower degree of mobility by interaction with the geochemical environment.

M. B. Alvarez · M. E. Malla
Departamento de Química e Ingeniería Química,
Universidad Nacional del Sur,
(8000) Bahía Blanca, Prov. de Buenos Aires, Argentina

D. A. Batistoni (✉)
Unidad de Actividad Química,
Gerencia Centro Atómico Constituyentes, CNEA,
Avenida del Libertador 8250, (1429) Buenos Aires, Argentina
and
INQUIMAE, Facultad de Ciencias Exactas y Naturales,
UBA, Buenos Aires, Argentina

Sequential leaching of sediments with solutions of increasing dissolving power allows a broad operational classification of the most important binding forms of metals, which can, in principle, be associated with the component solid phases. Because true specificity is almost impossible to achieve, the speciation results obtained by these means are generally described as “operationally defined”. Thus, the term “operational” is meant to indicate that the data are dependent on the experimental procedures employed, and that the forms or phases identified are only loosely defined.

Although somewhat far from ideal, sequential extraction schemes are frequently employed in environmental sciences to determine the chemical or physicochemical binding forms in natural solids. Some intrinsic limitations, such as redissolution or readsorption of metals during the successive extraction stages, make speciation measurements performed directly on the solid more desirable [3]. However, those measurements usually require sophisticated instrumentation, and are in many cases difficult to interpret.

A widely employed sequential scheme, originally proposed by Tessier et al. [4] classifies the metal fractions as: (a) exchangeable, (b) bound to carbonates, (c) bound to oxides of Fe and Mn, (d) bound to organic matter, and (e) residual (included in the crystal lattice). A similar method, described by Grimalt [5] includes a previous stage in which soluble metals, originally present in interstitial water, are extracted. Other procedures introduce also a water extraction step [6], or discriminate between metals associated with amorphous Fe and Mn oxides and those associated with crystalline oxides of Fe [7]. Additional information can be obtained from single extractions with specific complexing agents such as EDTA or acetic acid [8, 9] or from digestion / extraction with diluted strong acids (or acid mixtures) [10, 11]. Chemical fractionation is also frequently applied to substrates other than sediments, such as peat [12] or atmospheric particulate matter [13]. Possible sources of error associated with the procedures have been discussed [14, 15]. The need of adequate quality control of the sequential methods to allow the comparison of results is widely recognized. A three steps fractionation method has been proposed by the European Standards, Measurements and Testing Program (formerly BCR) [16, 17], aiming to improve the comparability while retaining the most significant empirical information generated. Standardized protocols, amenable to extensive testing via feasibility and interlaboratory studies, have been established. In particular, the preparation and certification of soil and sediment reference materials and the approaches for validation of single and multiple extraction schemes are thoroughly discussed by Quevauviller [17].

Due to their inherent multielemental capabilities to specifically detect and measure several elements at trace and subtrace levels, sequentially or simultaneously, atomic spectrometric techniques are particularly suited for the analysis of the relatively low volumes of the liquid phases resulting from the successive extraction steps. Applica-

tions of atomic absorption spectrometry, either with flame (FAAS) or electrothermal (ETAAS) atomization [6, 18–20], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [7, 21] and mass spectrometry with inductively coupled plasma source (ICP-MS) [7, 22] are described in the literature.

The objective of this work was to comparatively assess two widely employed sequential leaching methods [4, 5], with the purpose of establishing the feasibility of their application to distribution studies of heavy metal contaminants in coastal surface sediments. The methods were chosen because of their similarities and capacity to generate specific information on the type of materials considered. The study was focused on four elements of toxicological interest (Cd, Cr, Pb and Zn), that may be associated with industrial activities. Two representative sediment samples, collected in potentially contaminated sites, and a certified reference material (MURST-ISS-A1, Antarctic bottom sediment) for which previous information regarding the phase dependent composition is not available, were selected for evaluation.

2 Experimental

2.1 Reagents and instrumentation. All chemicals and reagents were of analytical reagent grade. Doubly distilled, demineralized water was used throughout. Before use all glass and plastic ware was soaked in 10% HNO₃ for 24 h. The washing was completed with a doubly distilled water rinse. Carlo Erba (Erbatron RSE) HF, HCl and HNO₃ were employed. Stock solutions of the analytes (1 g L⁻¹) were obtained from Carlo Erba Normex Standards. Multielement calibrant solutions of Cd, Zn and Pb were prepared in 0.5 mol L⁻¹ HNO₃. A single element solution was employed for Cr analyses by flame spectrometry because instability of the signals was verified if that analyte is included in the multielement solution [18]. Determination limits for the spectrochemical procedures were estimated from solutions containing the matrix components, i.e. simulating the composition of the solutions from each extraction step. Practical values were calculated as three times the IUPAC detection limit, defined as the ratio between three times the standard deviation of the blank signal (for $n = 10$) and the slope of the calibration line.

Atomic absorption measurements were performed with a Hitachi Z6100 Polarized Zeeman spectrometer, equipped with single element hollow-cathode lamps. The instrument was operated at maximum sensitivity with an air-acetylene flame. Analytical lines (nm) and determination limits ($\mu\text{g mL}^{-1}$) were: Cd 228.8/0.02; Pb 283.3/0.34; Zn 213.9/0.01 and Cr 359.3/0.1. A Shimadzu ICPS-1000 sequential plasma spectrometer was employed for atomic emission determinations. Operating RF power was 1.2 kW. A 12 mm ALC observation height was selected for the measurements, with the following argon gas flow rates (in L min⁻¹): plasma 14; auxiliary 1.2; nebulizer 1.0. Integration time was 5 s. Analytical wavelengths (nm) and instrumental determination limits ($\mu\text{g mL}^{-1}$) in solution for ICP were: Cd 226.57/0.01; Pb 220.42/0.15; Zn 213.92/0.01 and Cr 267.80/0.04.

A preliminary semiquantitative estimation of the total chemical composition of the samples was carried out by dc-arc atomic emission spectroscopy, employing a Jarrell-Ash Model 70.000, Ebert spectrograph. Plate calibration was performed with Spex G standards. A Siemens model D5000 diffractometer was employed for X-ray diffraction analysis. Radiation was from Cu at 1.5406 Å (graphite filter). Petrographic studies of samples PG-1 and PG-2 were performed by optical microscopy. The materials were suspended in nitrobenzene for microscopic observation.



Fig. 1 Geographical location of the sampling sites

2.2 Collection and pretreatment of samples. The samples studied were collected in the estuary zone of Bahía Blanca, a city located at the southern coast of the Buenos Aires province, in Argentina. The zone comprises an estuary that is fed by several channels and is characterized by the presence of fine sand, silt and clay surface

sediments. The coastal-marine zone hosts many ports and towns, with a population number of about 300000. The area receives the discharge of several streams and the run-off water from an agricultural area (4200 km²) as well as the input of municipal wastewater and direct industrial discharges. The two surface sediments (designated PG-1 and PG-2) selected for this study correspond to the Puerto Galván zone. The sampling area, located at 38° 46' S, 68° 18' W, is depicted in Fig. 1. Sampling sites are separated by a distance of about 700 m, and differ regarding their proximity to an industrial complex. Sample PG-2 is relatively closer to waste discharges.

The sample mass collected in each case was about 500 g. Sub-samples of the material were oven-dried at 50 °C during 24 h and sieved (250 mesh). The lower particle size fraction was homogenized by grinding in an agate mortar and stored in plastic bottles, which were kept refrigerated until the sequential leaching analyses were carried out.

2.3 Procedures. The successive chemical extraction steps involved in the sequential procedure employed are summarized in the flow-charts presented in Figs. 2 and 3. All the operations were carried out in 50 mL polypropylene centrifuge tubes provided with screw stoppers. The initial mass of sediment was 2.000 ± 0.001 g. The extracts were separated from the solid residue by centrifugation at 3000 rpm for 30 min. The residue was washed with water and the washings discarded before continuing the extraction sequence. The final solution volume was 25 mL. An additional fil-

Fig. 2 Flow chart of the Tessier sequential extraction scheme

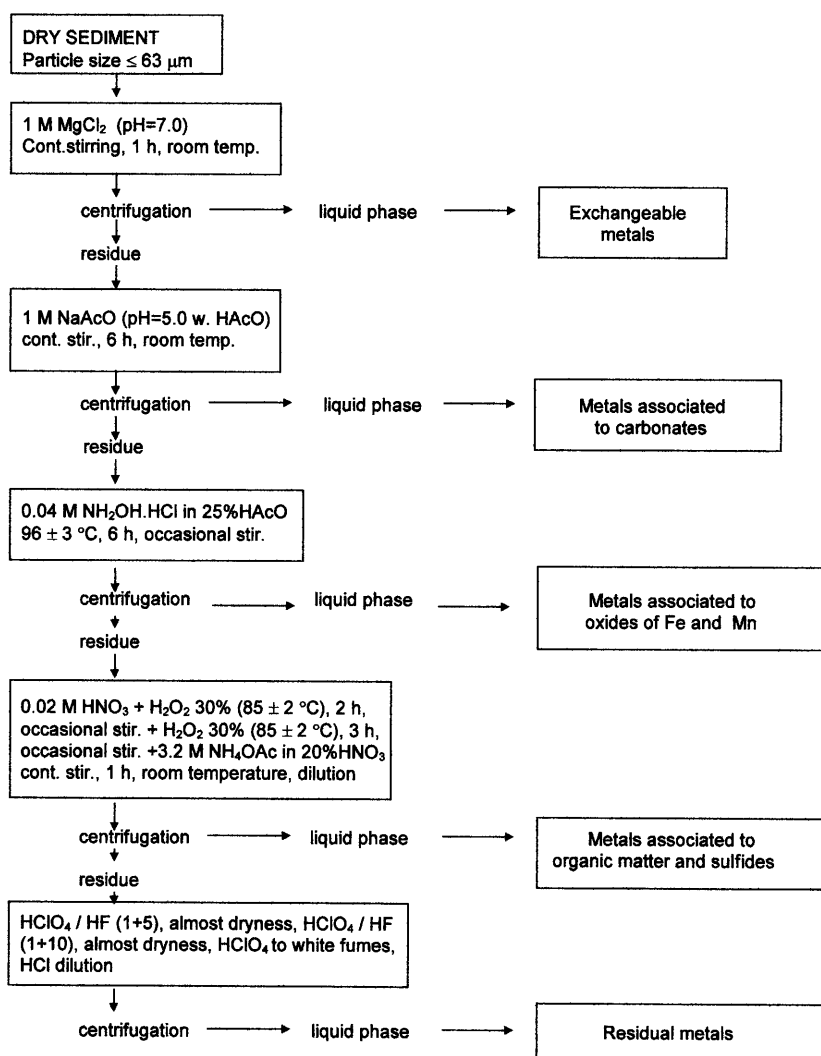
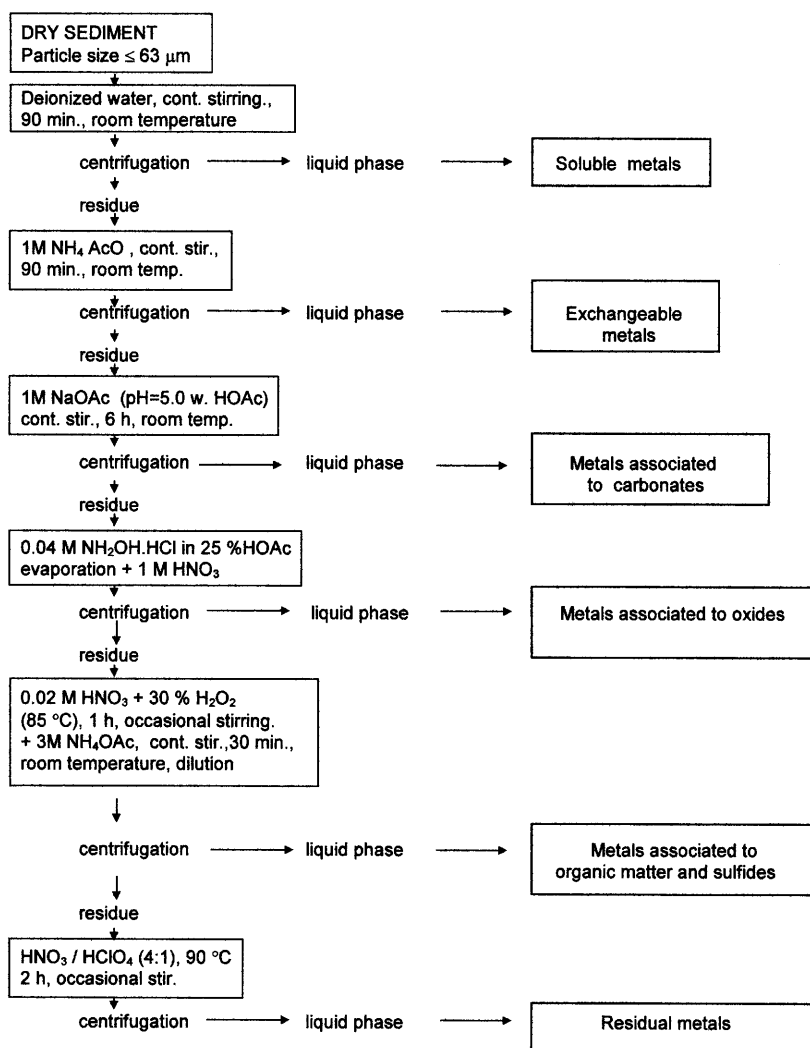


Fig. 3 Flow chart of the Grimalt sequential extraction scheme



tration step through Millipore 0.45 μm filter was introduced, in order to prevent the ICP nebulizer from blocking with microparticles potentially remaining in suspension. Analytical determinations were carried out on six independent replicates for both samples PG1 and PG2. Blanks were run simultaneously at all stages of the procedure. Only blank values below the instrumental limits of detection were considered acceptable.

For total metal measurements, dried sediment samples (1.000 ± 0.001 g) were digested as described in [4] in a PTFE container with 12 mL of (1 + 5) HClO_4/HF acid mixture, heating to near dryness. The process was repeated with 10 mL of a (1 + 10) mixture of the acids and the residue was treated with 2 mL of HClO_4 until white fumes. Redissolution of the residue was performed with 2 mL of conc. HCl, diluting with water to 25 mL. Sequential and total extractions were also performed on a certified reference material for trace elements (MURST-ISS-A1) provided by the Italian Research Program in Antarctica. This is a bottom sediment collected at a depth of 80 m.

3 Results and discussion

3.1 Bulk sample composition

A preliminary estimation of the bulk composition of surface sediment samples was performed by atomic emission spectrography. Semiquantitative results of the composition of both PG-1 and PG-2, obtained by dc-arc spectrochemical analysis and listed in Table 1, were similar. The four elements considered in this study appear as trace components. Major component concentrations (Si, Al, Fe, Ca, Mg and Ti) suggest, besides the obvious presence of silica, other silicoaluminates minerals, as well as the presence of iron oxides, and to a lesser extent, titanium containing mineral phases. The information on element composition was useful for the design of appropriate atomic

Table 1 Semiquantitative emission spectrographic analysis of PG-1 and PG-2 samples

Elements	Si, Al, Fe, Ca, Mg	Ti	Mn	Cu	Zn	Cd, Pb	Cr
% w/w	> 3	$\cong 3$	$\cong 0.03$	0.01–0.03	< 0.03	< 0.01	< 0.003

Table 2 Partition of metals among the different forms (Tessier method)

Fraction	$\mu\text{g/g} (\pm \text{SD})$																	
	PG-1						PG-2						MURST					
	Pb	Zn	Cd	Cr	Pb	Zn	Cd	Cr	Pb	Zn	Cd	Cr	Pb	Zn	Cd	Cr		
Exchangeable	< 2	< 0.2	0.55 \pm 0.03	< 0.5	< 2	0.50 \pm 0.02	0.63 \pm 0.05	< 0.5	< 2	0.84 \pm 0.04	0.57 \pm 0.03	< 0.5	< 2	4.2 \pm 0.2	< 0.15	< 0.5		
Bound carbonates	6.8 \pm 0.4	13.3 \pm 0.6	0.62 \pm 0.03	< 0.5	< 2	162 \pm 6	< 0.15	< 0.5	< 2	1.55 \pm 0.7	< 0.15	< 0.5	< 2	4.7 \pm 0.2	< 0.15	< 0.5		
Bound oxides	35.3 \pm 2.1	55.3 \pm 3.1	0.80 \pm 0.04	1.71 \pm 0.07	7.4 \pm 0.3	255 \pm 4	0.25 \pm 0.1	9.7 \pm 0.3	< 2	1.55 \pm 0.7	< 0.15	< 0.5	< 2	4.7 \pm 0.2	< 0.15	1.6 \pm 0.1		
Bound organic matter	15.1 \pm 2.2	4.6 \pm 0.7	0.64 \pm 0.03	< 0.5	9.7 \pm 0.4	81 \pm 5	< 0.15	6.6 \pm 0.1	< 2	4.7 \pm 0.2	< 0.15	< 0.5	< 2	4.7 \pm 0.2	< 0.15	1.6 \pm 0.1		
Residual	14.5 \pm 1.2	22.9 \pm 2.3	0.65 \pm 0.4	4.3 \pm 0.2	5.5 \pm 0.3	32 \pm 1	0.26 \pm 0.02	16.6 \pm 0.5	17.3 \pm 0.5	39.4 \pm 0.7	< 0.15	< 0.5	17.3 \pm 0.5	39.4 \pm 0.7	< 0.15	42.2 \pm 0.6		

Table 3 Partition of metals among the different forms (Grimalt method)

Fraction	$\mu\text{g/g} (\pm \text{SD})$																	
	PG-1						PG-2						MURST					
	Pb	Zn	Cd	Cr	Pb	Zn	Cd	Cr	Pb	Zn	Cd	Cr	Pb	Zn	Cd	Cr		
Soluble	< 2	< 0.2	< 0.15	< 0.5	< 2	0.60 \pm 0.08	< 0.15	< 0.5	< 2	0.27 \pm 0.02	< 0.15	< 0.5	< 2	0.71 \pm 0.05	0.49 \pm 0.03	< 0.5		
Exchangeable	< 2	< 0.2	0.32 \pm 0.03	< 0.5	< 2	18.9 \pm 1.1	< 0.15	< 0.5	< 2	4.0 \pm 0.1	< 0.15	< 0.5	< 2	4.2 \pm 0.1	< 0.15	< 0.5		
Bound carbonates	6.0 \pm 0.2	12.4 \pm 0.5	0.35 \pm 0.02	< 0.5	< 2	144 \pm 5	0.60 \pm 0.06	< 0.5	< 2	1.35 \pm 0.07	< 0.15	< 0.5	< 2	4.2 \pm 0.1	< 0.15	1.41 \pm 0.05		
Bound oxides	32.8 \pm 0.8	52.8 \pm 0.3	0.64 \pm 0.03	1.7 \pm 0.1	6.2 \pm 0.2	233 \pm 8	0.35 \pm 0.04	9.2 \pm 0.2	< 2	1.35 \pm 0.07	< 0.15	< 0.5	< 2	4.2 \pm 0.1	< 0.15	1.41 \pm 0.05		
Bound organic matter	17.9 \pm 0.5	6.8 \pm 0.4	0.60 \pm 0.02	< 0.5	12.7 \pm 0.6	90 \pm 5	< 0.15	10.6 \pm 0.3	< 2	4.2 \pm 0.1	< 0.15	< 0.5	< 2	4.2 \pm 0.1	< 0.15	1.41 \pm 0.05		
Residual	10.0 \pm 0.2	16.5 \pm 0.4	0.27 \pm 0.02	2.0 \pm 0.1	4.4 \pm 0.1	11.7 \pm 0.8	< 0.15	7.1 \pm 0.3	11.2 \pm 0.2	19.2 \pm 0.5	< 0.15	< 0.5	11.2 \pm 0.2	19.2 \pm 0.5	< 0.15	19.4 \pm 0.3		

flame and ICP spectroanalytical determination procedures employed. Co-extraction of elements in the leaching solutions may be a source of error due to inter-element interference effects. Analyte spiked samples of the digests, equivalent to sediment concentrations of 25 mg kg⁻¹ and 50 mg kg⁻¹, were employed to evaluate possible matrix and inter-element interferences. No significant effects (i.e. changes higher than ± 5% relative) were observed at the concentration levels tested.

3.2 Comparison of the leaching procedures

The results from the applied sequential leaching procedures, expressed on dry sample basis, are summarized in Tables 2 and 3. Repeatability is indicated as ± one standard deviation ($n = 6$). The minimum detectable concentrations reported are those obtained by plasma spectrometry. Because differences between element concentration values obtained by ZC-FAAS or ICP-AES were not significant at the 95% probability level, most of the results reported were obtained by the first technique. Precision of ICP-AES signals was relatively poorer in the case of the ammonium containing extracts (i.e. iron and manganese oxides fraction). A graphical depiction of distribution patterns as bar charts showing the proportions of elements associated with each of the defined forms is presented in Figs. 4 and 5.

Considering that the applied sequential schemes include a considerable number of manipulations, the resulting precision may be considered in general very good. Average values of RSD % corresponding to each given fraction and calculated for all the elements giving concentrations higher than the determination limits were compared. It was found that, apart from a relatively low precision for the soluble Grimalt's fraction that is detectable only in the PG-2 and MURST samples, most of the RSD's fell in the 2–8 % range. Larger departures were also observed for the organic matter fraction (12% average) in sediment PG-1 with the Tessier method and for the exchangeable fraction (9.9% average) in the same sample leached with the Gri-

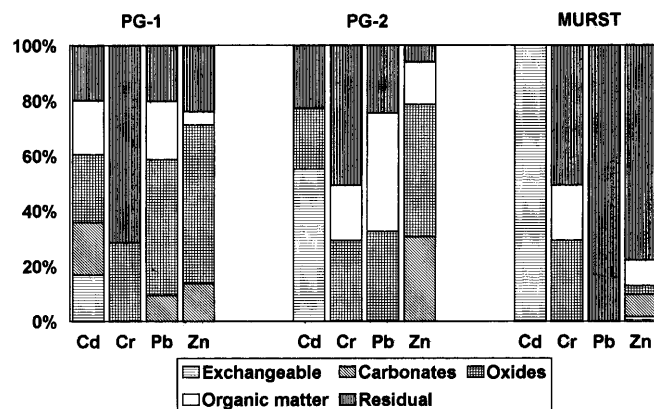


Fig. 4 Distribution of metals among the different phases obtained by the five steps procedure (Tessier)

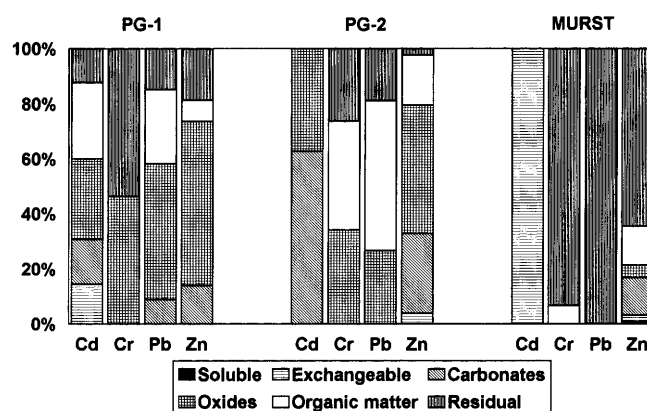


Fig. 5 Distribution of metals among the different phases obtained by the six steps procedure (Grimalt)

mal procedure. In addition, in the case of that sediment sample, nine tenths of the RSD values were similar or higher than the RSDs obtained for the MURST CRM sample, for both extraction schemes. The trend is not so well defined for the analyses performed on sample PG-2, for which identical proportions of RSD values are higher or lower than those measured with the MURST standard sample. A higher homogeneity of the reference material could be a possible explanation of these results, particularly in the case of sample PG-1. The total RSD (RSD_{tot}) can be considered as a convolution of three principal terms affecting repeatability, and expressed as:

$$RSD_{tot} = [(RSD_{extr})^2 + (RSD_{instr})^2 + (RSD_{heter})^2]^{1/2}$$

where:

RSD_{extr} corresponds to random contamination or losses of analyte, produced during the successive extraction stages; RSD_{instr} is determined by the repeatability of the instrumental measurement step; and

RSD_{heter} arises from variations originating from the possible non-homogeneity of the sample due to inadequate pretreatment of the solid.

The contribution from sample heterogeneity may be considered, in principle, non-significant for the reference sample due to the careful preparation reported for this material [23]. The instrumental variability of the spectroanalytical procedures employed is estimated to be not higher than 1% relative. Consequently, by considering a maximum RSD_{tot} value of 6% for that material, an average contribution from the chemical operations performed through the multiple extraction stages lower than 5.9% is expected. Thus, the contributions in excess arising for non-homogeneity of sample PG-1 are estimated to be (in average) about 10% for the organic matter phase (Tessier) and 7.8% for the exchangeable fraction (Grimalt). Because the experimental precision depends not only upon the care taken in performing the multiple extraction steps and the instrumental calibration and measurement, but also on the homogeneity of the treated material, these results are not unexpected [7].

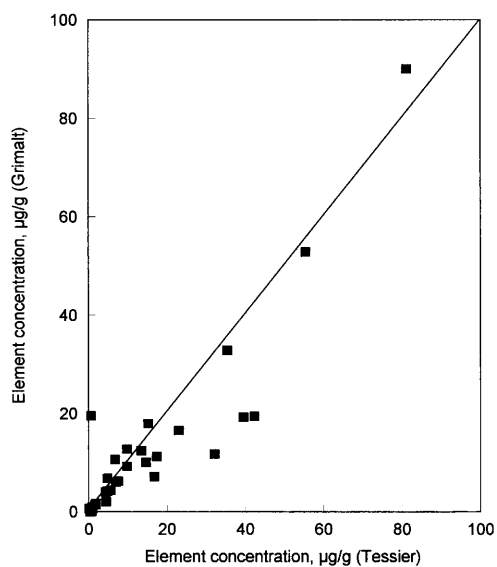


Fig. 6 Scatter plot of element concentrations obtained by both tested procedures (values higher than 100 $\mu\text{g/g}$ have not been included for clarity)

An overall consideration of the results presented in Tables 2 and 3 allows to conclude that acceptable correlation exists between both Tessier and Grimalt sequential methods for many elements and phases. Nevertheless, significant relative differences are apparent in some cases. A close scrutiny of the tables shows that differences are more noticeable for sample PG-2 in the Grimalt procedure. With this method a concentration of Zn similar to that obtained in the exchangeable fraction for the Tessier scheme was found in the soluble form, suggesting the presence of soluble metal in the interstitial water. However, a relatively larger concentration of the same element was measured in the exchangeable Grimalt fraction. Besides, no Cd was detected in the soluble/exchangeable Grimalt fractions of PG-2, but a relatively significant amount of element appears associated with carbonates. Instead, Cd was not detected in the bound to carbonates fraction of the Tessier procedure. These apparent inconsistencies remain unexplained.

Another more consistent departure occurs for elements associated with the residual phases. In some cases the differences are higher than 100% relative. These are the cases of Cr in sample PG-2 and Zn and Cr in the MURST reference sample. The statistical significance of this situation can be evaluated by means of a scatter plot of all metal concentrations obtained for all the considered phases by the Grimalt method vs. those resulting from the application of the Tessier scheme. The plot is presented in Fig. 6. In the case of Zn the concentrations from steps 1 and 2 of Grimalt were added and plotted vs. the concentrations from step 1 of the Tessier scheme. A linear model was fitted through the points by means of least squares procedure. A slope of 1.00 (shown as a solid line in Fig. 6) would indicate complete correlation. The calculated slope was 0.904 ± 0.021 , with a correlation coefficient (r^2) of

0.9881. The lower slope value reflects the trend of the Grimalt method to give lower results than Tessier's, probably due to the contribution of the points from residual phases. A further application of the Student's test to the fitted line population showed that the calculated slope differs significantly from the ideal slope of 1.00 at the 99.5% probability level (t , calculated = 4.57; t , tabulated [for $v = n-2 = 37$] = 2.7).

A rigorous validation of the complete sequential methods through assessment of accuracy was not possible because standard reference materials certified regarding the phase dependent composition were not available to us. It must be mentioned, however, that several sediments and soils have been recently certified, or the results of inter-laboratory comparisons published. Hall et al. [7] reported a detailed study of ten SRMs, based on a five steps sequential extraction scheme. In particular the already mentioned BCR procedure was applied to the certification of lake sediment BCR CRM 601, available from the European Standards, Measurements and Testing Program since 1997. This sample has also been employed to evaluate possible improvements in that procedure [24]. Other similar materials certified regarding standardized single and sequential extraction procedures include sewage sludge-amended soil (CRM 483), terra rossa soil (CRM 484) and calcareous soil (CRM 600) [16, 17].

Comparison between total concentrations obtained by an independent procedure (strong acid attack) and the sum of the individual concentrations in the fractions offers an alternative path to check for possible systematic errors arising from element losses, contamination or other undetermined causes during the numerous manipulations carried out in the course of chemical extractions. For the determination of total metal concentrations we applied a strong HF/HClO_4 attack on the sample, which is usually sufficient to solubilize most of the metals, even those included in the very stable, crystalline lattices of the mineralogical phases. Validation of the method was performed by similar analysis of the certified reference material (CRM). Obtained and reference concentration values have been included in Table 4. Acceptable agreement between the limits of experimental errors was generally achieved for the CRM. It must be mentioned, however, that this result is only a first approach to verify the general aptitude of the total digestion/dissolution procedure, because the mineral composition of the Antarctic sediment differs from that of the surface sediments studied.

A comparison of total metal concentrations and sum of fractions for both sequential leaching methods is shown in Table 4. Recovery is defined as $100 \times (\Sigma \text{ of fractions} / (\text{determined total concentration}))$. The degree of significance of differences in recoveries can be inferred from their estimated uncertainties, calculated from random error propagation. Generally good recoveries are achieved with the Tessier procedure. The lower value is $(87 \pm 7) \%$ for Cr in the PG-1 sample. This sample presents the lower concentration of that element. The highest recovery $(106 \pm 6) \%$ is observed for Cd in the CRM. With the Grimalt method, lower recoveries were found for Cr in the three samples

Table 4 Comparison between total metal concentrations and the sum of fractions

Sample		$\mu\text{g/g} (\pm \text{SD})^a$				
		Pb	Zn	Cd	Cr	
PG-1	Total Concentration		79.3 \pm 3.3	107 \pm 4	3.1 \pm 0.2	6.9 \pm 0.5
	Σ fractions	Tessier	71.7 \pm 3.3	96.1 \pm 3.9	3.26 \pm 0.08	6.0 \pm 0.2
		Grimalt	66.7 \pm 1.0	88.5 \pm 0.8	2.18 \pm 0.06	3.7 \pm 0.2
	% Recovery	Tessier	90.4 \pm 5.6	89.8 \pm 5.0	105.2 \pm 7.3	87.0 \pm 6.9
		Grimalt	84.1 \pm 3.7	82.7 \pm 3.2	70.3 \pm 4.9	53.6 \pm 4.8
PG-2	Total Concentration		23.2 \pm 0.9	507 \pm 15	1.16 \pm 0.03	36.2 \pm 1.1
	Σ fractions	Tessier	22.6 \pm 0.6	531 \pm 9	1.14 \pm 0.04	32.9 \pm 0.5
		Grimalt	23.3 \pm 0.6	498 \pm 11	0.95 \pm 0.07	26.9 \pm 0.5
	% Recovery	Tessier	97.4 \pm 4.6	104.7 \pm 3.6	98.3 \pm 4.3	90.9 \pm 3.1
		Grimalt	100.4 \pm 4.7	98.2 \pm 3.6	81.9 \pm 6.4	74.3 \pm 2.6
MURST-ISS-A1	Total Concentration		18.8 \pm 0.7	51.3 \pm 0.7	0.54 \pm 0.01	45.4 \pm 0.7
	Σ fractions	Tessier	17.3 \pm 0.5	50.7 \pm 0.8	0.57 \pm 0.03	43.9 \pm 0.7
		Grimalt	11.2 \pm 0.2	29.7 \pm 0.5	0.49 \pm 0.03	20.8 \pm 0.3
	% Recovery	Tessier	92.0 \pm 4.3	98.8 \pm 2.1	105.6 \pm 5.9	96.7 \pm 2.1
		Grimalt	59.8 \pm 2.5	57.9 \pm 1.3	90.7 \pm 5.8	45.8 \pm 1.0
	Certified Value ^b		21.0 \pm 2.1	51.9 \pm 3.2	0.54 \pm 0.02	42.1 \pm 2.5

^aNumber of replicates: 6–9

^bValue \pm reported uncertainty

and for all the elements in the reference material, with the exception of Cd. For the elements in the residual fraction this last result, in agreement with the negative departures consistently observed with the Grimalt method from Tessier's, seems to indicate that for the materials studied the last extraction stage of the Grimalt scheme is unable to remove elements strongly fixed in the crystalline lattice. It must be remarked that no HF is employed in that step, preventing an exhaustive attack of the residue. Thus, it can be concluded that the Tessier scheme provides in this case a more complete and reliable fractioning of the metals studied.

It is worth mentioning that when the results are depicted on a percentage basis, such as in the bar diagrams of Figs. 4 and 5, the general trends of the distributions for both methods remain qualitatively similar. Only the discrepancies associated with Cd and Zn in sample PG-2 emerge from the graphical depiction.

3.3 Petrographic and X-ray characterization of the sediments

The surface sediment samples were characterized by petrographic microscopy and X-ray diffraction. Due to the complexity of the materials, it is difficult to univocally establish a correlation between the specific geochemical phases present and the proportions of elements associated with the various binding forms deduced from distribution patterns. However, the verification of the presence, for example, of mineral substrates able to readily adsorb/exchange metals (such as feldspars) as of others with a ten-

dency to specifically adsorb metals (such as carbonates) or belonging to the easily reducible group (iron oxides and hydroxides) would contribute to a more complete characterization of the sediments.

Early sedimentological surveys of sand deposits corresponding to the sampling zones reported that textural and mineralogical data indicate a genesis derived from pyroclastic and volcanic rocks [25–28]. The presence of light and heavy minerals as well as magnetite and ilmenite, in variable proportions depending upon the distance from the associated water body, was also reported. Major components among light species include quartz, volcanic glass and paste (basic andesite and basalt) and minerals of the feldspar series, being albite and potash feldspar the most common. Reported identified heavy phases include augite, hypersthene, hornblende, granate and opaque minerals.

Microscopic observation of particles from sample PG-1 suspended in nitrobenzene showed clearly distinguished feldspar grains, whose composition could not be optically defined due to intense alteration, dispersed in a matrix of very fine clay minerals. Average grain sizes of 150 μm were estimated for plagioclase minerals of intermediate composition (oligoclase-andesine). Other components are materials of volcanic origin (glass pastes), carbonate fragments, microcrystalline quartz and glauconite. A fraction of non-transparent minerals observed corresponds to the iron oxides and hydroxides group. Reduced amounts of turmaline and rutile are also present. A similar study carried out on sample PG-2 demonstrated the presence of a more abundant fine silt-clay fraction, also containing feldspar grains. Rock pastes of volcanic origin and

feldspars almost completely altered to secondary minerals, with rarely present fresh components belonging to the plagioclase class, were found. Carbonate grains, principally arising from shell fragments, were identified. Quartz grains covered a size range from coarse sand to silt, and opaque iron oxide minerals were found to be present similarly as in sample PG-1. We did not attempt a petrographic study of the reference sample because of the very small size of the component particles.

Additional independent information on the component geochemical phases was obtained from X-ray diffraction diagrams. Due to the lack of sensitivity of the technique in the case of minor components, only major crystalline phases could be identified. Quartz, feldspars (such as albite / anorthite) and calcite were common to both surface sediment samples. A (Ca, Mg) silicate (braunite) in sample PG-1 and a Ca phosphate (brushite) in sample PG-2 were detected. Halite and minerals of the mica group (muscovite, phlogopite) together with quartz and albite in larger proportions were detected in the MURST reference material. Additionally, the presence of iron hydroxide group minerals, specifically goethite, in the three samples, could not be ruled out by the X-ray diffractometric analyses. The mineral composition of samples PG-1 and PG-2 agrees qualitatively with the element composition estimated by emission spectrography.

4 Conclusions

Results from the application of the Tessier sequential leaching scheme, summarized in Table 2 and Fig. 4, suggest noticeable differences among the studied materials, being more marked for the Antarctic sediment. The different origin of that sample (i.e. bottom sediment collected in a geographically differentiated area) should be in the first place an obvious explanation for that behavior. In addition, results might be affected by a lack of extractant selectivity, or by readsorption processes taking place on the remaining solid phases. These problems have been addressed by different authors [14, 15, 29], and were considered, at the present stage, out of the scope of our study. Bottom sediments are generally more complex than surface sediments, the first usually comprising detrital inorganic and organic substances, as well as products of diagenetic processes. In the case of the reference sample of the Antarctic sediment studied, aside from a relatively low proportion of Zn as exchangeable, Cd also appears totally present in the first extraction step, even considering that the total concentration in the material is very low. A possible explanation of this behavior may be the weak surface interaction existing between the Cd(II) in aqueous solution and some mineral phases such as those identified by X-ray diffractometry and petrography, as has been demonstrated by Farquhar et al. [30]. These authors also found that Pb(II) is strongly held by interaction with the mineral substrates albite and muscovite, which is consistent with the measured proportion of the metal in the residual phase of the Antarctic sediment.

Regarding total concentrations in surface samples, it was observed that total concentrations of Pb and Cd are higher in sample PG-1 than in PG-2, and that the inverse is true for Zn and Cr. When the element partition is considered, the exchangeable and residual fractions represent extreme situations regarding the potential influence of the binding forms of the elements on their mobility and availability by living organisms. The percentage of metals associated with easily exchangeable conditions is very low, with the exception of Cd. The fraction of Cd in that form is particularly significant in sample PG-2, suggesting a possible anthropogenic origin.

On the other hand, the residual phase of the surface sediment samples shows similar proportions of Pb and Cd, and variable amounts of Zn and Cr. In the Antarctic sediment, apart from the behavior of Cd already discussed, very significant proportions of the other metals are associated with the residual phase. In particular, Cr appears as more difficultly extractable from the three sediments. It is known that Cr³⁺ is readily substituted for Fe³⁺ in mineral structures, therefore requiring stronger conditions to be solubilized. Also, it is easily chemisorbed on oxides and silicate clays [31]. An important consequence is the reduced mobility of the Cr in the coastal sediments under changes in weathering conditions.

Both coastal sediment samples show measurable proportions of Pb and Zn bound to the organic form. In addition, about 20% of Cr appears associated with that phase in the PG-2 sample. The strong complexation properties of Cr³⁺ with organic matter is an effect already observed in soils [31]. On the whole, the organic matter phase as contaminant collector seems more important in that sample. Further studies regarding the proportion and characteristics of the present organic matter will be required to unambiguously associate those observations with neighboring industrial activities.

Regarding the remaining phases, the presence of carbonate type minerals is consistent with the proportions of metals associated with that form. Zn appears as more conspicuously bound to carbonates in the three samples, but no Cr is observed in that binding form. Besides, the bound to oxides / bound to carbonates ratio for Zn differs between samples, being 4.2 and 1.6 for samples PG-1 and PG-2, respectively. This suggests that a higher relative proportion of Zn may be readily available from sample PG-2, by example, under low pH conditions. Finally, significant fractions of the four metals appear as bound to oxides, in agreement with the occurrence of minerals of the iron oxide group observed by petrography and X-ray diffraction.

Although similarities in the distribution patterns resulting from both sequential leaching schemes were observed, the Tessier procedure seems to be more suitable for a complete characterization of the metal fractionation in the surface sediments studied and in the material of certified total concentration employed as reference. The principal limitation of the presented study as it has been carried out is the limited traceability of the tested sequential schemes, considering that no suitable CRM of known

fractionation characteristics was employed for that purpose. However, as previously described, the agreement between total concentrations and the acceptable recoveries obtained by comparison of these values with the sum of fractions could be considered a first approach in that direction.

Finally, the primary aim of this work was to test and evaluate metal fractionation methodologies required to face further sedimentological studies of a wider scope, i.e. on an extended coastal region possibly exposed to contamination of anthropogenic origin. These studies are intended to complement previous results reported for nearby areas [32], and are warranted by the fact that significant proportions of toxic metals, with the exception of Cr, were found in easily mobile forms. This could be considered as an indication of an anthropogenic input of metal contaminants into the estuary.

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References

- Chao TT (1984) *J Geochem Explor* 20: 101–135
- Hall GEM (1997) *J Geochem Explor* 61: 1–19
- Walter E, Calmano W, Mangold S, Tröger L (1999) *Fresenius J Anal Chem* 364: 238–244
- Tessier A, Campbell PGC, Bisson M (1979) *Anal Chem* 51: 844–851
- Grimalt JO (1989) Sampling, sample handling, and operational methods for the analysis of trace pollutants in the marine environment. In: Albaiges J (ed) *Marine pollution, Hemisphere, New York*, pp 258
- Gupta SK, Chen KY (1975) *Environ Lett* 10: 129–158
- Hall GEM, Gauthier G, Pelchat J-C, Pelchat P, Vaive JE (1996) *J Anal Atom Spectrom* 11: 787–796
- Quevauvillier P, Rauret G, Rubio R, López Sánchez JF, Ure A, Bacon J, Muntau H (1997) *Fresenius J Anal Chem* 357: 611–618
- Sahuquillo A, López-Sánchez JF, Rubio R, Rauret G (1995) *Mikrochim Acta* 119: 251–258
- Voutsinou-Taliadouri F (1995) *Mikrochim Acta* 119: 243–249
- Marr IL, Kluge P, Main L, Margerin V, Lescop C (1995) *Mikrochim Acta* 119: 219–232
- Twardowska I, Kyzioł J (1996) *Fresenius J Anal Chem* 354: 580–586
- Hlavay J, Polyák I, Bódog I, Molnár À, Mészáros E (1996) *Fresenius J Anal Chem* 354: 227–2326
- Kheboian C, Bauer CF (1987) *Anal Chem* 59: 1417–1423
- Belzile N, Laconte P, Tessier A (1989) *Environ Sci Technol* 23: 1015–1020
- Davidson CM, Thomas RP, McVey SE, Perala R, Littlejohn D, Ure AM (1994) *Anal Chim Acta* 291: 277–286
- Quevauvillier Ph (1998) *Trends Anal Chem* 17: 289–298, 17: 632–642
- Thomas RP, Rue AM, Davidson CM, Littlejohn D, Rauret G, Rubio R, López-Sánchez JF (1994) *Anal Chim Acta* 286: 423–429
- Rauret G, Rubio R, López Sánchez JF (1989) *Intern J Environ Anal Chem* 36: 69–83
- Campanella L, Dórazio D, Petronio BM, Pietrantonio E (1995) *Anal Chim Acta* 309: 387–393
- Li X, Coles BJ, Ramsey M, Thornton I (1995) *Analyst* 120: 1451–1419
- Howe SE, Davidson CM, McCartney M (1999) *J Anal Atom Spectrom* 14: 163–168
- Italian Research Program in Antarctica (updated December 1996) MURST-ISS-A1 Antarctic marine sediment certified reference material for trace elements
- Sahuquillo A, López Sánchez JF, Rubio R, Rauret G, Thomas RP, Davidson CM, Ure AM (1999) *Anal Chim Acta* 382: 317–327
- Teruggi ME (1959) LEMIT Report, La Plata, Provincia de Buenos Aires, Argentina, Serie II, N° 77
- Teruggi ME (1964) LEMIT Report, La Plata, Provincia de Buenos Aires, Argentina, Serie II, N° 81
- Angelelli V, Chaar E (1964) CNEA Report 122, Buenos Aires, Argentina
- Angelelli V, Chaar E (1967) CNEA Report 210, Buenos Aires, Argentina
- Tessier A, Campbell PCG (1988) Partitioning of trace metals in sediments. In: Kramer JR, Allen HE (eds) *Metal speciation: Theory, analysis and application*. Lewis Publishers, Chelsea, pp 183–199
- Farquhar ML, Vaughan DJ, Hughes CR, Charnock JM, England KER (1997) *Geochim Cosmochim Acta* 61: 3051–3064
- McBride MB (1994) *Environmental chemistry of soils*, Oxford University Press, New York, pp 331
- Ferrer L, Marcovecchio J, Pucci A (1996) Geochemical partitioning of chromium, zinc and manganese in surface sediments from Bahía Blanca estuary in Argentina. *Proceedings of International Conference on Pollution Processes in Coastal Environments, Mar del Plata, Argentina*, pp 238–242