

This article was downloaded by:

On: 17 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

Optimization of a Sequential Extraction Scheme for the Characterization of Heavy Metal Mobility in Iron Oxide Rich Sediments

José L. Gómez-Ariza^a; Inmaculada Giráldez^a; Daniel Sánchez-Rodas^a; Emilio Morales^a

^a Departamento de Química y Ciencia de los Materiales, Escuela Politécnica Superior, Universidad de Huelva, La Rábida, Huelva, Spain

To cite this Article Gómez-Ariza, José L. , Giráldez, Inmaculada , Sánchez-Rodas, Daniel and Morales, Emilio(1999) 'Optimization of a Sequential Extraction Scheme for the Characterization of Heavy Metal Mobility in Iron Oxide Rich Sediments', *International Journal of Environmental Analytical Chemistry*, 75: 1, 3 — 18

To link to this Article: DOI: 10.1080/03067319908047296

URL: <http://dx.doi.org/10.1080/03067319908047296>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

OPTIMIZATION OF A SEQUENTIAL EXTRACTION SCHEME FOR THE CHARACTERIZATION OF HEAVY METAL MOBILITY IN IRON OXIDE RICH SEDIMENTS

JOSÉ L. GÓMEZ-ARIZA*, INMACULADA GIRÁLDEZ,
DANIEL SÁNCHEZ-RODAS and EMILIO MORALES

*Departamento de Química y Ciencia de los Materiales, Escuela Politécnica Superior,
Universidad de Huelva, 21819 La Rábida, Huelva, Spain*

(Received 6 November 1998; In final form 23 April 1999)

Several parameters governing the extraction of metals from iron oxide rich sediments, using sequential extraction schemes were optimized. The mode of shaking, soil/extractant ratio and concentrations of $MgCl_2$ and $NH_2OH \cdot HCl$, for samples collected in the Odiel Marshes Natural Park (SW Spain), were considered. The concentration of $NH_2OH \cdot HCl$ deserved particular attention due to the nature of the studied sediments. A 0.4 M concentration of this extractant was needed to avoid readsorption of Cu and As in the samples. In addition, readsorption processes were studied using a candidate to reference material with a high organic matter content that was previously analyzed in an interlaboratory study.

Keywords: Sequential extraction; metals; marshes; readsorption

INTRODUCTION

Sediments are complex mixtures of mineral components which sometimes contain polluting chemical species bound to the matrix. Sediments of estuarine origin are in continuous equilibria with the aqueous column receiving inputs from both dissolved and non dissolved pollutants (adsorbed on suspended particles). Bioavailability of toxic metals and their interactions with water are strongly depending on their chemical form in the sediment. Therefore, the evaluation of trace metal associations with the major mineral components of the solid matrix,

* Corresponding author. Fax: +34-959-350311. E-mail: ariza@uhu.es

such as clays, carbonates, hydrous oxides of iron and manganese, and organic matter is of great interest.

In order to assess the mobility of heavy metals in sediments, various sequential extraction protocols have been developed using different reagents in a number of steps [1-3], the scheme proposed by Tessier *et al.* [4] being the most widely used. The specificity and reproducibility of the methods greatly depend upon the chemical properties of the element and the chemical composition of the sample. The results are influenced by experimental factors such as the sampling and sample preservation techniques [5], the choice of reagents, the extraction sequence, the contact time with the particulate material and the soil/extractant ratio [6,7]. Sequential extractions have been criticized [8] due to their "operational" character. Moreover, several problems associated to the use of this approach such as the specificity of the reagents and the release, redistribution and readsorption of the elements have also been considered in some studies, concluding that any scheme must be checked for each particular sample [9-13].

In this paper, the Odiel Marshes Natural Park (located SW of Spain, on the Atlantic coast) was considered as study area, in order to obtain a sequential extraction scheme suitable to the characteristics of the sedimentary samples in this area, particularly enriched in iron oxide.

The Park is placed in the junction of the Tinto and Odiel Rivers, and is rather polluted because of the effects from both the acid mine drainage (mainly Cu, Zn, Cd and Pb) and the disposal of industrial processing wastes (providing inputs of As) [14].

EXPERIMENTAL

Reagents and apparatus

All reagents were analytical grade or Suprapur quality (Merck, Darmstadt, Germany). Stock standard solutions were purchased from Merck and working solutions were daily prepared in 5% HNO₃. Milli-Q (Millipore, Bedford, MA, USA) was used in all the experiments. Cleaning of plastic and glassware was carried out by soaking in 14% (v/v) HNO₃ for 24 h and then rinsed with water.

Atomic absorption measurements were carried out using a Perkin-Elmer AAS (model 2380, Ontario, Canada) with double beam and background corrector. Hollow cathode lamps were used as radiation sources (Photron, Victoria, Australia). Either air-acetylene, nitrous oxide-acetylene flames or graphite furnace (Perkin-Elmer HGA-300) were used for sample atomization. The Hg and As analysis were carried out by means cold vapour (CV)-AAS and hydride genera-

tion (HG)-AAS (Perkin-Elmer MHS-10), respectively. Quantitative analysis of mercury and arsenic was achieved by standard addition at three different levels (doing duplicates for each level), whereas the quantifying of other metals was achieved with appropriate calibration curves obtained with the metals added to solutions containing either the reactants used for the extractions (sediment extracts) or the acid mixture used for digestion. Matrix did not have any influence on the measurements as was observed using standard additions for each metal in all the extracts. Organic matter was measured using molecular absorption measurements (UNICAM UV/VIS spectrometer, model 5625, Cambridge, UK). Two shaking systems were used, a home made end-over-end (40 rpm) and a vertical vibrator (Selecta Vibromatic, model 384, Barcelona, Spain).

Sample collection

The seven intertidal surface sediment samples (5 cm depth) used in the experiments were collected from the Odiel Marshes Natural Park (Figure 1, sampling stations from 1 to 7) using a plastic scoop and transferred to 1 l polypropylene containers. The samples were chosen to represent different types of sediments of the study area according to their contents of carbonates, Fe and Mn oxides, organic matter and particle-size distribution, as well as their spatial distribution. In the laboratory, the samples were dried at room temperature (22–25°C), mildly ground with a wooden roller to pass through a 2-mm sieve, homogenized and stored at 4°C in polypropylene until analysis.

Analytical procedures

Particle-size distribution was performed using the Bouyoucos hydrometer method [15]. Major components were determined after digestion of portions of 0.2 g (dry weight) of sediment using 20 ml of a 10/3/2/5 HF/HNO₃/HCl/HClO₄ mixture in air open teflon vessels, heating at 130°C just to dryness. This procedure was repeated a second time, and the residue was dissolved in 10 ml of 50% (v/v) HNO₃/H₂O, transferred to a 100 ml volumetric flask and diluted up to the mark with water. The concentrations of Fe, Mn, Ca and Mg were determined using an air-acetylene FAAS. Al and Ti were estimated using a nitrous oxide-acetylene FAAS device and Na and K using air-acetylene atomic emission. La₂O₃ solution was used as matrix modifier for Ca, Mg, Na, K and Al determinations. Phosphorus was determined by molybdate blue spectrophotometric method [16]. Silica analysis was performed after fusion at 400°C with NaOH of 0.1 g of sediment, redissolved in hot water and determination using the molyb-

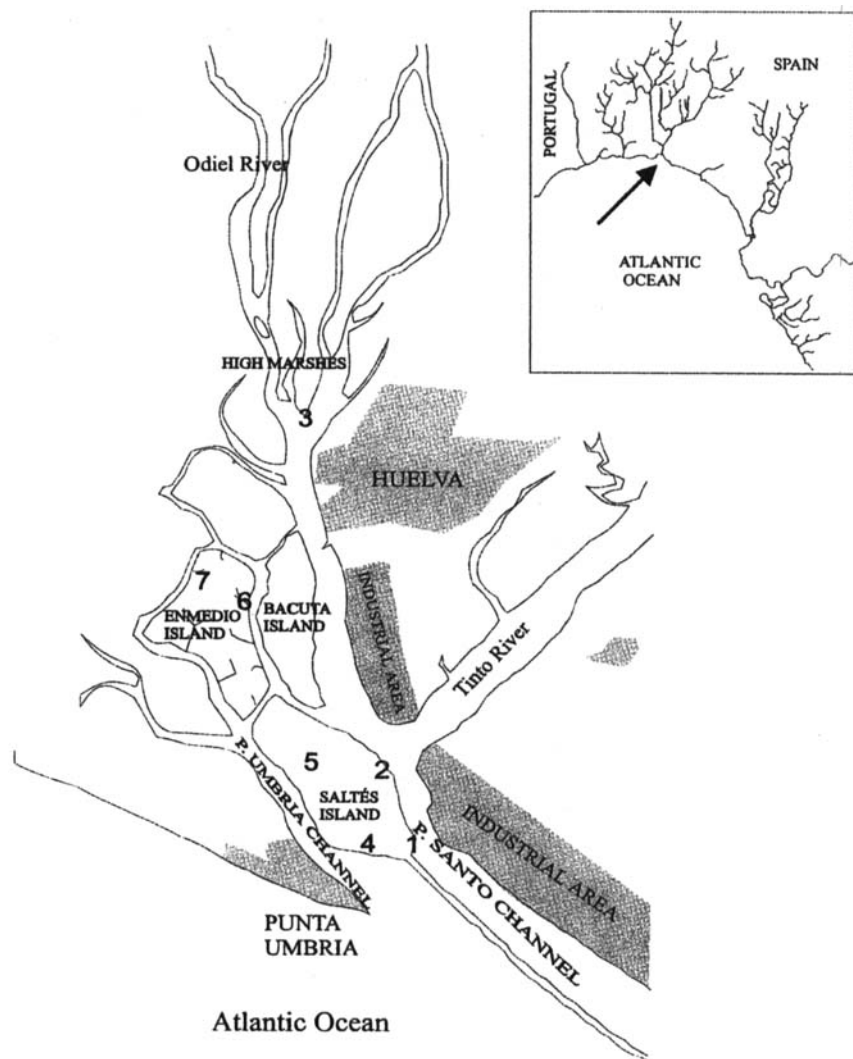


FIGURE 1 Map of the study area showing the sampling sites, numbered from 1 to 7. These numbers also correspond to the samples under study

date spectrophotometric method^[16]. Loss of ignition (LOI) was obtained heating a portion of 1 g of sample in a furnace at 900°C for 4 h^[15].

Carbonate content was determined with a Bernard calcimeter (volumetric measurement of the CO₂)^[15]. Organic matter was estimated by oxidation with an excess of potassium dichromate and back-titration with a standardized solu-

tion of Fe(II) ^[15]. Results are expressed as percentage of oxidizable organic matter (OM).

Table I summarizes the sequential extraction procedure used in this study, which was conducted in centrifuge tubes (polyethylene, 50 ml) stoppered with a screw cap. Between each successive extraction, separation was effected by centrifugation (SIGMA 4–10, Osteroder am Harz, Germany) at 10000 rpm for 10 min. The supernatant was decanted with a Pasteur pipet and stored at 4°C in stoppered polyethylene vessels until analysis, whereas the residue was washed with 8 ml of water. After centrifugation for 10 min. this second supernatant was discharged.

TABLE I Sequential extraction scheme for partitioning sediment samples (0.5 g sample)

<i>Fraction</i>	<i>Procedure</i>
Exchangeable (F1)	1M MgCl ₂ (8 ml), pH 7, 1 h. ca. 20°C, continuous agitation (end-over-end, 40 rpm)
Carbonate (F2)	1 M NaOAc (8 ml), pH 5, 5 h, ca. 20°C, continuous agitation (end-over-end, 40 rpm)
Fe-Mn oxide (F3)	0.4 M NH ₂ OH·HCl in 25 % acetic acid (20 ml), 6 h, 96°C, manual shaking every 30 min
Organic (F4)	0.02 M HNO ₃ (3 ml) + 30% H ₂ O ₂ (5 ml), pH 2, 2h, 85°C, manual shaking every 30 min; further 30% H ₂ O ₂ (3 ml), pH 2, 3 h, 85°C, manual shaking every 30 min; then 3.2 M NH ₄ OAc in 20 % HNO ₃ (5 ml). 0.5 h, ca. 20°C, continuous agitation (end-over-end, 40 rpm)
Residue (F5)	5/7.5/1 HF/HNO ₃ /HClO ₄ (13.5 ml), 5 h, 170°C

Analysis of both total metal content and residual elements (Table I) of the sediments were performed using a different digestion procedure than the one previously described for major components to allow the analysis of Hg and As. In this procedure 0.5 g of dry sample or the "residue" of the sequential extraction scheme treated with a 5/7.5/1 mixture of HF/HNO₃/HClO₄ in PTFE digesters, stoppered with PTFE screw caps and heated at 170°C for 5 h. After adding 2 g boric acid, the solution was transferred to a 25 ml volumetric flask and diluted up to the mark with water.

Quality control

Detection limits for each analyte in all the extractants are shown in Table II. The accuracy of the analytical procedures for total metal determinations (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) was checked with a certified reference material CRM-277 (estuarine sediment) provided by the BCR (Community Bureau of

Reference, Commission of the European Community). Replicate analysis of this CRM showed good accuracy, with all results comparable with certified values.

TABLE II AAS detection limits in sequential extraction reagents (mg kg^{-1} sediment dry mass); detection limits were calculated on the basis of 3s (blank solution)

<i>Fraction</i>	<i>As</i>	<i>Cd</i>	<i>Cr</i>	<i>Cu</i>	<i>Fe</i>	<i>Hg</i>	<i>Mn</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>
F1	0.02	0.5	3	2	3	0.006	3	0.3	4	0.01
F2	0.01	0.8	2	1	1	0.007	1	0.6	1	0.6
F3	0.02	0.002	0.04	8	5	0.05	2	0.1	9	1
F4	0.04	0.002	0.04	4	10	0.01	1	0.1	0.05	0.9
F5	0.03	0.002	3	2	9	0.01	2	1	5	0.09

Readsorption study of As and Cu during the sediment extraction with 0.04 M and 0.4 M $\text{NH}_2\text{OH}\cdot\text{HCl}\cdot\text{HOAc}$

The readsorption study was performed using the standard addition technique [13]. The experiments were designed to evaluate the importance of post-extraction readsorption of Cu and As using two concentrations of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in the third step of the sequential extraction scheme, under conditions similar to those normally found when such procedure is applied to natural sediments. Four sediments were selected for this study: three of them (named 2, 6 and 7) were collected from the study area and the fourth was a candidate to reference material (S12) [8] selected because of its high OM content (9.60 %).

Prior to the standard addition experiments, exchangeable and carbonate bound metals were extracted from the sediments and discharged. The resulting residues were then subjected to one of the two following treatments for each concentration of $\text{NH}_2\text{OH}\cdot\text{HCl}$:

- i. leaching with non-spiked extractant to determine the natural concentration of Cu and As in the "iron and manganese oxide" operational defined fraction (F3, Table I). The extractions served to establish the amount of each trace metal that had to be added as standard addition.
- ii. extraction with Cu and As spiked extractant, using a 100% of the amount of these elements evaluated in (i). Both trace metals were added as small volumes 50–200 μl) from stock solutions to the extraction reagent.

Finally, readsorption percentages were calculated as follows:

$$\% \text{ of readsorption} = \frac{(A+B-C)}{B} * 100$$

where B is the concentration ($\mu\text{g ml}^{-1}$) of the element added to the extractant in the treatment (ii), and A and C are the measured concentrations ($\mu\text{g ml}^{-1}$) of the element in the extracts obtained in treatment (i) and (ii), respectively.

Statistical analysis

The data were analyzed statistically using analysis of variance (ANOVA). Prior to analysis, all the data were tested for homogeneity of variance using the Barlett and Levene test. An α -value of 0.05 was adopted as the critical level for all statistical testing giving a 95% confidence level (CSS:STATISTICA™)

RESULTS

Optimization of the sequential extraction scheme

Data for total organic carbon and carbonate contents, particle-size distribution and chemical analysis of the sediments used for the sequential extraction procedure are presented in Table III. In general, these sediments present low carbonate and OM contents. Otherwise, they may be classified depending on the particle-size distribution in sand (samples 1 and 5), sand-silty (sample 4), clay (sample 2) and clay-silty (samples 3, 6 and 7). The samples classified as sand and sand-silty are characterized by low iron oxides content and low OM content, whereas the clay and clay-silty samples are characterized by higher iron oxides content and higher OM content. The optimized parameters were the type of shaker (for exchangeable (F1) and bound to carbonates (F2) fractions, which need a continuous shaking for the extraction), extractant volume to sediment weight ratio (for fraction F1, due to the exchange equilibrium involved), and the concentrations of MgCl_2 and $\text{NH}_2\text{OH}\cdot\text{HCl}$.

Two modes of shaking were tested for leaching both the exchangeable and carbonate phases: end-over-end and vertical vibrator shaking. The amounts of metals released using both methods were compared using ANOVA and the results indicated that there were no significant differences between both systems for any of the seven studied sediments ($p > 0.12$).

Several extractant volume to sediment weight ratios ranging from 8 to 48 were tested to evaluate exchangeable metals. A ratio of 16 was necessary to obtain good results for Cd, Ca, Cu and Zn (Table IV) and higher ratios did not improve the extraction (ANOVA. $p > 0.68$). Lead concentration was below the detection limit for all the samples studied and is not shown in the Table.

TABLE III Characteristics of study sediments from Odiel Marshes Natural Park

<i>Sample</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>S-12</i>
<i>Particle-size distribution (%)</i>								
Sand	80.7	4.0	11.2	55.7	79.8	6.9	6.2	---
Silty	4.8	5.0	49.7	27.3	4.3	48.7	47.8	---
Clay	14.4	91.0	38.8	17.0	15.9	44.4	46.0	---
<i>Major components (%)</i>								
SiO ₂	77.7	34.2	49.6	77.5	76.2	38.7	44.6	27.7
Al ₂ O ₃	4.71	13.2	12.7	5.76	6.67	14.9	12.2	7.71
Fe ₂ O ₃	2.22	17.4	13.5	2.35	2.14	15.7	13.9	3.43
MnO ₂	0.12	0.03	0.03	0.09	0.11	0.32	0.59	0.45
TiO ₂	0.00	0.32	0.22	0.46	0.59	0.59	0.60	0.36
CaO	3.57	2.18	1.44	2.77	1.10	0.51	0.61	22.5
MgO	1.60	1.91	1.89	1.57	1.69	2.39	2.15	2.32
Na ₂ O	4.30	3.27	2.18	4.48	4.30	4.68	4.04	0.42
K ₂ O	0.52	1.89	2.06	0.75	0.70	1.64	1.72	1.41
P ₂ O ₅	0.04	0.06	0.07	0.07	0.08	0.16	0.08	1.43
LOI	5.92	25.4	16.5	5.63	5.75	21.9	20.2	32.3
CO ₃ ⁼	6.59	0.76	1.01	4.51	0.65	0.20	0.43	20.0
OM	0.39	4.80	2.59	0.80	0.91	7.58	4.73	9.60

Concentrations of MgCl₂ between 1 and 5 M were tested for exchangeable metal extraction. No significant differences were found (ANOVA, $p > 0.88$), and 1 M concentration was used in further experiments because of the increased blank values found for higher concentrations of the extractant.

Concentrations of NH₂OH·HCl ranging from 0.04 to 0.4 M were tested for extraction of metals bound to the iron and manganese oxide phases. Results are shown in Table V. No significant differences were found for Mn which may indicate that a 0.04 M NH₂OH·HCl concentration is sufficient to dissolve all of the manganese oxides in the samples. However, the amounts of extracted Fe increased with increasing concentrations of NH₂OH·HCl. The amount of Fe released with 0.4 M NH₂OH·HCl was about 1.8 to 2.4 times higher than that obtained with 0.04 M NH₂OH·HCl. Moreover, increased metal amounts extracted at higher reagent concentrations were found for As, Cr, Cu, Pb and Zn.

However, it is not clear if iron and the rest of the metals are actually leached from the iron and manganese oxides, or they are also mobilized from the organic matter present in the sediment when 0.4 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ is used. In order to evaluate this hypothesis, the UV-visible spectra of the sediment extracts obtained both with 0.04 M and 0.4 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ were compared to those from model phases consisting of either 0.075 g of amorphous iron oxide prepared in the solution laboratory or 0.05 g of humic acid (Fluka, Buchs, Switzerland) extracted with 20 ml $\text{NH}_2\text{OH}\cdot\text{HCl}$. The maximum absorption peaks for humic acid and iron oxide in the model phases were 380 nm and 490 nm, respectively. When sediments were treated with 0.4 and 0.04 M, a maximum at 490 nm and a minimum at 380 nm were observed, indicating that no organic matter was extracted.

The readsorption experiments were only performed for As and Cu in the samples 2, 6, 7 and S-12 because of the lack of agreement found between the percentages extracted for these metals respect to those for iron when two different concentrations of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.04 and 0.4 M) were used. Results showed that both As and Cu were quantitatively readsorbed using 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}\cdot\text{HOAc}$ (> 90%) for all the samples. This indicated that iron oxide phase was not totally dissolved and, consequently, As and Cu were probably readsorbed on the remaining iron oxides. When the extractant concentration was increased to 0.4 M, no readsorption problems occurred in samples collected from Odiel Marshes, indicating that the dissolution of the iron oxide phase was probably complete. However, Cu was strongly readsorbed in the sample S-12 (more than 90%). This fact was attributed to the high organic matter content of this sample as far as a high Cu affinity for the organic matter has been described elsewhere [4,17,18]. Therefore, the use of 0.4 M $\text{NH}_2\text{OH}\cdot\text{HCl}\cdot\text{HOAc}$ as leaching agent for metals bound to the iron and manganese phase was chosen for the proposed sequential extraction scheme.

Application of the sequential extraction scheme to samples collected from Odiel Marshes

Results obtained from the use of the proposed scheme on seven samples collected at Odiel Marshes are shown in Figure 2. Different distribution patterns were observed for the different metals. Cr, Ni and Hg were mainly present in the residual fraction although significant amounts of these elements were also found in Fe-Mn oxide phase. Pb was also distributed between these two phases but an increased association with Fe-Mn oxide phase was observed. Arsenic was mainly bound to Fe-Mn oxides phase (60–78%) but its presence in the organic matter phase was also important. Cu and Zn were distributed among carbonate, iron-manganese oxide and organic matter phases. Finally, the distribution of Cd was dominated by the exchangeable fraction.

TABLE IV Metal concentration (mg kg^{-1}) \pm standard deviation from the exchangeable phase using several volume extractant-weight sample ratios

Volume/ weight	1	2	3	4	5	6	7
<i>Cadmium (mg kg^{-1})</i>							
8	<DL	3.5 ± 0.2	4.2 ± 0.3	<DL	<DL	<DL	<DL
16	<DL	4.7 ± 0.3	6.3 ± 0.3	<DL	<DL	<DL	<DL
32	<DL	51.1 ± 0.3	6.3 ± 0.3	<DL	<DL	<DL	<DL
48	<DL	<DL	6.5 ± 0.3	<DL	<DL	<DL	<DL
<i>Calcium (mg kg^{-1})</i>							
8	1700 ± 100	2700 ± 100	1900 ± 100	1280 ± 60	1060 ± 60	1900 ± 100	1720 ± 90
16	2900 ± 100	4500 ± 300	2700 ± 200	2600 ± 100	1840 ± 90	3700 ± 200	2900 ± 200
32	2800 ± 200	4500 ± 200	2700 ± 200	2500 ± 140	1800 ± 100	3600 ± 200	2900 ± 200
48	2900 ± 200	4400 ± 200	2800 ± 200	2500 ± 200	1900 ± 100	3700 ± 200	3000 ± 200
<i>Zinc (mg kg^{-1})</i>							
8	6.8 ± 0.4	64 ± 3	310 ± 20	5.9 ± 0.6	34 ± 3	110 ± 8	340 ± 20
16	7.0 ± 0.7	180 ± 10	460 ± 30	7.7 ± 0.5	60 ± 5	250 ± 20	560 ± 35
32	6.8 ± 0.6	180 ± 10	510 ± 30	7.7 ± 0.4	58 ± 4	230 ± 20	610 ± 30
48	7.1 ± 0.5	200 ± 10	500 ± 40	7.7 ± 0.4	61 ± 4	240 ± 20	635 ± 40
<i>Copper (mg kg^{-1})</i>							
8	<DL	12.6 ± 0.9	21 ± 1	<DL	<DL	<DL	7.7 ± 0.6
16	<DL	40 ± 3	69 ± 4	<DL	<DL	<DL	11 ± 1
32	<DL	44 ± 4	75 ± 5	<DL	<DL	<DL	0.8 ± 0.7
48	<DL	47 ± 4	81 ± 5	<DL	<DL	<DL	10.2 ± 0.7

DISCUSSION

The importance of the optimization of different operative parameters of the sequential extraction scheme in relation with the characteristics of the sediments under study has been reported by several authors [6,7]. The mode of shaking has been studied by Arunachalam *et al.* [19], who used both an horizontal and end-over-end shakers to extract metals from different sedimentary phases, extracting the metals with a sequential extraction scheme proposed by the same authors. No differences were found for Cd and Pb, but the extraction of Zn was affected by the type of shaker. In opposite to these results, Fiedler [20] reported

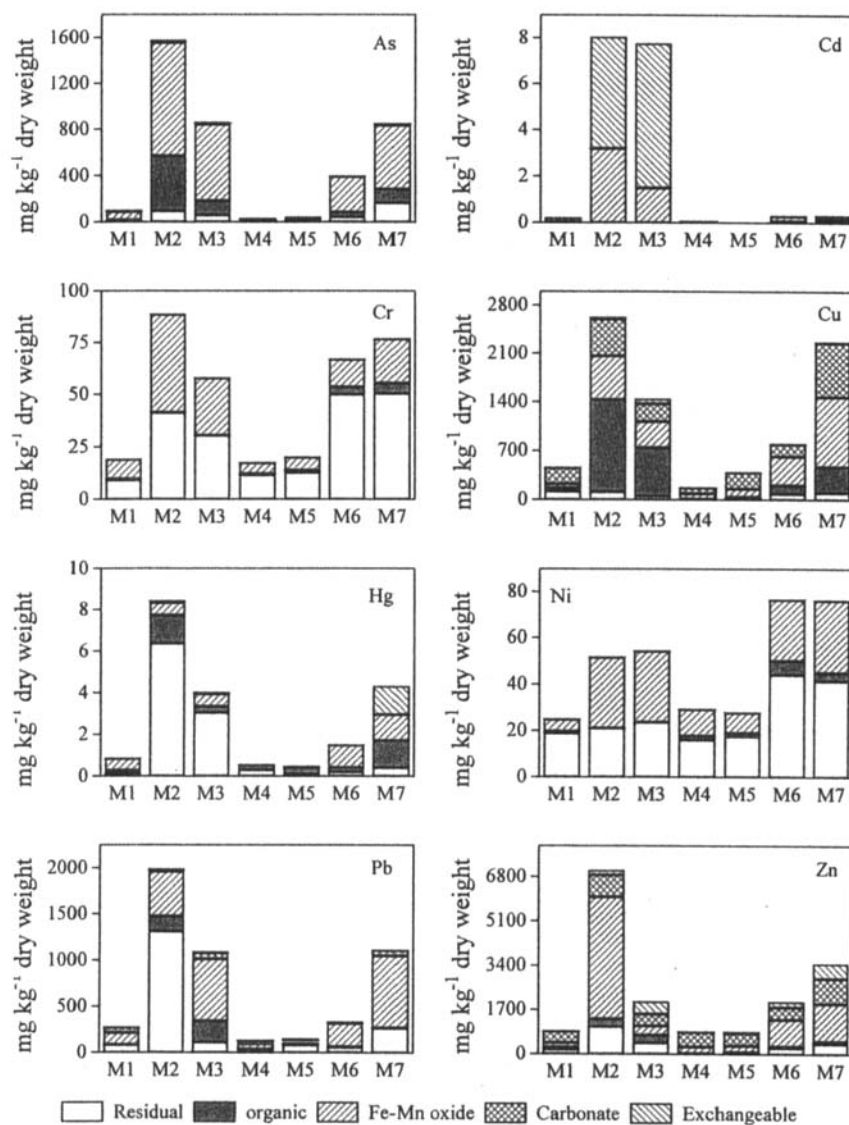


FIGURE 2 Metal distribution in Natural Park Odier Marshes sediment determined by the optimized sequential extraction

higher percentages in metal extraction, using the scheme proposed by BCR [3], when an end-over-end shaker was applied instead of the horizontal shaker. However, we did not find differences in the percentage extraction of several metals using both end-over-end and vertical vibrator shakers.

TABLE V Metal concentration (mg kg^{-1}) \pm standard deviation (3 replicates) extracted by using $\text{NH}_2\text{OH}\cdot\text{HCl}$

Concentration (M)	1	2	3	4	5	6	7
	<i>Arsenic</i>						
0.04	38 \pm 3	290 \pm 20	230 \pm 20	7.0 \pm 0.6	14 \pm 2	80 \pm 5	170 \pm 10
0.2	52 \pm 5	520 \pm 30	310 \pm 20	10 \pm 1	16 \pm 2	150 \pm 10	300 \pm 10
0.4	69 \pm 4	1060 \pm 90	670 \pm 40	14 \pm 1	18 \pm 2	340 \pm 10	530 \pm 30
	<i>Cadmium</i>						
0.04	0.17 \pm 0.01	3.60 \pm 0.2	1.49 \pm 0.04	<DL	<DL	0.20 \pm 0.01	0.15 \pm 0.01
0.2	0.18 \pm 0.01	3.9 \pm 0.1	1.4 \pm 0.1	<DL	<DL	0.19 \pm 0.01	0.18 \pm 0.01
0.4	0.16 \pm 0.01	3.2 \pm 0.2	1.5 \pm 0.2	<DL	<DL	0.21 \pm 0.02	0.15 \pm 0.01
	<i>Chromium</i>						
0.04	9 \pm 1	26 \pm 1	17 \pm 1	3.9 \pm 0.7	4.5 \pm 0.7	7.8 \pm 0.3	12.9 \pm 0.7
0.2	11.3 \pm 0.8	34 \pm 2	20 \pm 1	4.4 \pm 0.4	5.3 \pm 0.5	11.2 \pm 0.7	20 \pm 1
0.4	12.9 \pm 0.8	42 \pm 3	24 \pm 1	5.2 \pm 0.3	5.9 \pm 0.4	14 \pm 1	25 \pm 2
	<i>Copper</i>						
0.04	11.3 \pm 0.9	71 \pm 4	94 \pm 7	15 \pm 1	26 \pm 2	33 \pm 3	290 \pm 30
0.2	42 \pm 4	380 \pm 20	280 \pm 20	46 \pm 3	93 \pm 7	250 \pm 20	650 \pm 40
0.4	64 \pm 3	610 \pm 30	390 \pm 20	66 \pm 6	135 \pm 8	420 \pm 20	930 \pm 80
	<i>Iron</i>						
0.04	5.4 $\times 10^3 \pm 500$	1.3 $\times 10^4 \pm 1 \times 10^3$	9.5 $\times 10^3 \pm 1 \times 10^3$	5.6 $\times 10^3 \pm 500$	5.1 $\times 10^3 \pm 500$	3.3 $\times 10^4 \pm 2 \times 10^3$	2.4 $\times 10^4 \pm 2 \times 10^3$
0.2	9.1 $\times 10^3 \pm 700$	2.3 $\times 10^4 \pm 2 \times 10^3$	1.5 $\times 10^4 \pm 2 \times 10^3$	8.7 $\times 10^3 \pm 700$	8.5 $\times 10^3 \pm 500$	5.8 $\times 10^4 \pm 6 \times 10^3$	3.7 $\times 10^4 \pm 2 \times 10^3$

SEQUENTIAL EXTRACTION

	$1.0 \times 10^4 \pm 900$	$3.0 \times 10^4 \pm 2 \times 10^3$	$1.7 \times 10^4 \pm 1 \times 10^3$	$9.9 \times 10^3 \pm 900$	$9.3 \times 10^3 \pm 800$	$6.6 \times 10^4 \pm 5 \times 10^3$	$4.6 \times 10^4 \pm 2 \times 10^3$
0.4							
<i>Manganese</i>							
0.04	35 ± 3	59 ± 5	56 ± 6	59 ± 6	41 ± 4	320 ± 30	1340 ± 90
0.2	38 ± 3	72 ± 8	56 ± 6	60 ± 6	46 ± 5	340 ± 30	1400 ± 100
0.4	43 ± 4	90 ± 10	69 ± 7	68 ± 7	40 ± 4	330 ± 30	1300 ± 100
<i>Nickel</i>							
0.04	4.4 ± 0.4	33 ± 3	20 ± 2	8.3 ± 0.6	6.0 ± 0.4	12.4 ± 0.9	21 ± 2
0.2	4.9 ± 0.4	39 ± 3	25 ± 2	10.7 ± 0.6	7.7 ± 0.5	20 ± 1	28 ± 2
0.4	5.0 ± 0.4	34 ± 3	28 ± 2	11.8 ± 0.8	8.9 ± 0.6	25 ± 2	34 ± 3
<i>Lead</i>							
0.04	65 ± 3	230 ± 10	390 ± 20	54 ± 3	23 ± 2	95 ± 8	460 ± 30
0.2	102 ± 5	410 ± 20	540 ± 30	57 ± 3	29 ± 2	160 ± 10	640 ± 50
0.4	123 ± 6	510 ± 20	640 ± 30	62 ± 4	33 ± 2	250 ± 30	830 ± 50
<i>Zinc</i>							
0.04	180 ± 10	3800 ± 200	300 ± 20	230 ± 10	260 ± 20	790 ± 70	1200 ± 100
0.2	200 ± 10	4500 ± 200	320 ± 20	230 ± 10	290 ± 20	950 ± 50	1400 ± 100
0.4	200 ± 10	4400 ± 200	340 ± 20	240 ± 20	280 ± 20	1120 ± 30	1400 ± 100

Results using different extractant volume to sample mass ratios showed that this parameter is also critical to obtain quantitative extraction of metals from sediments. Similar findings were reported by Rauret *et al.* [7] who studied the metal extraction from river sediments checking that a 50:1 extractant volume-sediment weight ratio, was much more effective than the smaller ratio proposed in the Tessier's scheme for Cu, Pb, Cr and Ni.

The high percentage of iron oxides (13–18%) generally present in the sediments from Odiel Marshes made necessary to increase the $\text{NH}_2\text{OH}\cdot\text{HCl}$ concentration proposed in the Tessier's procedure (0.04 M) in order to reduce quantitatively all the amorphous iron oxides [1,21]. Higher extraction yields were obtained in these sediments. However, the results have to be considered with caution, because organic matter could also be partially dissolved with higher concentrations of $\text{NH}_2\text{OH}\cdot\text{HCl}$ releasing the bound metals [22]. Two interpretations have been proposed to explain the simultaneous extraction of organic matter by $\text{NH}_2\text{OH}\cdot\text{HCl}$: (i) the tendency for oxidation and subsequently dissolution of humic acids by ferric ions at $\text{pH} < 3$ [23]; and (ii) the dissolution of metal-organic matter complexes coated by iron and manganese oxides when this phase is removed [24]. However, it has been found in the present study that both the pH of the medium did not change significantly when $\text{NH}_2\text{OH}\cdot\text{HCl}$ concentration changed from 0.04 M (pH 1.37) to 0.4 M (pH 1.72) and that the UV-visible spectra of the 0.4 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ extract obtained from both sediments and amorphous iron oxide showed the absence of the maximum at 380 nm which characterised the organic matter.

Readsorption of As and Cu during the extraction with 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ could explain the lower percentages found for these elements [25]. This extractant seems selective for the solubilization of amorphous iron oxides, but not for the release of trace elements associated to this phase. Our results showed that both Cu and As were readsorbed when 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ was used. However, no readsorption problems were observed using higher reagent concentrations which justified the higher metal amount extracted with 0.4 M $\text{NH}_2\text{OH}\cdot\text{HCl}$. This readsorption problem is related to the sediment characteristics since other authors reported the absence of readsorption when using both 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ and the standard addition technique [13].

When the sequential extraction method was applied to several sediments from Odiel Marshes, Cr, Ni and Hg remained in the residue, this fact being also observed by several authors in other areas, indicating that these metals used to be in non-available form in natural sediments [26–35]. On the other hand, Cd was found in the exchangeable phase, which is in according to the findings of different authors [35–38] and implies that may be easily taken up by plants growing in intertidal areas and soils [39]. Finally, according with several authors, we have

found Pb and Zn associated with Fe and Mn oxides and carbonates [27,29,37,40–44], mobilized Zn being usually precipitated or adsorbed on carbonate surfaces of sediments with pH > 6 [38].

CONCLUSION

Results obtained in the present study showed that the optimization of the several parameters controlling the extraction is necessary when a particular scheme has to be applied to environmental samples, taking into account the characteristics of the study area. For iron oxide rich sediments (>13% of Fe₂O₃) an increase of the NH₂OH·HCl concentration prescribed in the procedure of Tessier (0.04 M) is necessary to extract metals bound to the iron oxide phases and avoid readsorption problems.

Acknowledgements

The authors express their thanks to the DGICYT (Dirección General de Investigación Científica y Técnica) for Grant No PB95–0731, as well as the A.M.A. (Agencia de Medio Ambiente de Andalucía, Spain).

References

- [1] N. Meguellati, D. Robbe, P. Marchandise and M. Astruc in: *Proc. Int. Conf. on Heavy Metals in the Environment* (Edimburgo, 1983), pp. 1090–1093.
- [2] F. Rapin and U. Förstner in: *Proc. Int. Conf. on Heavy Metals in the Environment* (Edimburgo, 1983), pp. 1074–1077.
- [3] P. Quevauviller, G. Rauret, H. Muntau, A.M. Ure, R. Rubio, J.F. López-Sánchez, H.D. Fieldler and B. Griepink, *Fresenius J. Anal. Chem.*, **349**, 808–814 (1994).
- [4] A. Tessier, P.G.C. Campbell and M. Bisson, *Anal. Chem.*, **51**, 844–852 (1979).
- [5] I. Rapin, A. Tessier, P.G.C. Campbell and R. Carignan, *Environ. Sci. Technol.*, **20**, 836–840 (1986).
- [6] U. Förstner, *Intern. J. Anal. Chem.*, **51**, 5–23 (1993).
- [7] G. Rauret, R. Rubio and J.F. Lopez-Sanchez, *Intern. J. Environ. Anal. Chem.*, **36**, 69–83 (1989).
- [8] P.M.V. Niren and F.M.M. Morel, *Wat. Res.*, **24**, 1055–1056 (1990).
- [9] S. Xiao-Quang and C. Bin, *Anal. Chem.*, **65**, 802–807 (1993).
- [10] C. Kheboian and C.F. Bauer, *Anal. Chem.*, **59**, 1417–1423 (1987).
- [11] E. Tipping, N.B. Hetherington, J. Gilton, D.W. Thompson, E. Bowels and J.H. Taylor, *Anal. Chem.*, **57**, 1944–1946 (1985).
- [12] P.S. Rendell and G. E. Batley, *Environ. Sci. Technol.*, **14**, 314–318 (1980).
- [13] N. Belzile, P. Lecomte and A. Tessier, *Environ. Sci. Technol.*, **23**, 1015–1020 (1989).
- [14] A.M.A. (Agencia de Medio Ambiente de Andalucía, Spain). *Plan de Policía de Aguas del litoral Andaluz*, (A.M.A., Sevilla, Spain, 1994).
- [15] E. Primo-Yufere and J.M. Carrasco-Dorrien, in: *Química Agrícola I: suelos y fertilizantes* (Alhambra, Madrid, Spain 1973).
- [16] L.S. Clesceri, A.E. Greenberg and R.R. Trussell, in: *Métodos Normalizados para análisis de aguas potables y residuales* (Díaz de Santos, Madrid, Spain 1992).
- [17] V. Samanidou and K. Fytianos, *Sci. Total Environ.*, **67**, 279–285 (1987).

- [18] T. Qiang, S. Xiao-quan and N. Zhe-ming, *Sci. Total Environ.*, **151**, 159–165 (1994).
- [19] J. Arunachalam, H. Emons, B. Krasnodebska and C. Mohl, *Sci. Total Environ.*, **181**, 147–159 (1996).
- [20] H.D.L. Fiedler in: *Método común de extracciones secuenciales de metales en sedimentos: Estudio sobre la preparación de un material de referencia certificado* (Tesis Doctoral, Universitat de Barcelona, 1995).
- [21] A. Tessier and P.G.C. Campbell, *Anal. Chem.*, **60**, 475–476 (1988).
- [22] S. Karlsson, K. Hakansson and B. Allard, 987. *J. Environ. Sci. Health*, **A22(6)**, 549–562 (1987).
- [23] B.A. Goodman and M.V. Cheshire, *J. Soil Sci.*, **30**, 85–91 (1979).
- [24] W.A. Maher, *Bull. Environ. Contam. Toxicol.*, **32**, 339–334 (1984).
- [25] K.A. Gruebel, J.A. Dabis and J.O. Leckie, *Soil Sci. Soc. Am. J.*, **52**, 390–397 (1988).
- [26] C. Izquierdo, J. Usero and I. Gracia, *Mar. Pollut. Bull.*, **34**, 123–128 (1997).
- [27] B. Jones and A. Turki, *Mar. Pollut. Bull.*, **34**, 768–779 (1997).
- [28] A.U. Belazi, C. M. Davidson, G.E. Keating, D. Littlejohn and M. McCartney *J. Anal. At. Spectr.*, **10**, 233–240 (1995).
- [29] B. Nowak, *Analyst*, **120**, 737–739 (1995).
- [30] G. Rauret, R. Rubio, J.F. Lopez-Sanchez and E. Casassas, *Intern. J. Environ. Anal. Chem.*, **35**, 89–100 (1989).
- [31] I.H. Elsokkary and G. Müller. *Sci. Total Environ.*, **97/98**, 455–463 (1990).
- [32] S.K. Gupta and K. Y. Chen, *Environ. Let.*, **10**, 129–158 (1975).
- [33] R. Giordano, L. Musmeci, L. Ciaralli, I. Vernillo, M. Chirico, A. Piccioni and S. Costantini, *Mar. Pollut. Bull.*, **24**, 350–357 (1992).
- [34] A. Abu-Hilal, *Mar. Pollut. Bull.*, **26**, 85–90 (1993).
- [35] E. Helios-Rybicka, *Miner. Petrogr. Acta*, **XXXV-A**, 297–305 (1992).
- [36] I.H. Elsokkary and J. Lag., *Acta Agric. Scand.*, **28**, 262–268 (1978).
- [37] L. Ramos, L.M. Hernández and M.J. González, *J. Environ. Qual.*, **23**, 50–57 (1994).
- [38] A. Chlopecka, J.R. Bacon, M.J. Wilson and J. Kay, *J. Environ. Qual.*, **25**, 69–79 (1996).
- [39] A. Andersson, *Swed. J. Agric. Res.*, **7**, 79–83 (1977).
- [40] S. Kuo, P.E. Heilman and A.S. Baker, *Soil Sci.*, **135**, 101–109 (1983).
- [41] F. Rapin, U. Förstner, I.J. García and G. Nembrini, in: *VI Journées Etud. Pollutions* (Cannes, C.I.E.S.M., 1982) pp. 107–114.
- [42] G. Sposito, L.J. Lund and A.C. Chang, *Soil Sci. Soc. Am. J.*, **46**, 260–264 (1982).
- [43] S. Dudka and A. Chlopecka, *Wat. Air Soil Pollut.* **51**, 153–160 (1990).
- [44] R. Pardo, E. Barrado, L. Perez and M. Vega, *Wat. Res.*, **24**, 373–379 (1990).