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Pollution in intertidal sediments of San Simón Bay (Inner Ria de Vigo, NW of Spain): total heavy metal concentrations and speciation

P. Álvarez-Iglesias, B. Rubio *, F. Vilas

Departamento de Geociencias Marinas y Ordenación del Territorio, Facultad de Ciencias, Universidad de Vigo, 36200 Vigo (Pontevedra), Spain

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San Simón Bay constitutes the inner part of the Ria de Vigo (Fig. 1a), and is 7 km long and 3.5 km wide with a surface area of 19.5 km². Its average depth is less than 7 m, except in the Rande Strait where the depth reaches 30 m. Tidal range is 2–4 m (mesotidal). This bay has two well defined sectors (Fig. 1b): one subtidal and another intertidal. Orientation and morphological characteristics of the Bay make it a low hydrodynamic energy area, which allows for the development of intertidal flats and marshes. The intertidal sector presents two sedimentary environments: estuary and intertidal flat, the limit between both environments being gradual and irregular. The Eastern intertidal sector area is dominated by the Oitabén-Verdugo River (Nombela and Vilas, 1986–1987). Intertidal areas are usually sinks for trace metals of natural or anthropogenic origin. San Simón Bay, together with the rest of the Ria de Vigo constitutes a coastal ecosystem of high biological productivity, due to upwelling processes which are common in all the Galician Rias (Fraga, 1981; Prego, 1993). Upwelling makes possible extensive marine cultures, giving this area a great economical importance.

The San Simón Bay environment is affected by urban and industrial wastes from towns and cities around its coastline. In particular, a ceramic factory located close to the Oitabén-Verdugo river mouth dumps wastes directly into the Bay (Fig. 1b). The main objectives of this research were to evaluate the influence of this factory on the Bay; to determine the influence of diagenetic processes; and to identify metal concentrations, with some ecological importance, over background levels. For these purposes, total metal concentrations of Al, Cu, Fe, Mn, Pb and Zn, and metal speciation of selected elements (Fe, Pb and Zn) were determined. Al, Fe and Mn were chosen as indicators of sediment characteristics. Cu, Pb and Zn were selected because they are trace metals which usually have an anthropogenic origin.

Sediment samples were collected in the San Simón Bay intertidal area, near the Oitabén-Verdugo River mouth and near the ceramic factory (Fig. 1b). They consisted of three cores of about 25 cm (C1, C2 and C3) in the intertidal flat and three surficial samples in the waste channel of the factory (P3, P4 and P5). The cores were collected to study the influence of the different sample characteristics over metal content and to evaluate the influence of diagenetic processes, while the waste channel samples were collected to evaluate the influence of the ceramic factory on the Bay. Core pipes were cut

* Corresponding author. Tel.: +34-986-812649; fax: +34-986-812556.

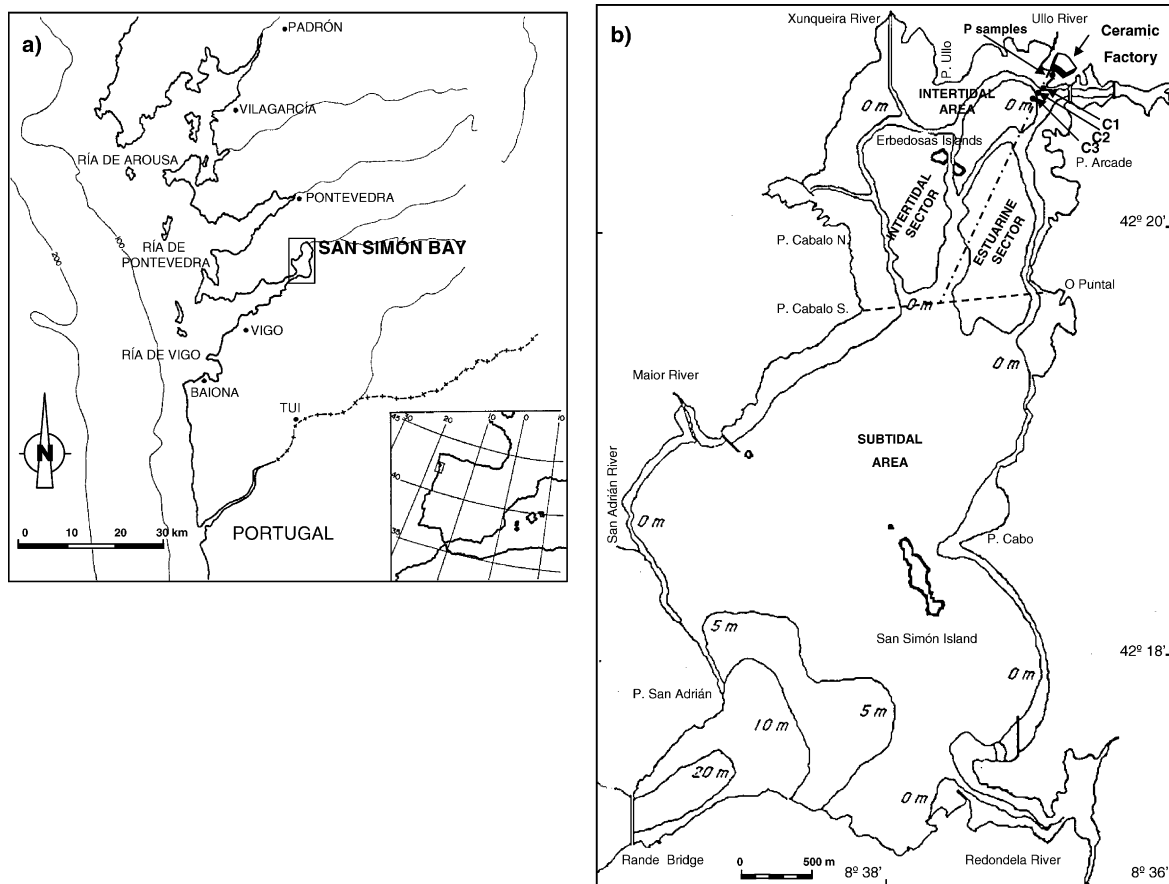*E-mail address:* brubio@uvigo.es (B. Rubio).

Fig. 1. Location of the study area. (a) General view, (b) detail with the location of sediment samples in the study area (C: cores, P: waste channel samples).

longitudinally, and 1-cm thick slices were sampled at the centre for X-ray radiography, using a Hewlett Packard, 43805 N model Faxitron. Textural, mineralogical and geochemical analyses were performed every 2 cm.

Grain size was determined by dry and wet sieving (Folk, 1974). Geochemical (pH, organic carbon, calcium carbonate, total metal content and its speciation) and mineralogical analyses were performed on the fraction smaller than 63 μm, which was finely powdered using an agate mortar. Use of this fraction in pollution studies is recommended by several authors (Förstner, 1989; Soares et al., 1999). Organic carbon was determined by wet digestion and calcium carbonate by using a Bernard calcimeter (Guitián and Carballás, 1976). Mineralogical

phases of the sediments (<63 μm fraction) were determined by X-ray diffraction (XRD).

Total metal contents (Al, Cu, Fe, Mn, Pb and Zn) were determined by triacid digestion (HF, HNO_3 and HCl) in a microwave oven (CEM, MDS 2000 Microwave Digestion System) with two heating steps separated by one airing step (Barreiro, 1991; Carral Vilariño, 1992; Marcet Miramontes et al., 1997). This intermediate step was used to release pressure, avoiding gas explosion hazards caused by digestion. Data accuracy and precision were checked by analysing the reference material MESS-1, indicating good agreement between certified and analytical values (recovery was over 80%; Table 1).

Table 1
Comparison of the analytical results of the reference material (MESS-1) with the certified data

Element	Certified value	Measured value[a]
Al (%)	5.84 ± 0.20	3.71 ± 2.14
Fe (%)	3.05 ± 0.17	2.47 ± 0.12
Mn (μg g^{-1})	513 ± 25.0	403.53 ± 35.23
Cu (μg g^{-1})	25.1 ± 3.8	23.84 ± 2.17
Pb (μg g^{-1})	34.0 ± 6.1	36.50 ± 7.24
Zn (μg g^{-1})	191.0 ± 17.0	161.54 ± 15.37

[a] Metal concentration mean values calculated for 10 replicates, except for Pb (seven replicates) and Zn (six replicates).

Table 2
Detection limits for total and fractions metal concentrations

Metal/fraction	Detection limit ($\mu g\,g^{-1}$)
Al, Fe, Pb, Zn	25
Cu, Mn	10
CuA	0.32
CuB	0.32
CuC	0.8
CuD	1.0
CuE	2.0
FeA, PbA, ZnA	0.8
FeB, PbB, ZnB	0.8
FeC, PbC, ZnC	2.0
FeD, PbD, ZnD	2.5
FeE, PbE, ZnE	5.0

Metal speciation of selected elements (Fe, Pb and Zn) was obtained according to the Tessier et al. (1979) sequential extraction method modified by Álvarez-Iglesias et al. (2000). Pb and Zn were selected in view of their anthropogenic character and Fe, because of its sensitivity to diagenetic changes. This method separates total concentrations in five fractions: exchangeable (A), bound to carbonates (B), bound to Fe–Mn oxyhydroxides or reducible (C), bound to organic matter-sulphides or oxidizable (D) and residual (E). Metal concentrations in all the extracts were determined by atomic absorption spectrometry (AAS). Detection limits for the metal extracts are shown in Table 2.

One of the most prominent characteristics of cores was a lack of lamination in comparison with other intertidal areas (Allen, 2000; Vos and van Kesteren, 2000), caused by an intense activity of organisms in the study area (Nombela et al., 1995). Bioturbation chiefly consists of a few centimetres deep galleries formed by polychaetes of the genus *Nereis*. Another prominent characteristic was high sand content (>30%) in the cores and low mud contents (1–58%) contrasting with the mud-rich sediments in the Ria de Vigo (>80%: Marcet Miramontes, 1994; Rubio et al., 2000a,b). High proportions of gravel and sand in core samples are consistent with closeness to the Oitabén-Verdugo River. Both fractions exceeded 80% of the total weight in cores C1 and C3 while in core C2 they were about 63%. This core was more distant than the others to the estuarine channel. Samples closer to the river mouth (C1) had a higher gravel content ($38.71 \pm 14.43\%$). Texturally, the core samples can be classified as sandy-gravel for C1, gravelly muddy sand for C2 and gravelly-sand for C3 (Folk, 1954). Waste channel samples (P) were very different from core samples. These mainly comprised fine materials, except for sample P4. This sample consisted of a piece of greenish coloured amorphous material, of industrial origin (the dumping of vitreous materials used in ceramic manufacture). The other samples (P3 and P5) had a whitish colouration, similar to that of the sediments near the ceramic factory.

All samples showed similar pH values, being close to neutral (7.33 ± 0.20) and between the expected range for most subaqueous marine and non-marine sediments (6–8; Berner, 1981).

Organic matter content was high in the cores (7–15%) with an average value of $10.36 \pm 2.26\%$. Core C2 showed the highest values ($12.84 \pm 1.38\%$). These high levels are characteristic of the inner part of Galician Rias (Vilas et al., 1995, 1996, 1999) and are similar to those found by other authors for the Ria de Vigo (Nombela and Vilas, 1986–1987; Marcet Miramontes et al., 1997; Rubio et al., 2000a,b). These contents are probably related to (1) organic matter inputs from the Oitabén-Verdugo River, (2) to the richness of marine flora (*Zostera marina* and *Z. noltii*) in the area and (3) to biological production. Waste channel samples showed very low organic matter content (about 0.5%).

Calcium carbonate estimations were very low (<1%) in contrast with the high proportions observed in other areas inside the ria (Rubio et al., 2000b). Calcareous shell fragments were scarce, and mainly gastropods (*Hydrobia ulvae*), which tend to concentrate at the surface.

The main mineralogical constituents of the mud fraction of cores were quartz, muscovite and feldspars (plagioclases and orthoclases). It is important to mention the presence of kaolinite and minerals at 14 Å. Gibbsite was also detected in trace quantities. This mineralogy is coincident with those obtained in other areas of the bay and river suspended load composition (Macías, 1981; Pazos et al., 2000), indicating a continental origin. In contrast, the main constituent of P3 was gypsum.

Total metal concentration in cores varied, in general, in a short range for Al, Cu, Fe and Zn, while for Mn and Pb a clear differentiation was observed for different cores (Fig. 2) even when they showed similar distributions. Lower samples reached similar concentrations for Fe ($2.32 \pm 0.10\%$) and Pb (about 500 $\mu g\,g^{-1}$). This was not the case for Cu and Zn or Al and Mn. Cu and Zn presented the highest concentrations for all cores at the bottom of core C1: about 90 $\mu g\,g^{-1}$ for Cu and 370 $\mu g\,g^{-1}$ for Zn. This core also presented the highest concentrations of Mn (about 370 $\mu g\,g^{-1}$). The highest Al concentrations were presented at the bottom of core C2 (about 13.16%). Of particular note were the high Pb concentrations present in core C2 (about 6000 $\mu g\,g^{-1}$ in the surface). This core, together with core C3, showed a fairly marked Pb content decrease with depth. The most likely explanation for this trend would be the increase of anthropogenic inputs with time. Conversely, organic matter content, which is one possible ligand for trace metals, decreased to the bottom of the cores.

Waste channel samples (P) presented anomalous values (very high or very low) in comparison with core samples. Concentrations of Al, Cu, Fe, Mn and Zn in P samples were very low or below the detection limit (Fig. 3), except in sample P3 for Zn (about 930 $\mu g\,g^{-1}$) and in
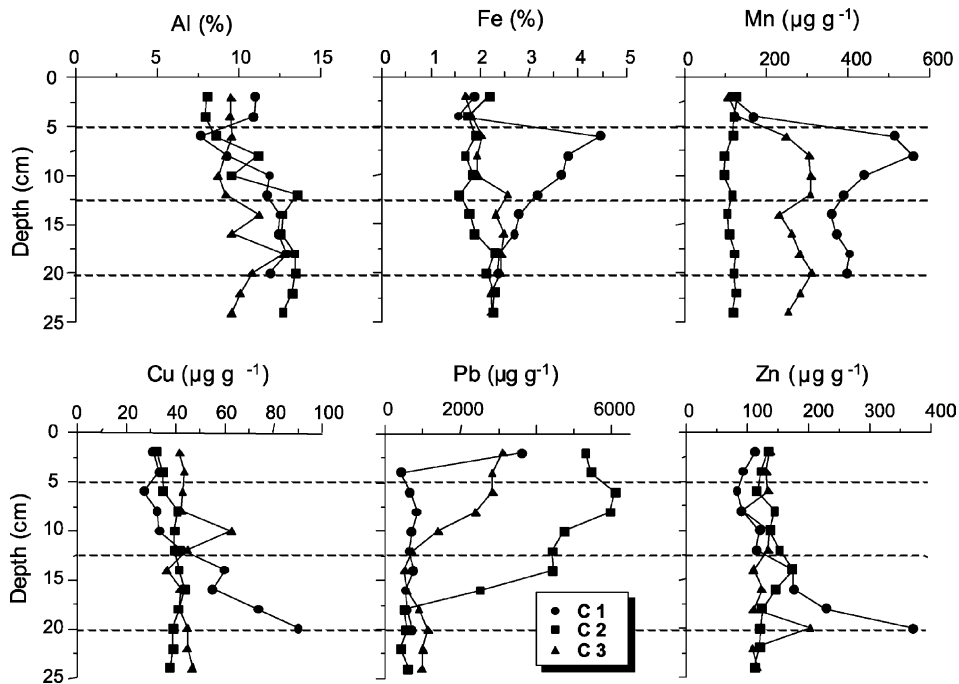
Fig. 2. Depth profiles of total metal concentrations (Al, Cu, Fe, Mn, Pb and Zn). Concentrations are given in $\mu g\,g^{-1}$, except for Al and Fe (%).
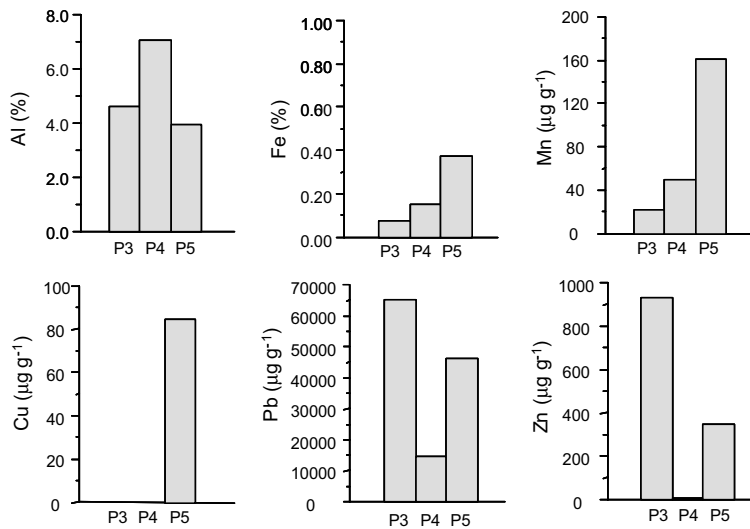

Fig. 3. Total metal concentration in waste channel samples (P).

sample P5 for Cu ($>85\ \mu g\,g^{-1}$), Mn (about $160\ \mu g\,g^{-1}$) and Zn ($>200\ \mu g\,g^{-1}$). Pb concentrations were extremely high (more than $65400\ \mu g\,g^{-1}$ in sample P3).

Metal concentrations were compared with those found by several authors in sediments from the adjacent Ria de Vigo and the subtidal area of San Simón Bay (Nombela et al., 1994; Belzunce-Segarra et al., 1997; Rubio et al., 2000a). The most prominent fact was the anomalously high Pb concentrations measured in San Simón Bay, indicating an important input of this metal.

Several indices were applied to evaluate sediment pollution including contamination factor (CF), enrichment factor (EF) and geoaccumulation index (Igeo),

(Zoller et al., 1974; Müller, 1979; Hakanson, 1980). Al was used as the normalization element, as recommended for the Galician Rias (Carral Vilariño, 1992; Nombela et al., 1994; Rubio et al., 2000a). Results were dependent on chosen background levels (Rubio et al., 2000a). It is recommended that background levels are obtained by similar analytical procedures to those applied on the samples studied. In this study, the background levels established by Rubio et al. (2000b) for sediments in the Ria de Vigo were applied (Table 3). These authors established background values based on metal concentrations determined by different techniques for a long core. The three indices used gave similar results

Table 3
Mean, standard deviation (SD) and extreme values for the chosen indexes: contamination factor (CF), enrichment factor (EF) and geoaccumulation index (Igeo). Considered background levels (B) established by Rubio et al. (2000b)

B		Index	C1			C2			C3			P		
			Mean ± SD	Maximum	Minimum	Mean ± SD	Maximum	Minimum	Mean ± SD	Maximum	Minimum	Mean ± SD	Maximum	Minimum
Fe	3.51	CF	0.82 ± 0.26	1.27	0.45	0.57 ± 0.07	0.66	0.45	0.63 ± 0.08	0.73	0.49	0.06 ± 0.04	0.11	0.02
		EF	0.50 ± 0.26	1.08	0.27	0.33 ± 0.08	0.50	0.22	0.41 ± 0.05	0.52	0.33	0.08 ± 0.08	0.18	0.03
		Igeo	−0.93 ± 0.46	−0.24	−1.75	−1.42 ± 0.18	−1.18	−1.72	−1.27 ± 0.19	−1.03	−1.16	−5.04 ± 1.18	−3.81	−6.20
Mn	244.33	CF	1.53 ± 0.56	2.30	0.48	0.48 ± 0.04	0.53	0.40	1.04 ± 0.28	1.28	0.45	0.32 ± 0.30	0.66	0.09
		EF	0.92 ± 0.46	1.78	0.28	0.28 ± 0.07	0.43	0.22	0.68 ± 0.20	0.94	0.30	0.46 ± 0.54	1.08	0.12
		Igeo	−0.10 ± 0.71	0.62	−1.65	−1.66 ± 0.13	−1.50	−1.90	−0.60 ± 0.50	−0.23	−1.75	−2.72 ± 1.45	−1.19	−4.09
Cu	20	CF	2.40 ± 1.06	4.51	1.36	1.94 ± 0.16	2.02	1.62	2.23 ± 0.62	3.14	1.82	–	4.23	nd
		EF	1.36 ± 0.49	2.46	0.91	1.13 ± 0.18	1.41	0.94	1.48 ± 0.32	2.33	1.05	–	6.96	nd
		Igeo	0.56 ± 0.59	1.59	−0.14	0.36 ± 0.13	0.55	0.11	0.56 ± 0.18	1.07	0.28	–	1.50	nd
Pb	25	CF	37.29 ± 37.76	143.92	16.33	136.4 ± 93.25	243.4	15.77	61.08 ± 39.08	124.6	20.21	1686 ± 1023	2618	592
		EF	22.11 ± 22.38	84.55	9.7	88.67 ± 69.61	183.55	7.72	40.97 ± 27.57	84.8	11.64	2428 ± 1666	3703	544
		Igeo	4.3 ± 0.85	6.58	3.44	5.89 ± 1.63	7.34	3.39	5.07 ± 0.94	6.38	3.75	9.89 ± 1.12	10.77	8.62
Zn	105.34	CF	1.48 ± 0.84	3.51	0.78	1.26 ± 0.17	1.65	1.06	1.21 ± 0.26	1.92	0.86	4.07 ± 4.45	8.86	0.07
		EF	0.83 ± 0.42	1.91	0.52	0.74 ± 0.16	1.01	0.54	0.79 ± 0.17	1.15	0.53	6.00 ± 6.26	12.53	0.06
		Igeo	−0.19 ± 0.69	1.23	−0.94	−0.26 ± 0.19	0.14	−0.50	−0.34 ± 0.28	0.36	−0.80	−0.25 ± 3.70	2.56	−4.45

nd: concentration under the detection limit.

(Table 3). The most important results were that the sediments studied were contaminated by Pb. Pollution can be classified from high to very high, with concentrations which surpass from 16 to 243 times the local background levels in core samples, and up to 2600 times for surficial samples. Previous papers (Marcet Miramontes, 1994; Belzunce-Segarra et al., 1997) pointed towards traffic pollution as the main source of Pb input into the bay. However, as use of leaded gas has been substantially reduced in the last decades, a decrease toward the core tops could be expected. Consequently, industrial disposal of wastes to the bay was investigated. A ceramic factory close to the Oitabén-Verdugo mouth was the most obvious source amongst the other industries. Pb is often used in ceramic factories (Barlattani et al., 1995; Larsson et al., 1999) and in this case, is corroborated by the extremely high Pb concentrations found in glass fragments (P4), deriving from the company. This fact could explain the high Pb concentrations in the waste channel samples (P), which were located closer to the industry. The Pb concentrations in San Simón Bay, when compared with other places worldwide catalogued as contaminated (Bryan and Langston, 1992; Tkalin et al., 1996; Jones and Turky, 1997) are substantially higher.

A moderate contamination by Cu and Zn was also observed, although less notable for the latter element. Slightly high concentrations were detected for Mn in cores C1 and C3. Nevertheless, surpassing of the background level is not always an indication of pollution. An enrichment of Mn can be caused by diagenetic processes, because some compounds of this element, such as the oxyhydroxides, are very sensitive to redox changes. In the case of Fe, background levels were not exceeded, which indicates no contamination and, therefore, confirms its utility as a diagenetic indicator. As noted earlier, Fe and Mn give information about diagenetic processes. Considering total concentrations of Fe and Mn (Fig. 2), subsurficial maximum values were observed in core C1 (between 6 and 8 cm) and in cores C2 and C3 (at 10–12 cm). These maxima are due to Fe–Mn oxyhydroxides dissolution under reduced conditions. An upward migration of Fe and Mn ions is generated and their reprecipitation near the oxic-suboxic interface re-

sults. Similar distributions have been found by several authors (Barreiro, 1991; Zwolsman et al., 1993). Increases were more intense for Mn than for Fe and were more marked in cores C1 and C3 than in core C2. This is probably due to an easier migration of the liberated ions in coarse than in fine sediments. Also, the increase is stronger in core C1 than in C3, the former having a higher gravel content. This would also explain the slight enrichment of Mn detected in these two cores when CF was calculated.

Metal speciation for Pb, Zn and Fe was studied in all C samples (Figs. 4 and 5). Sample P3 was selected for waste channel sample determinations for its proximity to the ceramic industry. The Tessier et al. (1979) method was selected for chemical speciation as being the most widely applied (Allen et al., 1990; Fernandes, 1997; Mortimer and Rae, 2000; Morera et al., 2001; Ngiam and Lim, 2001; Fan et al., 2002). In spite of its well known limitations, this method is a useful tool to evaluate bioavailability, potential mobility of metals and diagenetic processes (Luoma and Bryan, 1981; Tessier and Campbell, 1987; Förstner, 1987). The lack of reference materials for these extraction methods can be overcome by comparing the sum of the concentrations obtained in each individual step with total metal concentration (Ramos et al., 1994; Fernandes, 1997). In this case, a mean variability of 10% for Pb and near 20% for Fe and Zn was obtained.

Considering core samples, fractions A and B represented the lowest contribution to total metal concentration (Fig. 4), fraction B having a slightly higher contribution. The other fractions (C, D and E) were the most abundant fractions for all the studied metals. However, the relative importance of each depended on each particular metal. For Pb, fraction E (PbE) was the most important (about 56%), followed by PbC and PbD (which constituted approximately a similar percentage: 18–20%). For Zn, fractions C and D were the most abundant and had similar contributions (35–36%). Fe showed similar distributions although in this case FeD was the most abundant (about 56%). These data showed the capacity of Fe–Mn oxyhydroxides (C) and organic matter-sulphides (D) to retain trace metals (Tessier et al., 1979; Ramos et al., 1994; Mortimer and Rae, 2000).
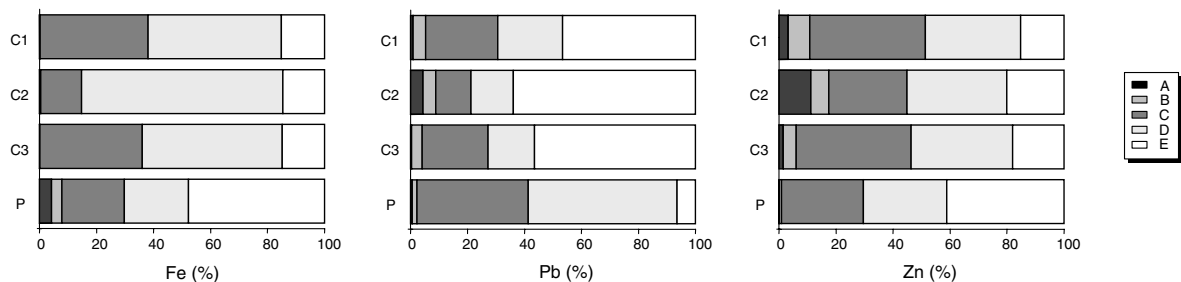

Fig. 4. Mean partitioning range of the different sedimentary fractions for core samples (C) and waste channel samples (P).

Waste channel samples showed a very different pattern to that of core samples. This could be a consequence of the very high concentrations of Pb and Zn detected. The most important fractions of Pb were PbC (about 40%) and PbD (about 50%). In waste channel samples, the residual fraction was not as abundant. This indicates that Pb in these samples was in more bioavailable fractions. Considering the ceramic industry located near the mouth of Oitabén-Verdugo River as a source of Pb input into the Bay, these results would indicate retention of Pb by sediments and redistribution among the different sedimentary compartments. Conversely, the most labile fractions (PbA and PbB) constituted less than 2% of total Pb. However, in terms of concentration they represent very high levels (365.78 ± 13.06 and 1132.91 ± 82.73 μg g^{-1}, respectively) and consequently they must not be neglected when evaluating bioavailability potential. For Zn and Fe, the residual fraction is the most important, followed by fractions C and D. This indicated, as for the case of Pb, a redistribution of Zn among the different sedimentary fractions. Concentrations in these fractions, C and D, were higher than those of the core samples, so their potential effects on biota also has to be considered. For the case of Fe, the contribution of

the most labile fractions (A and B) was higher than in core samples and they together reached about 8%.

Considering core samples in more detail, the contribution of the different fractions to total metal concentrations varied with depth for Pb and Zn, while for Fe it was quite constant (Fig. 5). Exchangeable fraction (A) in general showed the largest concentrations for Pb and Zn in core C2 (129.89 ± 112.77 and 17.63 ± 7.59 μg g^{-1}, respectively). This was the core that presented the highest organic matter and mud content. However, the highest concentrations of Fe were those of core C3 (10.70 ± 21.14 μg g^{-1}). In general terms, fraction B presented bigger concentrations than those of fraction A. Although calcium carbonate content in samples was very low, other carbonates could bind metals and appear in the samples. Pb concentrations found in this fraction were probably caused by the presence of cerussite (a highly insoluble Pb carbonate) which tends to precipitate at pH values (>6) like those of the study area (cf. Maskall and Thorton, 1998). Both fractions, A and B, correspond to metal concentrations usually bound to exchange sites of organic matter and clays and to carbonates. Metals associated with these fractions can be easily remobilized by changes in environmental
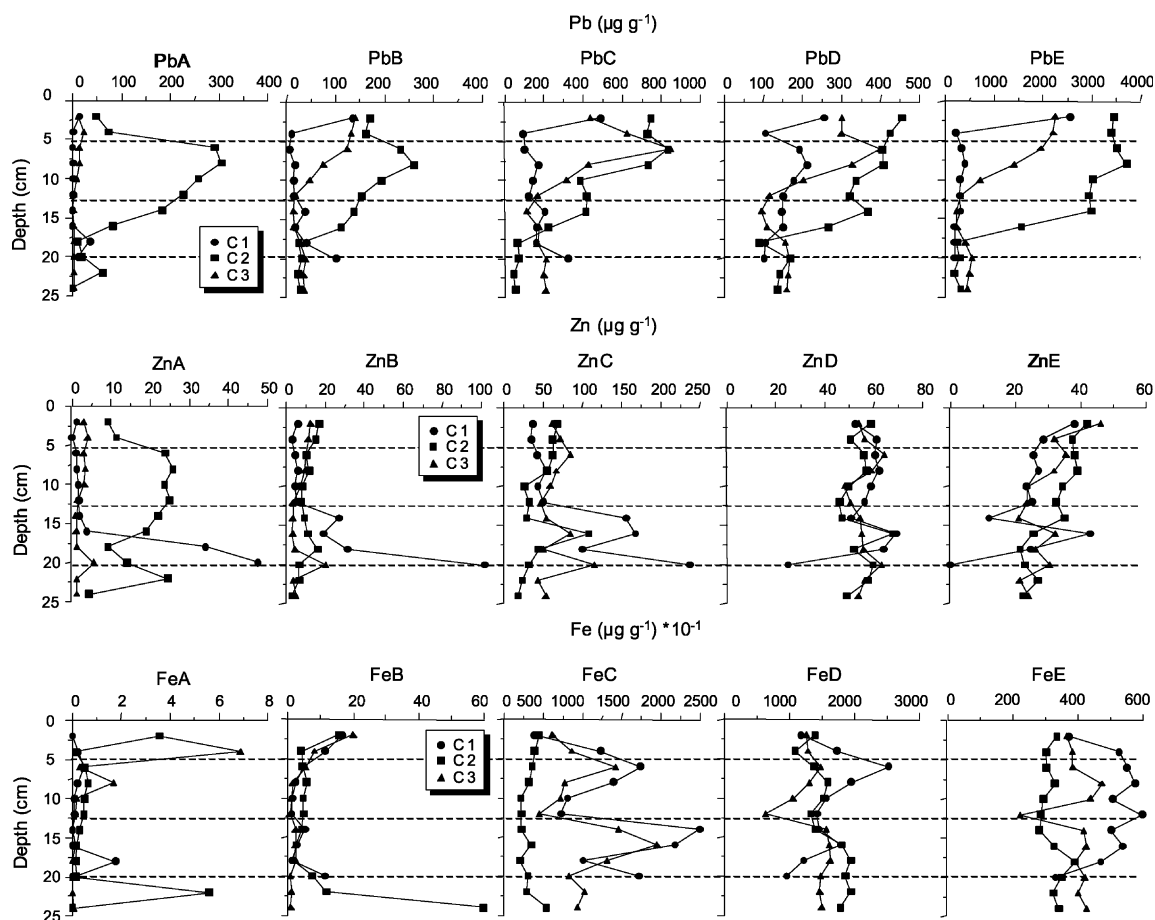

Fig. 5. Variation with depth of metal concentrations (μg g^{-1}) for the different geochemical fractions in core samples.
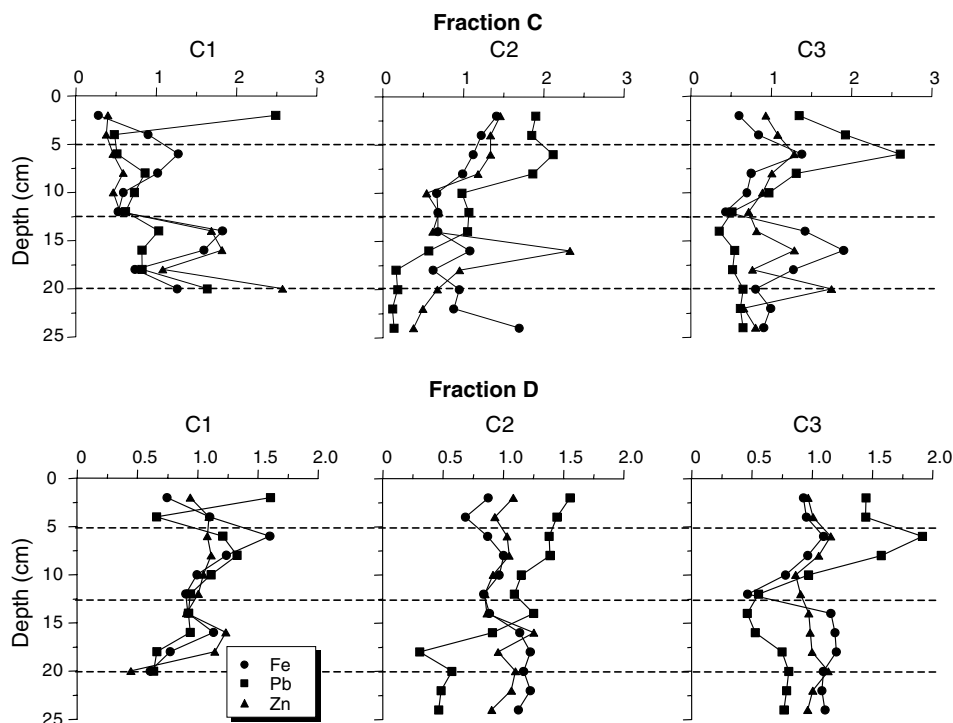
Fig. 6. Ratio between measured concentrations for fractions C and D and their mean value for every core.

conditions such as salinity or temperature (Tessier et al., 1979; Izquierdo et al., 1997), and therefore they are very susceptible to becoming bioavailable. Changes in ionic composition will basically affect the exchangeable fraction, while pH variations will affect the fraction bound to carbonates. Metal concentrations in both fractions represented a low percentage (about 0.3% for Fe, 6% for Pb and 11.5% for Zn), while Pb concentrations (Fig. 5) were on average five times over the selected background level (25 µg^{-1}). These fractions are highly bioavailable. The effects on flora and fauna within the study area were previously studied by Álvarez-Iglesias et al. (2000).

Fractions C and D distributions showed similar trends, which were observed in all cores (Fig. 6). A succession of maximum and minimum values is observed at 6–8 and 14–16 cm, enhanced when the ratio between measured concentrations and their mean value is represented to facilitate their comparison (Fig. 6). These fluctuations were interpreted as different oxidized-reduced levels, characteristic in the sediments of the study area. They were observable as an alternation of reddish and blackish thin bands, and could be interpreted as a consequence of the periodical tidal inundation that causes cyclical variations from oxidizing to reducing conditions. Bioturbation can be clearly observed in radiographies, where low energy parallel lamination, characteristic of these areas were more or less perturbed. These fractions (C and D) are affected by changes in pH, mainly for fraction C during early diagenesis. Both fractions (C and D) together constituted a

fairly constant percentage for Fe (84.87 ± 2.65%), while when considering each one separately they presented a higher standard deviation (28.83 ± 13.81% for FeC and 56.04 ± 13.01% for FeD). This could indicate a transfer of Fe from one fraction to the other, since fractions A and B represented a low percentage, and the residual fraction had in general a short variability. For example, in core C2, FeC content decreased (while FeD content increased) with depth. This could be caused by the dissolution of oxyhydroxides under reduced conditions generated by tidal inundation. When dissolution happens, adsorbed and coprecipitated ions of these compounds are liberated to interstitial water and could become part of another sedimentary phases (sulphides, carbonates) or be liberated to the solution. In marine environments under anoxic conditions, sulphide anions (generated by sulphate reduction) are likely to be present. Liberated ions can react with these sulphide anions and generate the corresponding metallic sulphide (the majority or these compounds are insoluble). So, it is probable that a metallic transfer from fraction C to fraction D takes place. The opposite process could also occur in two different ways. First, the oxygenation of anoxic sediments may occur, during which sulphides will be oxidized to sulphates and accompanying ions will be liberated. These ions could be caught by Fe–Mn oxyhydroxides (neoformed or present in the sediment in upper levels). Second, in oxic sediments the liberated metal ions, generated by organic matter decomposition, would be captured by oxyhydroxides among other
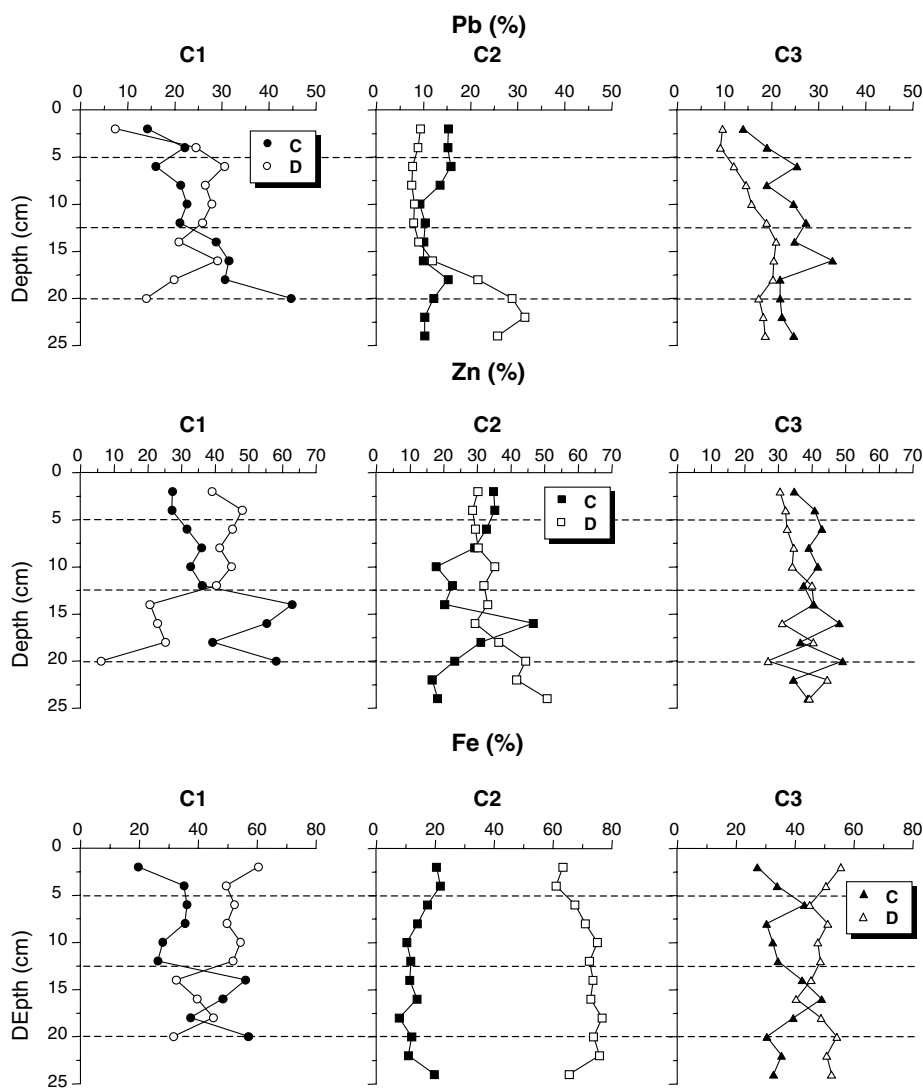
Fig. 7. Partitioning range of fractions C and D for every metal and core.

possible ligands. This could be the case for core C1, where FeD content decreased with an increase in depth, whereas FeC content as well as the organic matter content increased. Therefore, an opposite relationship could be expected between sedimentary fractions C and D. This can be clearly observed by comparison of percentage distributions of fractions C and D for every metal (Fig. 7). Zn showed a similar behaviour to that of Fe. This was not the case for Pb: PbC ($19.94 \pm 4.76\%$) and PbD ($17.65 \pm 4.16\%$) together represented $37.58 \pm 8.12\%$, and both fractions simultaneously increased their contribution with depth. This would indicate a mobilization of this metal from the residual fraction to more labile fractions (C and D) because in the marine environment Pb precipitates as sulphide in organic matter rich sediments, and is adsorbed and concentrated in oxyhydroxides (Marcet Miramontes et al., 1997). As these two fractions are affected by oxi-

dation–reduction processes, metal concentrations bound to them have to be considered when evaluating bioavailability due to their potential mobility.

Finally, the residual fraction (E) corresponding with the metal fraction in the mineral crystalline matrix, is strongly retained, and its liberation into solution under natural environmental conditions is not expected (Tessier et al., 1979). This was the most abundant fraction for Pb. Contribution of this fraction to total Pb decreased with depth: at the surface it represented 75% of total Pb, decreasing to 50% for cores C2 and C3 and to 25% for core C1. This indicates, as previously suggested, a liberation of these metals to more bioavailable fractions. This also happened to ZnE, mainly in core C1. By way of contrast, FeE represented a fairly constant percentage for all cores (about 15% of total Fe).

Data were subjected to simple statistical analysis in order to study possible associations between different
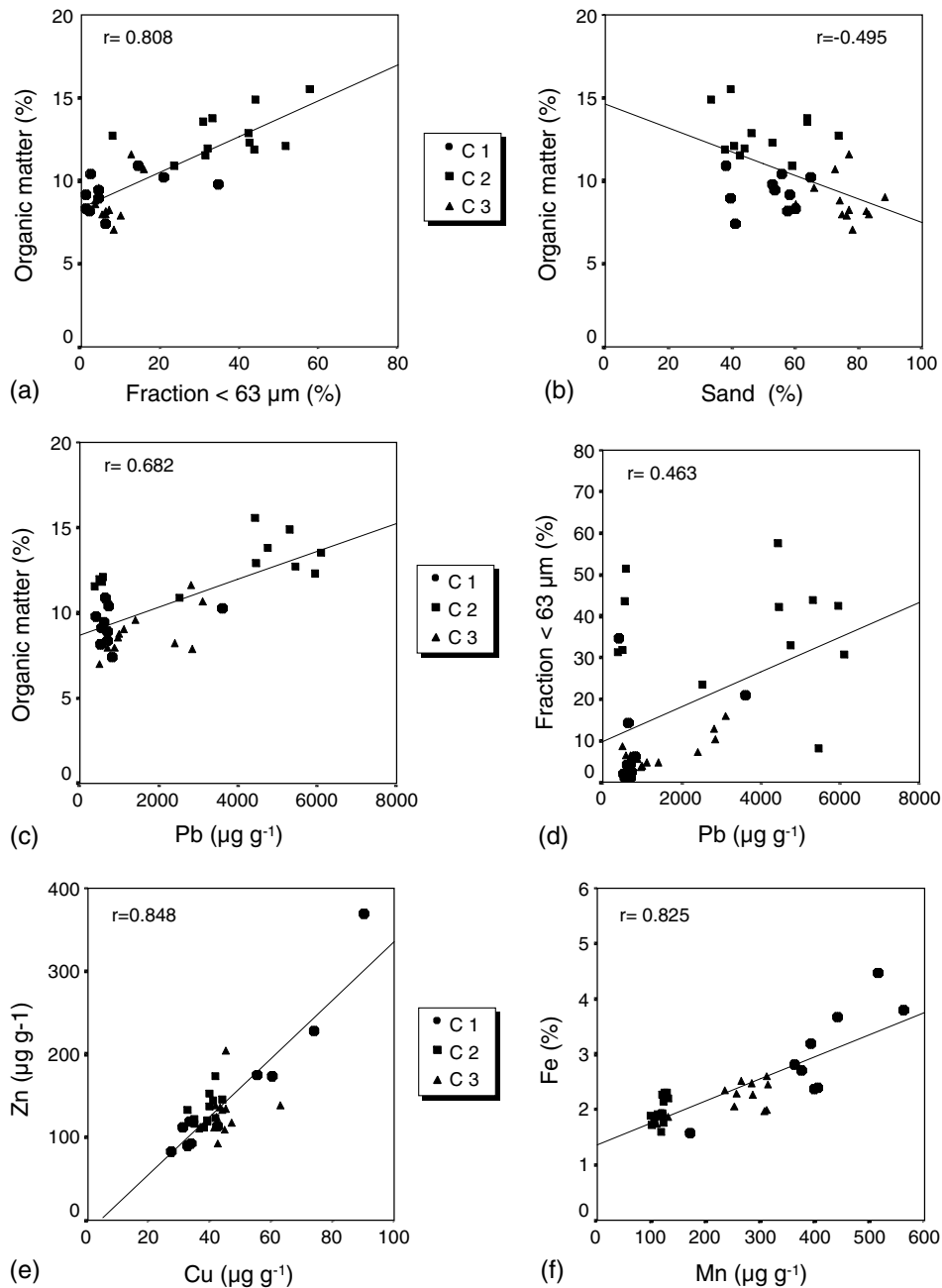
Fig. 8. Scatter plots showing the relationships between (a) organic matter and mud contents ($p < 0.001$), (b) organic matter and sand percentages $p \leqslant 0.003$, (c) total Pb content and organic matter content ($p < 0.001$), (d) total Pb content and mud percentage ($p < 0.001$), (e) total concentrations of Cu and Zn ($p < 0.001$), and (f) total concentrations of Fe and Mn ($p < 0.001$) for the three cores.

variables. The most relevant relations are shown in Fig. 8. Results showed a positive correlation between organic matter and <63 µm fraction content (Fig. 8a). This reflected an incorporation of organic matter to the finest fractions of sediments by adsorption phenomena (Salomons and Förstner, 1984), i.e., organic matter content increases when grain size decreases. This is also confirmed by the negative relationship between organic matter and sand (Fig. 8b) and gravel fractions ($r = -0.399$, $p \leqslant 0.019$).

Significant and positive relationships of total Pb with organic matter (Fig. 8c) and <63 µm fraction content (Fig. 8d) reflected that organic matter and fine materials tend to act as heavy metal binders (Salomons and Förstner, 1984; Soares et al., 1999). The inverse correlation between organic matter and Mn concentration ($r = -0.661$, $p = 0.001$) may be highlighted. This also was observed in other sediments in the Ria de Vigo (Marcet Miramontes, 1994) due to Mn association with carbonates, which are related to coarse fractions showing

low organic matter contents. Exchangeable fractions (A) of Pb and Zn showed positive and statistically significant correlations mainly with organic matter and, to a lesser extent, with mud content. This indicates the main contribution of organic matter, and the secondary contribution of fine grain size fraction to the exchange sites of these two metals. There was also a good correlation between exchangeable fractions (A) of Pb and Zn ($r = 0.558$, $p = 0.002$). Other metal correlations (total metal concentrations and metal fractions) with organic matter and mud contents were not statistically significant. This indicates that a better correlation would be obtained considering a combination of both factors (organic matter and mud content) or that other factors have to participate in binding these metals to the sediment (as for example, carbonates). If a combination of both variables is considered, a better correlation is obtained.

Considering total metal concentrations, the most noticeable positive correlations were obtained for Cu vs Zn (Fig. 8e) and Fe vs Mn (Fig. 8f). This indicated that each pair of elements has a similar origin and behaviour. Also, an opposite relationship was found between Pb and Fe, and Pb and Mn. This is probably due to the different origin of these elements: Pb content has an anthropogenic origin while Fe and Mn have a lithogenic origin.

Regarding sedimentary fractions, relationships for Fe and Zn between fractions C ($r = 0.607$, $p = 0.001$) and D ($r = 0.475$, $p = 0.005$) can be emphasized. This is related to the reported presence of alternating redox levels in sediments. A similar relationship for Pb was not found because this metal and its different fractions were highly related to organic matter content, as indicated above. Profiles of the different fractions of Pb were similar and showed significant and positive correlations between them. This could be indicative of an equilibrated distribution of the high concentrations measured between the different sediment compartments.

In order to obtain a global view of the results, principal component analysis (PCA) was applied over the data logarithmically transformed. This transformation was performed, on the one hand, to eliminate errors

Table 4
PCA results applied to logarithmically transformed metal data

Factor	Eigenvalue	Explained variance (%)	Accumulated variance (%)
1	5.854	39.023	39.023
2	2.969	19.796	58.820
3	2.027	13.513	72.333
4	1.478	9.853	82.186
5	1.050	6.998	89.184

caused by the high Pb concentrations, and on the other hand, to satisfy the assumption of constant normality and variance (Schropp and Windom, 1988; Otte et al., 1991). The use of this analysis makes it possible to reduce the number of studied variables and facilitates the interpretation of a large volume of data. Five principal components (factors) have been identified (eigenvalue = 1), explaining 89% of the data variance (Table 4). The first three factors accounted for about the 72% of the total variance. Particularly, the first factor explains 39%, the second one almost 20% and the third one, about 13.5%.

The two first factors loading plot (Fig. 9a) made it possible to differentiate between metals and between the different sediment fractions. The first factor could be interpreted as an indicator of anthropogenic influence and bioavailability, while the second factor can be envisaged as an indicator of variability in the redox level in the sediment column. Factor 1 separated Pb and Zn with positive loads (anthropogenic origin), higher for Pb than for Zn on the one side and Fe on the other. This factor also grouped the most bioavailable fractions for all metals, A and B, with high positive loadings for all metals, whereas those fractions most influenced by redox variations in sediments, C and D, showed negative loadings in the case of Fe and Zn, and lower than those of fractions A and B in the case of Pb. Factor 2 allowed differentiation between C and D fractions: the more negative the values the more the oxidizing conditions (C) whereas the more positive the values, the more reduced the conditions (D).
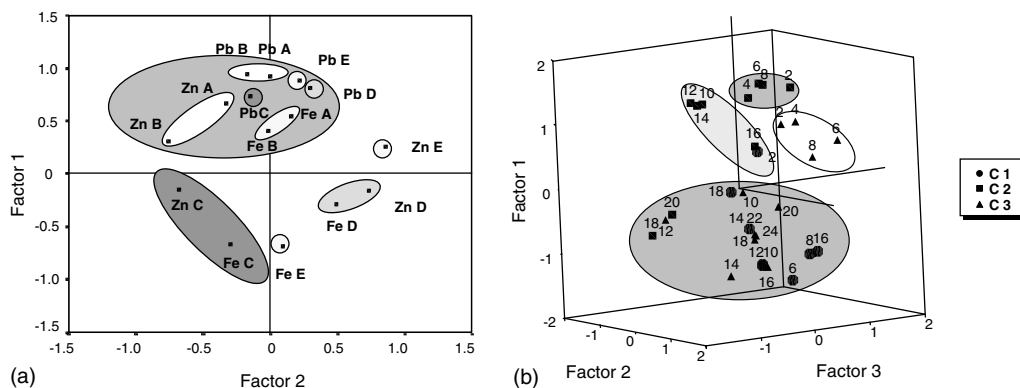

Fig. 9. PCA results: (a) Two first factors loading plot obtained in the analysis. (b) Three first factors scores plot obtained in the analysis.

Factor scores for each variable studied were represented in the plane defined by the three first components or factors (Fig. 9b). This gives a distribution of variables in three groups interpreted as three concentration levels: samples with high, intermediate or relatively low concentrations. The first group includes surficial samples (0–2 cm for core C1, 0–8 cm for core C2 and C3) which had the highest metal concentrations. A second group is formed by the intermediate samples of core C2 (8–16 cm), which had intermediate concentrations. A third group would be constituted by the rest of the samples, which can be grouped by core following the importance of measured concentrations (C2, C3 and C1, in this order, from higher to lower concentrations). This reflected that not only the closeness to the ceramic industry determines the sample metal concentration, but also sediment characteristics (mud and organic matter content, for example) and river influence are important.

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References

Allen, J.R.L., 2000. Morphodynamics of Holocene salt marshes: a review sketch from the Atlantic and Southern North Sea coasts of Europe. Quaternary Science Reviews 19, 1155–1231.

Allen, J.R.L., Rae, J.E., Zanin, P.C., 1990. Metal speciation (Cu, Zn, Pb) and organic matter in an anoxic salt marsh, Severn Estuary, Southwest Britain. Marine Pollution Bulletin 21 (12), 574–580.

Álvarez-Iglesias, P., Rubio, B., Vilas, F., 2000. Especiación de plomo en sedimentos y niveles de concentración en organismos de la zona intermareal de la Ensenada de San Simón (Ría de Vigo, NO España). Thalassas 16, 79–94.

Barlattani, M., Ferrandi, L., Fiocchi, G., Portaro, N., Triolo, L., Zappa, G., Lorenzini, G., Soldatini, G.F., 1995. Fluoride and lead environmental dispersion from a ceramic factory in the Emilia Romagna region. In: Lorenzini, G., Soldatini, G.F. (Eds.), Responses of Plants to Air Pollution: Biological and Economic Aspects. Pacini Editore, Pisa, Italy, pp. 211–215.

Barreiro Lozano, B., 1991. Estudio de metales pesados en medio y organismos de un ecosistema de Ría (Pontedeume, A Coruña). PhD, Universidad de Santiago de Compostela, 227 pp.

Belzunce-Segarra, M.J., Bacon, J.R., Prego, R., Wilson, M.J., 1997. Chemical forms of heavy metals in surface sediments of the San Simón inlet, Ría de Vigo, Galicia. Journal of Environmental Science and Health A 32, 1271–1292.

Berner, R.A., 1981. A new geochemical classification of sedimentary environments. Journal of Sedimentary Petrology 51 (2), 359–365.

Bryan, G.W., Langston, W.J., 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom Estuaries: a review. Environmental Pollution 76, 89–131.

Carral Vilariño, E., 1992. Estado de conservación de los complejos hidrolitorales de Galicia: nutrientes y metales pesados en sedimentos y organismos. PhD, Universidad de Santiago de Compostela, 164 pp.

Fan, W., Wang, W.-X., Chen, J., Li, X., Yen, Y.-F., 2002. Cu, Ni, and Pb speciation in surface sediments from a contaminated bay of Northern China. Marine Pollution Bulletin 44, 816–832.

Fernandes, H.M., 1997. Heavy metal distribution in sediments and ecological risk assessment: the role of diagenetic processes in reducing metal toxicity in bottom sediments. Environmental pollution 97 (3), 317–325.

Folk, R.L., 1954. The distinction between grain size and mineral composition in sedimentary rock nomenclature. Journal of Geology 62, 344–369.

Folk, R.L., 1974. Petrology of sedimentary rocks. Hemphill Publishing, Austin, TX, 182 pp.

Förstner, U., 1987. Sediment-associated contaminants-an overview of bases for developing remedial options. Hydrobiologia 149, 221–246.

Förstner, U., 1989. Contaminated Sediments. In: Lecture notes on Earth Science, 21. Springer-Verlag, London, 157 pp.

Fraga, F., 1981. Upwelling off the Galician Coast, NE Spain. In: Richards, F.A. (Ed.), Coastal Upwelling. American Geophysical Union, Washington, DC.

Guitián, F., Carballás, T., 1976. Técnicas de análisis de suelos. Editorial Pico Sacro, Santiago de Compostela, 288 pp.

Hakanson, L., 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Research 14, 975–1001.

Izquierdo, C., Usero, J., Gracia, I., 1997. Speciation of heavy metals in sediments from salt marshes on the Southern Atlantic Coast of Spain. Marine Pollution Bulletin 34 (2), 123–128.

Jones, B., Turky, A., 1997. Distribution and Speciation of heavy metals in surficial sediments from the Tees Estuary, North-East England. Marine Pollution Bulletin 34 (10), 768–779.

Larsson, S., Bergback, B., Eklund, M., Lohm, U., 1999. Historical emissions from Swedish crystal-glass production and future scenario of soil-lead pollution. Environmental Reviews 7 (2), 53–61.

Luoma, S.N., Bryan, G.W., 1981. A statistical assessment of the form of trace metals in oxidized estuarine sediment employing chemical extractants. The Science of the Total Environment 17, 165–196.

Macías Vázquez, F., 1981. Formation of gibbsite in soils and saprolites of temperate-humid zones. Clay Minerals 16, 43–52.

Marcet Miramontes, M.P., 1994. Contribución al estudio de la contaminación de la Ría de Vigo. Contenido y distribución de nutrientes y metales pesados en sedimentos someros. PhD, Universidad de Vigo, Vigo, 287 pp.

Marcet Miramontes, P., Couce, M.L., Montero Vilariño, M.J., 1997. Contenido y enriquecimiento de metales en sedimentos de la Ría de Vigo (España). Thalassas 13, 87–97.

Maskall, J.E., Thorton, I., 1998. Chemical partitioning of heavy metals in soils, clays and rocks at historical lead smelting sites. Water, Air and Soil Pollution 108, 391–409.

Morera, M.Y., Echevarría, J.C., Mazkiarán, C., Garrido, J.J., 2001. Isotherms and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils. Environmental Pollution 113, 135–144.

Mortimer, R.J.G., Rae, J.E., 2000. Metal speciation (Cu, Zn, Pb, Cd) and organic matter in oxic to suboxic salt marsh sediments, Severn Estuary, Southwest Britain. Marine Pollution Bulletin 40 (5), 337–386.

Müller, G., 1979. Schwermetalle in den sedimenten des Rheins-Veränderungen seitt 1971. Umschan 79, 778–783.

Ngiam, L.-S., Lim, P.-E., 2001. Speciation patterns of heavy metals in tropical estuarine anoxic and oxidized sediments by different sequential extraction schemes. The Science of the Total Environment 275, 53–61.

Nombela, M.A., Vilas, F., 1986–1987. Medios y submedios en el sector intermareal de la Ensenada de San Simón. Ría de Vigo Pontevedra: secuencias sedimentarias características. Acta Geológica Hispánica 21–22, 223–231.

Nombela, M.A., Vilas, F., García-Gil, S., García-Gil, E., Alejo, I., Rubio, B., Pazos, O., 1994. Metales pesados en el registro sedimentario reciente en la Ensenada de San Simón, parte interna de la Ría de Vigo (Galicia, España). Gaia 8, 149–156.

Nombela, M.A., Vilas, F., Evans, G., 1995. Sedimentation in the mesotidal Rias Bajas of Galicia (North-Western Spain): Ensenada de San Simón, Inner Ría de Vigo. Special Publications International Association of Sedimentologists 24, 133–149.

Otte, M.L., Bestebroer, S.J., Van Der Linden, J.M., Rozema, J., Broekman, R.A., 1991. A survey of zinc, copper and cadmium concentrations in salt marsh plants along the Dutch Coast. Environmental Pollution 72, 175–189.

Pazos, O., Nombela, M.A., Vilas, F., 2000. Continental contribution of suspended sediment to an estuary: Ría de Vigo. Scientia Marina 64 (3), 295–302.

Prego, R., 1993. General aspects of carbon biogeochemistry in the Ria of Vigo, Northwestern Spain. Geochimica et Cosmochimica Acta 57, 2041–2052.

Ramos, L., Hernández, L.M., González, M.J., 1994. Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Doñana National Park. Journal of Environmental Quality 23, 50–57.

Rubio, B., Nombela, M.A., Vilas, F., 2000a. Geochemistry of major and trace elements in sediments of the Ría de Vigo (NW Spain): an assessment of metal pollution. Marine Pollution Bulletin 40 (11), 968–980.

Rubio, B., Nombela, M.A., Vilas, F., 2000b. La contaminación por metales pesados en las Rías Bajas gallegas: nuevos valores de fondo para la Ría de Vigo (NO de España). Journal of Iberian Geology 26, 121–149.

Salomons, W., Förstner, U., 1984. Metals in the Hydrocycle. Springer-Verlag, Berlin, Heilderberg, New York, Tokyo, 349 pp.

Schropp, S.J., Windom, H.L., 1988. A guide to the interpretation of metal concentrations in estuarine sediments. Coastal Zone Management Section, Department of Environmental Regulation, Florida, 74 pp.

Soares, H.M.V.M., Boaventura, R.A.R., Machado, A.A.S.C., Esteves da Silva, J.G.G., 1999. Sediments as monitors of heavy metal contamination in the Ave river basin (Portugal): multivariate analysis of data. Environmental Pollution 105, 311–323.

Tessier, A., Campbell, P.G.C., 1987. Partitioning of trace metals in sediments: relationships with bioavailability. Hydrobiologia 149, 43–52.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metal. Analytical Chemistry 51, 844–851.

Tkalin, A.V., Presley, B.J., Boothe, P.N., 1996. Spatial and temporal variations of trace metals in bottom sediments of Peter the Great Bay, the Sea of Japan. Environmental Pollution 92 (1), 73–78.

Vilas, F., Nombela, M.A., García-Gil, E., García-Gil, S., Alejo, I., Rubio, B., Pazos, O., 1995. Cartografía de sedimentos submarinos, Ría de Vigo, E: 1:50000. Xunta de Galicia, 40 pp.

Vilas, F., García-Gil, E., García-Gil, S., Nombela, M.A., Alejo, I., Rubio, B., Pazos, O., 1996. Cartografía de sedimentos submarinos, Ría de Pontevedra, E: 1:50000. Xunta de Galicia, Santiago de Compostela, 40 pp.

Vilas, F., García-Gil, S., García-Gil, E., Nombela, M.A., Alejo, I., Francés, G., Méndez, G., 1999. Cartografía de sedimentos submarinos, Ría de Arousa, E: 1:50000. Xunta de Galicia, 31 pp.

Vos, P.C., van Kesteren, W.P., 2000. The long-term evolution of intertidal mudflats in the northern Netherlands during the Holocene; natural and anthropogenic processes. Continental Shelf Research 20 (12–13), 1687–1710.

Zoller, W.H., Gladney, E.S., Gordon, G.E., Bors, J.J., 1974. Emissions of trace elements from coal fired power plants. In: Hemphill, D.D. (Ed.), Trace Substances in Environmental Health (8). Rolla, University of Missouri, Colombia, pp. 167–172.

Zwolsman, J.J.G., Berger, G.W., Van Eck, G.T.M., 1993. Sediment accumulation rates, historical input, postdepositional mobility and retention of major elements and trace metals in salt marsh sediments of the Scheldt Estuary, SW Netherlands. Marine Chemistry 44, 73–94.

Heavy metal levels in bottlenose and striped dolphins off the Mediterranean coast of Israel

Mia Roditi-Elasar [a], Dan Kerem [a,*], Hava Hornung [b], Nurit Kress [b], Efrat Shoham-Frider [b], Oz Goffman [a], Ehud Spanier [a]

[a] *Israel Marine Mammal Research & Assistance Center, The Leon Recanati Institute for Maritime Studies and Department for Maritime Civilizations, The University of Haifa, Mt. Carmel, Haifa 31905, Israel*
[b] *Israel Oceanographic and Limnological Research, National Institute of Oceanography, Tel-Shikmona, P.O. Box 8030, Haifa 31080, Israel*

* Corresponding author. Fax: +972-4-8240493.
E-mail address: dankerem@research.haifa.ac.il (D. Kerem).

Very little is known about heavy metal concentrations in tissues of cetaceans inhabiting the Eastern Mediterranean. This report presents such data for two Delphinid species: the bottlenose dolphin (*Tursiops truncatus*)