

## Metal speciation in surface sediments of the Vigo Ria (NW Iberian Peninsula)

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**SUMMARY:** Total concentrations and chemical forms of metals in surface sediments of the Vigo Ria (NW Iberian Peninsula) were determined following the sequential extraction method proposed by Tessier *et al.* (1979). Total values ranged from 7 to 14  $\mu\text{gCo g}^{-1}$ , 52 to 76  $\mu\text{gCr g}^{-1}$ , 18 to 82  $\mu\text{gCu g}^{-1}$ , 136 to 209  $\mu\text{gMn g}^{-1}$ , 18 to 30  $\mu\text{gNi g}^{-1}$ , 24 to 112  $\mu\text{gPb g}^{-1}$ , 62 to 185  $\mu\text{gZn g}^{-1}$  and 18 to 34  $\text{mg g}^{-1}$  for Fe. The distribution of metals is strongly influenced by the presence of urban and industrial centres. A decreasing concentration trend was observed towards (i) the outer-oceanic part of the ria and (ii) the northern shore in the middle part. Cobalt, Cr, Fe, Mn, and Ni were found to be strongly associated with the residual fraction of the sediment (65-78%), whereas Cu is significantly present in the oxidisable phase (34-72%) and Pb and Zn are found in both the reducible (14-49%) and the oxidisable (14-39%) phases. The speciation patterns reflect natural uncontaminated conditions in the outer part of the ria. However, a significant fraction of the Cu, Pb, and Zn in the sediments of the southern margin of the middle part of the ria, which supports most of the population and industrial activities, is present in labile forms, so a potential pollution risk may exist.

**Keywords:** sediment, metals, speciation, Tessier sequential extraction, Vigo Ria.

**RESUMEN:** ESPECIACIÓN DE METALES EN SEDIMENTOS SUPERFICIALES DE LA RÍA DE VIGO (NW DE LA PENÍNSULA IBÉRICA). – La concentración total y las formas químicas de los metales se determinaron en sedimentos superficiales de la Ría de Vigo (NW de la Península Ibérica) siguiendo el procedimiento de Tessier *et al.* (1979). La concentración total dio valores entre 7 y 14  $\mu\text{gCo g}^{-1}$ , 52 y 76  $\mu\text{gCr g}^{-1}$ , 18 y 82  $\mu\text{gCu g}^{-1}$ , 136 y 209  $\mu\text{gMn g}^{-1}$ , 18 y 30  $\mu\text{gNi g}^{-1}$ , 24 y 112  $\mu\text{gPb g}^{-1}$ , 62 y 185  $\mu\text{gZn g}^{-1}$  y entre 18 y 34  $\text{mg g}^{-1}$  de Fe. La distribución de metales está fuertemente influenciada por la presencia de núcleos urbanos e industriales y, consecuentemente, se constató un gradiente decreciente de las concentraciones hacia (i) la parte exterior de la ría y hacia (ii) la zona media de la orilla norte. El cobalto, Cr, Fe, Mn y Ni se encuentran fuertemente asociados a la fracción residual del sedimento (65-78%), mientras que el Cu esta significativamente presente en la fase oxidable (34-72%) y Pb y Zn se encuentran en las fases reducibles (14-49%) y oxidables (14-39%). Las formas de especiación de los metales reflejan condiciones naturales no contaminadas en la parte exterior de la ría; sin embargo, una fracción significativa de Cu, Pb y Zn en los sedimentos de la zona media de la ría, en su margen sur, que soporta la mayor parte de la población y de las actividades industriales, se presenta en formas lábiles y, por tanto, con un riesgo potencial de contaminación.

**Palabras clave:** sedimento, metales, especiación, extracción secuencial de Tessier, ría de Vigo.

### INTRODUCTION

The nature of the marine environment and the dominant biogeochemical processes in sediments is particularly important in coastal areas supporting

urban and industrial activities where aquaculture activities are also present. This is the case of Vigo Ria, one of the four biggest Western Galician Rias located south of Finisterre Cape (NW Spain). This ria supports the influence of a large urban centre, Vigo

city, with approximately 400000 inhabitants, and its surrounding industries (mainly fisheries, shipyards, mussel farms and automobile industries). The anthropogenic activities may influence the nature of the sediments and metal concentrations and their speciation, leading to their accumulation or mobilisation (Förstner and Salomons, 1991). Sediments may therefore act as either sources or sinks for metal, and this is strongly dependent on their chemical forms. Sequential extraction analysis is a technique developed for the overall assessment of the speciation and potential mobility of metals in sediments (Calmano *et al.*, 1996) and, despite its inherent limitations, it is still recognised as being useful and is widely used.

In accordance with the recent overview by Prego and Cobelo-García (2003), only the HCl-extractable fraction (Langston *et al.*, 1999) has been reported for any Galician ria sediments (Real *et al.*, 1993; Carballeira *et al.*, 2000). A more complete procedure for studying the metal speciation in sediments is the sequential extraction proposed by Tessier *et al.* (1979). This method, which estimates the strength with which the metal is bound to the sediment, has been applied for the sediments of the San Simon inlet (Fig. 1; Belzunce-Segarra *et al.*, 1997), and the existence of potential contamination sources from industrial activities was suggested. Furthermore, Beiras *et al.* (2003) observed a potential toxic effect on marine biota of the metals present in sediments of several parts of the Vigo Ria.

The term ria defines an incised valley in which the estuarine zone can move according to climatic changes (Evans and Prego, 2003). The Vigo Ria is a classic example of a drowned river valley which gradually narrows and becomes shallower inland. The geology of the hinterland of the Ria is remarkably uniform and consists predominantly of granites, granitic gneiss, micaceous schists and occasional interbedded quartzites. Focusing particularly on the metals, mineralogical and chemical studies of the surface sediments show the overwhelming influence of detritus inputs in both cases (Belzunce-Segarra *et al.*, 2002; Howarth *et al.*, 2005).

Total metal concentrations of the sediments in the western Galician rias have been reported (Prego and Cobelo-García, 2003), particularly in the Vigo Ria (Prego and Cobelo-García, 2002), but very little is still known about their metal speciation, especially compared with other world coastal areas (e.g. Bryan and Langston, 1992). The aim of this study was there-

fore: (i) to study the spatial distribution of metals in the sediments of the Vigo Ria and (ii) to determine their chemical forms following the Tessier (Tessier *et al.*, 1979) sequential extraction procedure.

## MATERIALS AND METHODS

### Sampling

Sixteen surface sediment (<5 cm depth, oxic zone) samples were taken using a grab sampler at the sites shown in Figure 1 in March 1997 onboard the Lampadena boat (IIM-CSIC). Eight of these samples (Stations 1-8) were sampled along the longitudinal axis of the ria, where the fine-grained sediments are predominant. The remaining 8 samples were taken from both the northern (Sts. 21-24) and southern (Sts. 11-14) margins of the ria. Potential sources of contamination are associated with Vigo city urban inputs (St. 12), the River Lagares, which collects about 40% of the total sewage from the urban area and flows into the outer ria zone, La Guía shipyard (Sts. 2, 3), and the mussel farms near the Rande Strait (Sts. 11, 21). The samples represent the external and middle zones of the ria, where marine conditions are dominant and the influence of fluvial discharge is low.

### Sample preparation

The sediment samples were oven-dried at 60°C for 24 h and the coarser material (>2000 µm) was removed by sieving. The remaining fine fraction was finely ground in an electrical agate mortar to <20 µm before chemical treatment (Tessier *et al.*, 1979).

### C, N Analysis

Total N and organic C were determined by combustion at 1020°C in a Carlo Erba Nitrogen Analyzer 1500 apparatus. Prior to analysis, the inorganic carbon was eliminated following the method described by Nieuwenhuize *et al.* (1994).

### Total metal analysis

Sediment samples (1 g, dry weight) were digested in platinum crucibles using an acid mixture of 2 mL of concentrated HClO<sub>4</sub> and 10 mL of concentrated HF, and heated on a hot plate until almost dry-

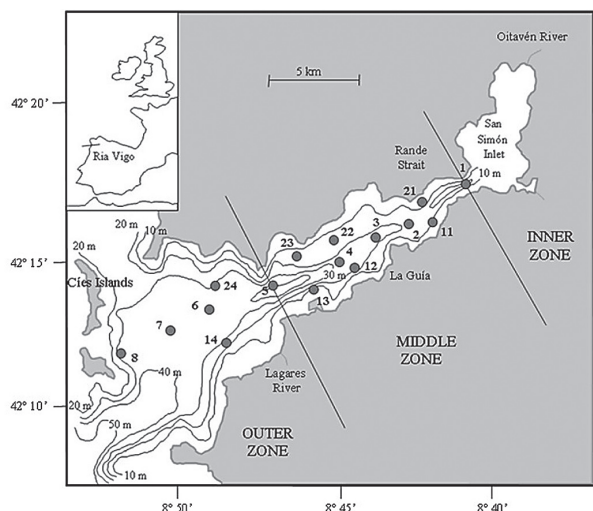


FIG. 1. – Bathymetry and location of samples in the Vigo Ria. The ria is 33 km long and has a surface area of 176 km<sup>2</sup>.

ness. Then a further 1 mL of HClO<sub>4</sub> and 10 mL of HF were added and the mixture heated again until dryness. Finally, 1 mL of HClO<sub>4</sub> was added and the mixture heated until evaporation with the appearance of white fumes. The final residue was dissolved with 12 M HCl, filtered (Whatman No. 540) and diluted to 50 mL. Digests were then stored for metal analysis by inductively coupled plasma (ICP) atomic emission spectroscopy (ARL 3580 B). Analysis of a Certificate Reference Material (PACS-2, Canada) for metals in sediments using this procedure yielded 95–105% recovery from the certified concentrations.

### Sequential extraction

The sequential extraction method defined by Tessier *et al.* (1979) was followed to determine the partitioning of metals, divided into five operationally defined fractions as follows:

I.- Exchangeable, extracted with magnesium chloride.

II.- Acid-extractable (bound to carbonates), extracted with sodium acetate.

III.- Reducible (bound to Fe/Mn oxides), extracted with hydroxylamine hydrochloride/acetic acid.

IV.- Oxidisable (bound to organic matter and/or sulphides), extracted with nitric acid/hydrogen peroxide/ammonium acetate.

V.- Residual, extracted with hydrochloric/perchloric acids (following the same procedure used for the total metal analysis described above).

At the end of each extraction, the extractable fraction was separated by centrifugation at 10400 rpm

for 30 min. The supernatant was pipetted and stored in plastic containers in a cool room (4°C) until analysis. Before starting each extraction step, the residue was washed with 8 mL of deionised water, shaken for 30 min and centrifuged at 10400 rpm for 30 min. The supernatant was removed and discarded.

All the material used for the experiments was carefully washed with 5% Decon and 0.6 M HNO<sub>3</sub>. Milli-Q water (Millipore) was used. All reagents used in this study were analytical grade. Metal concentrations in the extracts were determined by ICP-AES. The total recovery by sequential extraction with respect to the total digestion was around 102 ± 6% for Co, Cr, Cu, Fe and Mn, while for the remaining elements (Ni, Pb and Zn) it was always higher than the total digestion, being in the range of 110 ± 8%.

## RESULTS AND DISCUSSION

### Total metal concentrations

The metal concentrations and distribution in the <2 mm fraction of the surface sediment samples are shown in Figure 2. When these values, whose average concentrations and ranges are indicated in Table 1, are compared to uncontaminated sediments of other world estuaries (see Table 2) (UK: Bryan and Langston, 1992; USA: Hornberger *et al.*, 1999; Australia: Doherty *et al.*, 2000) their levels could be considered uncontaminated for Co, Mn and Ni, locally contaminated for Cu, Pb and Zn, and higher than reference concentrations for Fe and Cr. However, if the regional background concentrations obtained in the Galician rias (Cobelo-García and Prego, 2003) are considered, then the sediments of the Vigo Ria cannot be considered contaminated by Fe and Cr. Elements with a potential risk of pollution are therefore Cu, Pb and Zn, which is in accordance with the list of contaminating metals proposed by Prego and Cobelo-García (2003) for this ria.

These three metals show a non-homogeneous distribution, with the highest total concentrations in the middle part of the ria: the axis (Sts. 2–4) and southern margin (Sts. 11–13), where the highest values (81 µgCu g<sup>-1</sup>, 112 µgPb g<sup>-1</sup> and 185 µgZn g<sup>-1</sup>; Fig. 2) are found. Compared with the San Simón inlet sediments, Pb concentrations are significantly lower since the inner part of the ria is contaminated by Pb (Evans *et al.*, 2003). The lowest values of Cu,

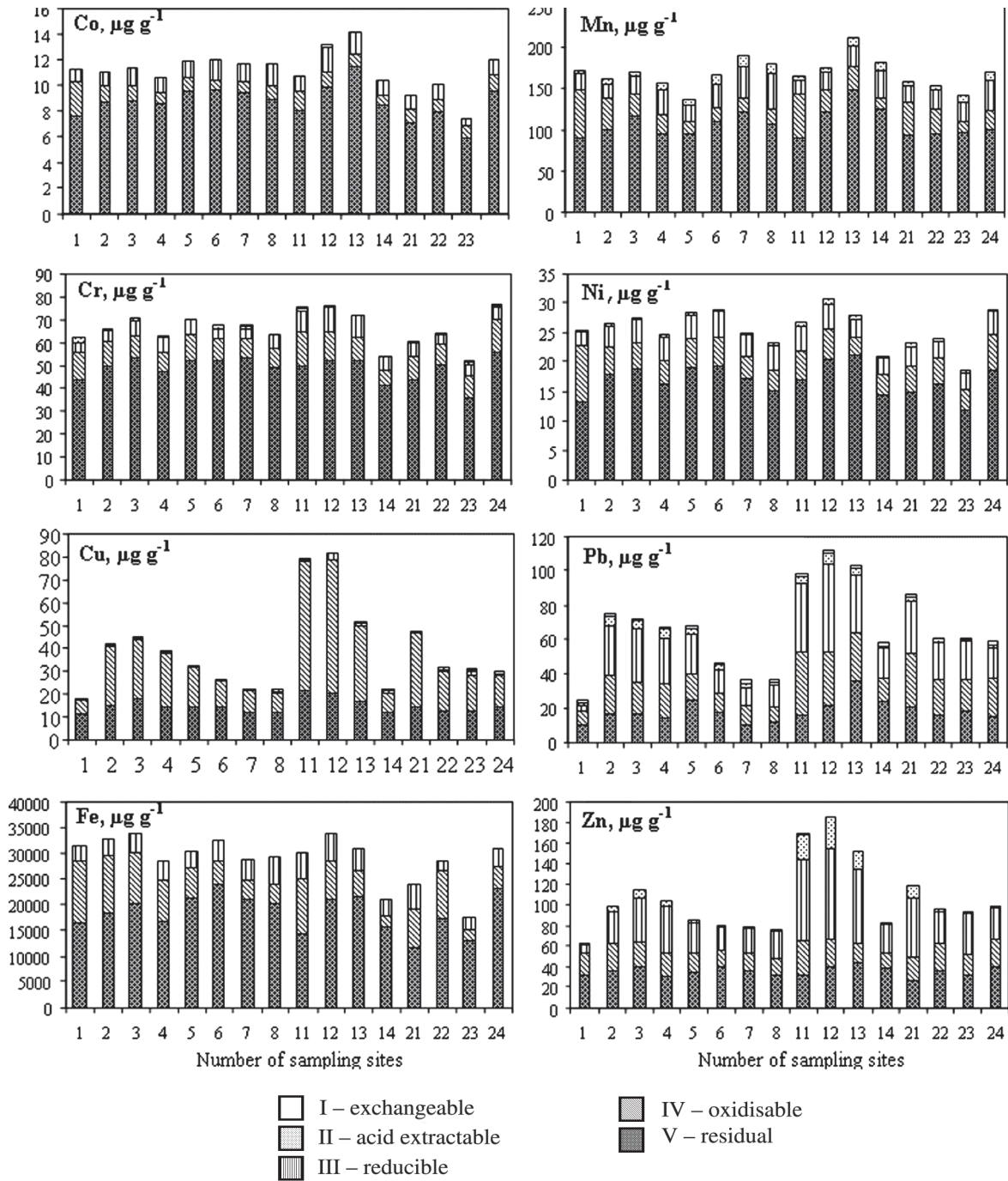


FIG. 2. – Distribution of total metals and their speciation in the Vigo Ria sediments in each chemical fraction. Units are expressed in  $\mu\text{g g}^{-1}$ .

Pb and Zn are found in the northern (free of shipyard industry) and external (dominated by offshore seawater) parts of the Vigo Ria. Earlier concentrations for the Vigo Ria reported by Barreiro *et al.* (1988) in the <2 mm fraction of sediments collected in the early 1980s were lower than 31, 80 and 117  $\mu\text{g g}^{-1}$  for Cu, Pb and Zn, respectively. Our results, corresponding to sediments sampled in 1997, sug-

gests an increase in the ria contamination in the last 20 years of the twentieth century. The other elements (Co, Cr, Fe, Mn and Ni) show a homogeneous distribution among the samples, although a slight increase in their concentrations is found near the shipyard area of the city of Vigo, corresponding to the most contaminated area of the ria (Rubio *et al.*, 2000).

TABLE 1. – Averages and ranges (between brackets) of total metal concentrations ( $\mu\text{g g}^{-1}$ ) and the amount (%) of metals in each chemically-defined fraction (Tessier *et al.*, 1979) in the Vigo Ria sediments.

Metal	Total	Exchangeable	Carbonate	Reducible	Oxidisable	Residual
Co	11.2 (7-13)	0.0	0.1	11.4 (8-15)	10.7 (6-24)	77.8 (74-81)
Cr	66.1 (52-76)	0.2 (0-1)	1.4 (0-3)	9.4 (7-14)	15.6 (12-20)	73.5 (66-79)
Cu	38.6 (18-82)	0.0	2.0 (0.9-3.5)	2.3 (1-7)	54.0 (34-72)	41.7 (24-61)
Fe	29000 (17800-33800)	0.0	0.02	13.4 (8-21)	22.7 (11-39)	64.0 (48-73)
Mn	168 (141-210)	0.0	4.5 (3-7)	15.8 (11-24)	16.6 (8-33)	63.0 (52-70)
Ni	25.6 (19-31)	0.0	1.7 (1-3)	14.3 (9-18)	18.3 (10-37)	65.8 (53-76)
Pb	66.3 (24-103)	2.7 (1-7)	4.7 (1.6-8.0)	34.3 (14-45)	30.0 (23-39)	28.3 (15-40)
Zn	106 (62-185)	0.1	5.1 (1-16)	37.1 (16-49)	21.7 (14-32)	36.0 (19-52)

TABLE 2. – Average concentration of heavy metals ( $\mu\text{g g}^{-1}$  dry wt) in sediments from different regions and from the study area.

Country	Region	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
UK	Axe Estuary	7	27	12	18361	326	14	26	76	Bryan and Langston, 1992
UK	Solvay Estuary	6	30	7	14816	577	17	25	59	Bryan and Langston, 1992
USA	San Francisco Bay	–	129	–	39000	465	87	–	–	Hornberger <i>et al.</i> , 1999
USA	Tomales Bay	–	150	–	37000	324	116	–	–	Hornberger <i>et al.</i> , 1999
Australia	Cocoa Creek	11	–	10	24406	599	16	14	38	Doherty <i>et al.</i> , 2000
Australia	Gordon Creek	8	–	12	20218	423	11	12	35	Doherty <i>et al.</i> , 2000
Spain	Ferrol Ria	6	63	12	2400	....	26	27	55	Cobelo-García and Prego, 2003
Spain	Vigo Ria	11	66	39	29000	168	26	66	106	Present paper

### Metal partitioning

Figure 2 illustrates the different distribution of the eight metals under study among the five chemically-defined fractions, and their averages are shown in Table 1. From the distributions in the five different operationally defined phases, two groups could be then distinguished:

(i) One group includes Cu, Pb and Zn. Copper is mainly found in the oxidisable fraction (Fig. 2), where it is probably associated with organic matter and/or with sulphides. Near the coast, this fraction accounts for more than 60% of the total, but in the open part of the ria, it is reduced to around 45%. Only up to 7% of Cu is represented in the other non-residual phases, most of the remaining Cu occurring as a residual component. Lead is distributed among all the mobile phases (Fig. 2) but particularly in the oxidisable and reducible fractions with mean percentages up to 29 and 35%, respectively. A mean value of 28% is found for the residual form and up to 9% associated with exchangeable cations and carbonates (Table 1). Zinc is principally present in the reducible, oxidisable and residual fractions, with mean values of 37, 21 and 37%, respectively (Table 1).

(ii) The other group is formed by Co, Cr, Fe, Mn and Ni. These elements are mainly found in the residual fraction, with mean values of 78% for Co, 74% for Cr and about 65% for Fe, Mn and Ni (Table 1). They are probably associated with the silicate matrices of the sediments. However, they are also found in the reducible and oxidisable forms, and a significant percentage of Mn is associated with carbonate phases (up to 7%). The oxidisable form is more important for Fe than for the other elements, with a mean value of 28% for samples in the inner and middle part of the ria and 15% for samples situated in the external zone. The distribution of Fe in reducible phases (Fe/Mn oxides) is much more homogeneous. The content of oxidisable Mn is highest at Sts. 1, 2, 11 and 21 located in the inner part of the ria and, conversely, the reducible fraction is slightly higher in samples from the external and middle part of the ria.

In general, the different fractions of Co, Cr and Ni are homogeneously distributed in the ria sediments and 64 to 78% of these metals occur in the stable matrices of the minerals. Their pattern is similar to that observed in the innermost ria zone (Belzunce *et al.*, 1997). On the other hand, the first group of metals is concentrated in the non-residual fractions. Thus,

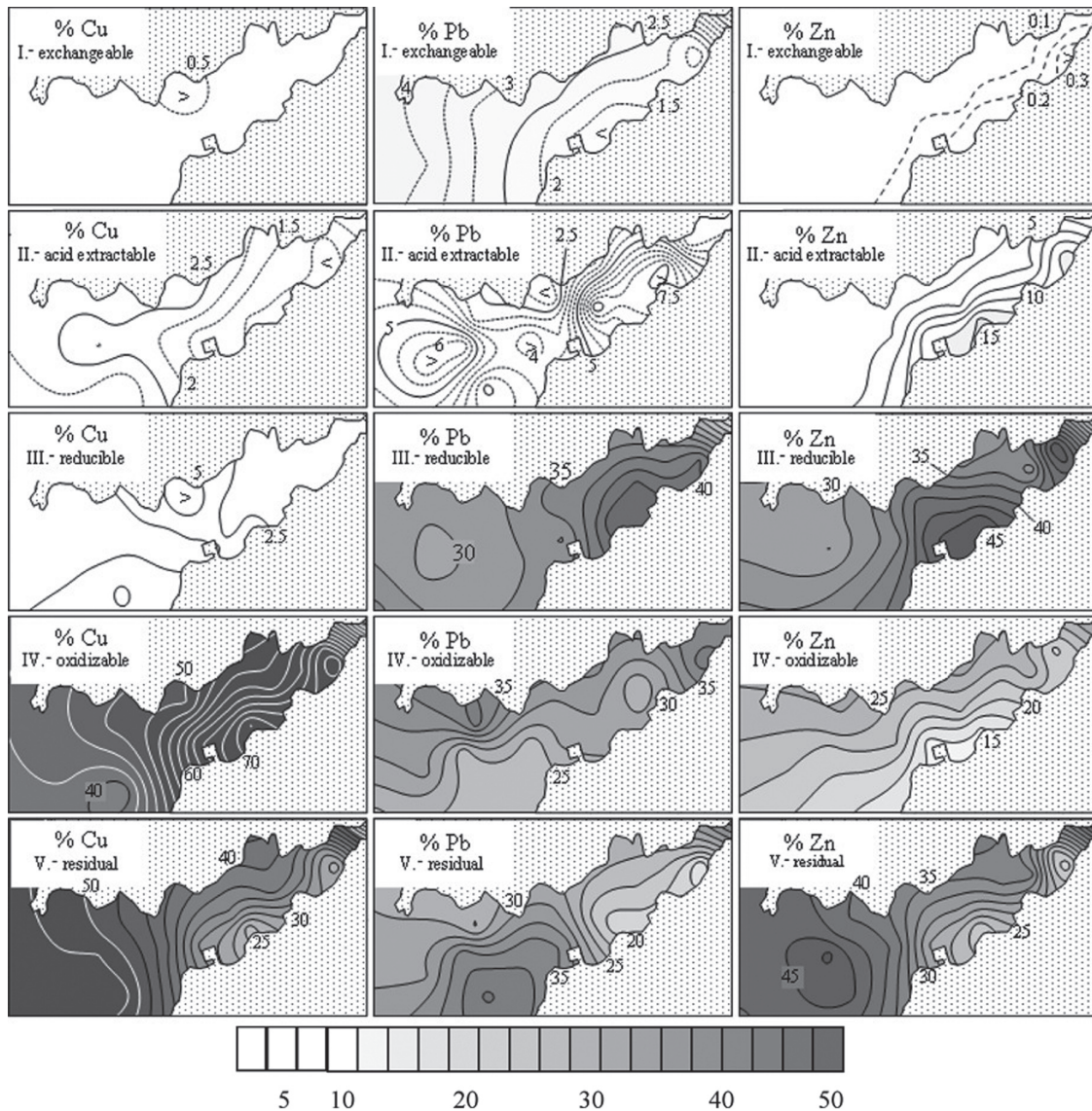


FIG. 3. – Isolines maps of the distribution of Cu, Pb and Zn in each chemical fraction in the Vigo Ria sediments.

for Cu, Pb and Zn, more than 50% of them (up to 72% for Pb) is found associated with the potentially mobile fractions. This division resulting from metal speciation has already been considered in estuaries in relation to anthropogenic influences (v.g. Allen *et al.*, 1990). The forms of these three metals involve a potential risk of contamination in the ria because a large fraction of these trace metals could be remobilised in estuaries (Mortimer and Rae, 2000).

### Spatial changes in the metal speciation

Regarding the group of metals with the potentially more mobile fractions in the ria sediments, two areas are clearly distinguished:

(i) The southern margin and Rande Strait in the middle part of the ria show the highest contents of Cu, Pb and Zn associated with the mobile phases (Figs. 2 and 3). Both areas are dominated by mud- and organic-rich sediments (Bernárdez *et al.*, 2005). The analysis of C and N showed values in this area of 2.1-4.2 % (w/w) for C and 0.24-0.49 % (w/w) for N. The highest organic carbon values were measured at Sts. 11 and 21 near the Rande Strait, decreasing from the middle to the outer part of the ria, in accordance with the decrease in primary production in the water column and the opal in sediments observed towards the open sea (Prego, 1993; Bernárdez *et al.*, 2005), and suggesting a predominant natural origin of the organic matter. On the other hand, in the

middle zone, there is a C and N increase from the north to south littoral zone. This distribution is affected by the domestic inputs from the city of Vigo, whose origin is anthropogenic. The distribution pattern observed for C/N ratios (from 7.3 to 11.3) also confirms the influence of external inputs. In this area dominated by organic-rich sediments, a significant enrichment of Cu in the oxidisable fraction was observed (Fig. 3), whereas the enrichment of Pb in the sediments is related to an increase in this metal in both oxidisable and reducible fractions (Fig. 3), but the exchangeable Pb is high in Rande Strait (7% at St. 1 and 4% at Sts. 7 and 8). The highest contents of Zn were associated with reducible and acid-extractable (carbonate) phases (Fig. 3).

(ii) The external and middle-north areas of the ria (Sts. 6, 7, 8, 14, 22, 23 and 24) contain the lowest concentrations of Cu, Pb and Zn, and the highest percentages associated with the residual fraction. The southern-middle part of the ria is the most contaminated and has the highest proportions of metals in the labile fraction, probably associated with the anthropogenic influence (Li *et al.*, 2001). Sewage discharges and industrial inputs from the city of Vigo and the harbour and shipyard activities are the main reason for this pattern in the ria for Cu, Pb and Zn. Their natural speciation observed in the outer ria zone and in non-impacted estuaries (Bryan and Turki, 1997) has changed in the southern margin of the middle ria to a distribution clearly related to, or influenced by, the proximity to the urban and industrial point sources.

In summary, surface sediments in the Vigo Ria are moderately contaminated by metals, although the highest concentrations of Cu, Pb and Zn are localised in the sediments closest to contamination point-sources, i.e. the mouth of the River Lagares, and the city of Vigo/harbour-shipyard area. This area also shows the highest amount of metals in the most mobile phases of the sediments, which are therefore reactive and bioavailable, strongly suggesting both a significant anthropogenic contribution and a potential pollution risk. On the other hand, Co, Cr, Fe, Mn and Ni show a fairly uniform distribution in the Vigo Ria sediments and are mainly associated with the residual fraction, suggesting a predominant lithogenic origin and a low contamination risk.

This information, reported for the first time for the middle and outer parts of a Galician ria, constitutes a baseline of metal speciation in sediments and a reference for future studies on the changes of la-

bile and residual metal fractions over time. It also reports a sampling strategy guideline for studying the hazardous effects of metals in the sediments. Their potential toxicity has also been indicated by Beiras *et al.* (2003) for the Galician Rias by means of bioassays using sediments collected near the Rande Strait (Vigo Ria) and different species of bivalves and ascidians.

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