

Distribution and Geochemical Partitioning of Heavy Metals in Sediments of the Bahía Blanca Estuary, Argentina

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ABSTRACT

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A long-term study programme has evaluated heavy metals in the Bahía Blanca estuary, considering occurrence, concentration and distribution in the estuarine sediments, as well as their corresponding geochemical partitioning in the <62 µm grain size fraction of the sediment. Total concentrations of heavy metals (Cd, Zn, Cu, Cr, Pb, Fe) have been determined through flameless atomic absorption spectrophotometry (AAS). Geochemical partitioning of these metals was determined following a sequential extraction technique. Furthermore, heavy metal distribution was studied against organic matter concentration within the sediments.

The results allow the characterization of the spatial distribution of the metals, together with their accumulation areas and potential sources. Bahía Blanca estuarine sediments have low to medium heavy metal concentrations. The geochemical partitioning indicated that many bioavailable species occur within the system, including those of highly toxic elements such as cadmium. Moreover, a theoretical scheme of transference of these metals to other compartments within the system was proposed. Finally, the environmental status of the estuary was addressed within the described framework.

ADDITIONAL INDEX WORDS: *Heavy metals, estuarine sediments, accumulation processes, anthropic sources.*

INTRODUCTION

Trace metals have been shown to be significantly hazardous pollutants in aquatic environments, even at very low concentrations (SALOMONS and FÖRSTNER, 1984; NRIAGU and PACYNA, 1988; SALOMONS and STIGLIANI, 1995). In this sense, the study of the occurrence, fate and distribution of trace metals in coastal marine and estuarine environments has received major attention, mainly because of the persistent toxic effects of heavy metals (LACERDA *et al.*, 1988), as well as their ability to be accumulated within compartments of these environments (LACERDA and ABRÃO, 1984). Thus, a large amount of environmental monitoring programmes have been carried out assessing metal distribution within coastal ecosystems (*i.e.*, JICKELS and KNAP, 1984; PATCHINEELAM *et al.*, 1988; FOWLER, 1990; LACERDA *et al.*, 1999). The physical or physico-chemical processes controlling the behaviour of heavy metals, and the geochemical partitioning of these elements in sediments are basic to understand potentially toxic events in the considered environments. Research pro-

grammes directed to address these topics have been developed in different ecosystems, including Latin American ones (*i.e.*, SOUZA *et al.*, 1986; PONCE-VELEZ and BOTELLO, 1991; BARCELLOS *et al.*, 1991). However, the combined analysis of both kinds of processes on the distribution of heavy metals has still been scarce and is limited to a few papers (LACERDA, 1996; LACERDA *et al.*, 1996; ALLER, 1999). In the particular case of the Bahía Blanca estuary in Argentina, background data on heavy metal contents and the distribution of its sediments include studies developed during the '80s (*i.e.*, MARCOVECCHIO *et al.*, 1986; VILLA and PUCCI, 1987; PUCCI, 1988) as well as the '90s (*i.e.*, FERRER *et al.*, 1996a; ANDRADE *et al.*, 1996). In addition, data on geochemical partitioning of heavy metals in Bahía Blanca sediments have been opportunely reported (FERRER *et al.*, 1996a, b).

The present paper deals with the analysis of several heavy metal (*i.e.*, cadmium, zinc, copper, chromium, iron and lead) concentration and distribution in Bahía Blanca estuary sediments, not only in the total sediment fraction but also in the one corresponding to the <62 µm grain-size, as well as with the determination of the geochemical partitioning of the mentioned metals in the sediments. Finally, metal levels were correlated with organic matter contents within sediments,

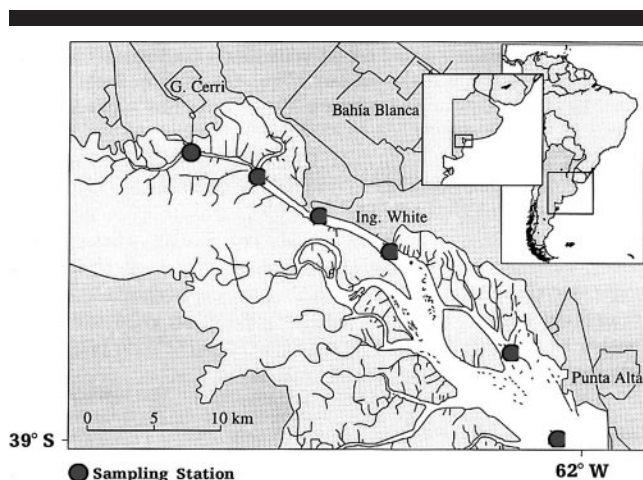


Figure 1. Location of sampling stations within Bahía Blanca estuary.

keeping in mind that is a significant scavenger of metals in both coastal and estuarine environments (SALOMONS and STIGLIANI, 1995). The information was integrated to determine the health status of this environment.

MATERIALS AND METHODS

Description of Studied Area

Bahía Blanca is a mesotidal coastal plain estuary (PERILLO *et al.*, 2001) located between 38°45' and 39°40'S, and 61°45' and 62°30'W, in the southeastern area of Buenos Aires Province within Argentina (Figure 1). It has an elongated form, northwestern–southeastern directed, about 80 km long within the Main Channel, and numerous streams which separate islands and tidal flats (PERILLO and PICCOLO, 1991). Water interchange within the bay is influenced by a semidiurnal tidal regime. The bay encompasses an area of 400 km², and at high tide the total area is close to 1300 km² (VILLA and PUCCI, 1987). The hydrography of the estuary is strongly influenced by climatic conditions (FREIJE *et al.*, 1981). Several streams and channels flow into the bay, most of them affected by anthropogenic activities. The freshwater contribution is approximately 4000 m³day⁻¹. Tidal oscillations of 3 m and predominant northwesterly winds create strong tidal currents which facilitate water mixing, leading to a uniform vertical distribution of the main oceanographic parameters (PICCOLO and PERILLO, 1990).

Various ports, towns (with a population exceeding 300,000 inhabitants) and industries are located at the northern boundaries of the estuary, and several streams discharge into the area. Oil refineries and terminals, petrochemical industries, meat factories, leather plants, fish factories, textile plants, wool washing plants, silos and cereal mills discharge their processing residues into the streams or directly into the estuary. Nearly 10 m³day⁻¹ of raw sewage is discharged into the study area (PUCCI, 1988; ANDRADE, 2001; FERRER, 2001). This estuary is extensively used by fishing boats, oil tankers and cargo vessels and requires regular dredging. So, this coastal marine system receives contaminant inputs from mu-

nicipal waste-waters, direct industrial discharges, harbour related operations, runoff water which carries materials from land development areas and aerial fallout from atmospheric pollutants.

Six sample stations have been established along the estuary (Figure 1), including different areas influenced by the above mentioned potential sources of pollution.

Sampling and Analytical Treatment of Samples

Oceanographic surveys were carried out within the Bahía Blanca estuary, using a transect which included six (6) sampling stations along the Main Navigation Channel (Figure 1). Surface sediment samples were obtained in these places using a stainless steel sediment sampler. On board, sediment samples were kept in plastic bags and stored in a freezer at -20°C until treated in the laboratory.

In a first step sediment samples were oven dried at low temperature (50 ± 5°C) overnight up to constant weight. After this, two sub-samples were separated: One of them was sieved through stainless steel meshes in order to separate sediment with grain size <62 μm; this fraction was stored in acid-cleaned glass bottles in a dessicator, prior to analytical treatment. The other sub-sample was homogenized in a porcelain mortar and also stored in acid-cleaned glass bottles in a dessicator, prior to analytical treatment; moreover, sediment samples for organic matter determination as well as for geological characterization were removed from this second mentioned sub-sample.

Total metal concentrations (Cd, Zn, Cu, Cr, Pb, Fe) within total sediments were determined following the method opportunely described by MARCOVECCHIO *et al.* (1988). This technique includes a sediment mineralization within a strong acid mixture (HClO₄:HNO₃, 1:3) under controlled temperature (110 ± 5°C). The residue was diluted in 0.7% (v/v) HNO₃ up to 10 ml. Metal concentrations in these solutions were measured using AAS with air-acetylene flame and deuterium background correction (D₂BGC).

For the study of heavy metal geochemical fractioning in Bahía Blanca sediments (<62 μm fraction), a sequential extraction method was applied, following the modification of LACERDA *et al.* (1988b) and MADDOCK and LOPES (1988) on the technique proposed by MEGALATTI *et al.* (1983a,b). This methodology has provided information on the metal content of five geochemical fractions: (i) F₁, exchangeable adsorbed metals; (ii) F₂, oxidisable metal complexes; (iii) F₃, metals in carbonates; (iv) F₄, metals in reducible compounds; and, (v) F₅, residual metals.

Organic matter content in analyzed sediments was determined following the method originally described by STRICKLAND and PARSONS (1968), which includes a wet oxidation of organic carbon with acidic potassium dichromate and measurement through spectrophotometry.

A Perkin Elmer AA-2380 atomic absorption spectrophotometer was used for metal determinations. Analytical grade reagents were utilized for sediment mineralization as well as for blanks and calibration curve standards build ups. In all cases bidistilled water was used to prepare the corresponding solutions.

Table 1. Heavy metal concentrations ($\mu\text{g}\cdot\text{g}^{-1}$, d.w.) in total sediments of Bahía Blanca estuary. (Fe concentrations in $\text{mg}\cdot\text{g}^{-1}$, d.w.) (mean value \pm standard deviation).

Sampling Station	Total Heavy Metal Concentrations ($\mu\text{g}\cdot\text{g}^{-1}$, d.w.)					
	Cd	Zn	Cu	Cr	Pb	Fe ($\text{mg}\cdot\text{g}^{-1}$)
Station #1	0.15 ± 0.08	25.73 ± 4.92	5.88 ± 1.73	3.56 ± 1.45	8.53 ± 2.12	12.34 ± 2.38
Station #2	0.96 ± 0.24	48.06 ± 5.27	13.83 ± 2.65	6.45 ± 1.53	14.42 ± 2.30	16.19 ± 2.87
Station #3	2.06 ± 0.30	59.02 ± 5.43	16.46 ± 2.08	9.21 ± 1.64	18.45 ± 2.67	19.51 ± 2.91
Station #4	2.23 ± 0.31	60.21 ± 4.86	18.10 ± 1.88	8.73 ± 1.53	19.82 ± 2.23	20.68 ± 2.98
Station #5	0.77 ± 0.14	52.34 ± 5.82	14.85 ± 1.88	8.44 ± 1.51	17.76 ± 2.98	18.89 ± 2.82
Station #6	0.62 ± 0.15	52.96 ± 5.67	16.01 ± 1.85	7.86 ± 1.65	15.72 ± 2.86	18.96 ± 2.31

Analytical quality was checked against international reference materials (*pond sediment flour*, R.M.N^o2) provided by The National Institute for Environmental Studies (NIES) from Tsukuba University (Japan). For all metals analyzed, recovery percentages concurred with official NIES calibration exercises.

Statistical comparisons were developed using analysis of variance (ANOVA), mean values assessment (Tukey's test), correlation analysis and single linear regression analysis (SOKAL and ROHLF, 1979).

RESULTS

Total Metal Concentrations

Selected metal (Cd, Zn, Cu, Cr, Pb, Fe) concentrations were determined in Bahía Blanca estuarine sediments (Table 1, Figure 2).

Cadmium levels varied between non detectable values and

up to $2.50 \mu\text{g}\cdot\text{g}^{-1}$, with average values at individual stations varying between 0.15 ± 0.08 and $2.23 \pm 0.31 \mu\text{g}\cdot\text{g}^{-1}$ (Table 1). One factor ANOVA carried out showed that Cd levels in sediments from Station #1 were significantly different ($p < 0.01$) from those of the other sampling stations. On the other hand, levels from Station #2 were different ($p < 0.01$) from those of Station #3; levels from Station #5 were different ($p < 0.01$) from the levels at Stations #3 and #4; and, those from Station #6 were different ($p < 0.01$) from the values of Stations #2, #3 and #4.

In the case of zinc, mean values at individual stations varied between 25.73 ± 4.92 and $60.21 \pm 4.86 \mu\text{g}\cdot\text{g}^{-1}$ (Table 1), with a minimum and a maximum of 0.61 and $70.03 \mu\text{g}\cdot\text{g}^{-1}$, respectively. ANOVA has shown that Zn values at Station #1 were significantly different ($p < 0.01$) from those of the other sampling stations. Moreover, Zn levels at Station #2 were different ($p < 0.01$) from those of Stations #3 and #4; levels from Station #5 were also different ($p < 0.01$) from those of Stations #3 and #4; and, Station #6 showed levels different from those of Station #4 ($p < 0.01$) and Station #3 ($p < 0.05$).

Copper concentrations presented a variation range between 3.51 and $20.99 \mu\text{g}\cdot\text{g}^{-1}$, with an average variation at individual stations between 5.88 ± 1.73 and $18.10 \mu\text{g}\cdot\text{g}^{-1}$ (Table 1). Cu levels in Station #1 sediments have been significantly different ($p < 0.01$) from those of all the other stations. Furthermore, values at Station #2 were different from those of Stations #3 and #4 ($p < 0.01$); levels from Station #5 were different from those of Station #4 ($p < 0.01$), while, levels from Station #6 were different from Station #4 levels ($p < 0.05$).

Chromium mean values at individual stations have been ranged from 3.56 ± 1.45 to $9.21 \pm 1.64 \mu\text{g}\cdot\text{g}^{-1}$ (Table 1), with a minimum of $1.58 \mu\text{g}\cdot\text{g}^{-1}$ and a maximum of $12.16 \mu\text{g}\cdot\text{g}^{-1}$. Application of ANOVA has shown that Cr concentrations in sediments from Station #1 were always different ($p < 0.01$) from those corresponding to the other sampling stations. Also, values from Station #2 were different ($p < 0.01$) from those of Stations #3, #4 and #5.

In the analysis of lead concentrations in Bahía Blanca sediments, a variation range between 4.18 and $27.72 \mu\text{g}\cdot\text{g}^{-1}$ was observed, with an average range at individual stations between 8.53 ± 2.12 and $19.82 \pm 2.23 \mu\text{g}\cdot\text{g}^{-1}$ (Table 1). Also in this case ANOVA has shown that Pb concentrations at Station #1 were always different ($p < 0.01$) from those of the other sampling stations. Simultaneously, Pb concentrations at Station #2 were different ($p < 0.01$) from those of Stations #3, #4 and #5.

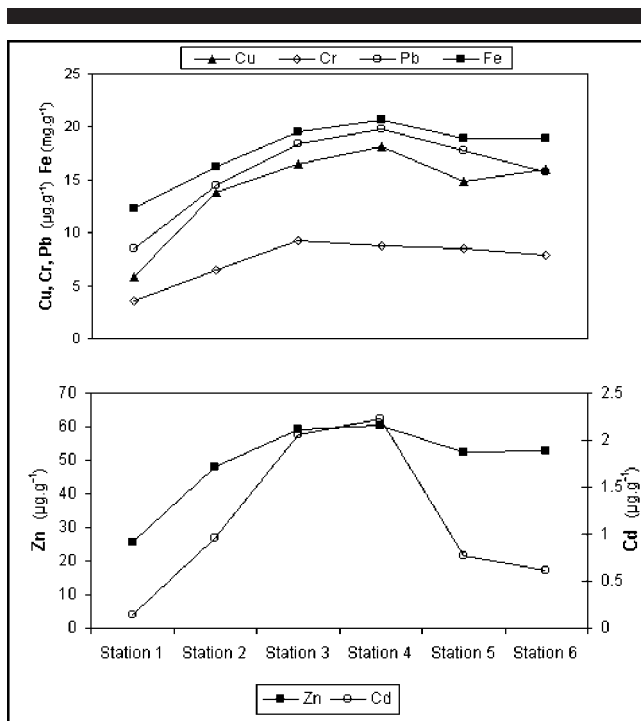


Figure 2. Total metals distribution in total sediments from Bahía Blanca estuary.

Finally, when iron concentrations were studied it was observed that mean values at individual stations varied between 12.34 ± 2.38 and 20.68 ± 2.98 $\text{mg}\cdot\text{g}^{-1}$ (Table 1), with corresponding minimum and maximum levels of 9.25 $\text{mg}\cdot\text{g}^{-1}$ and 26.29 $\text{mg}\cdot\text{g}^{-1}$, respectively. ANOVA has shown that Fe contents in sediments from Station #1 were always different ($p < 0.01$) from those of the other sampling stations, while values at Station #2 were also different ($p < 0.01$) from those at Stations #3 and #4.

Metals Geochemical Partitioning

Geochemical partitioning of heavy metals within the finest fraction (<63 μm) of Bahía Blanca estuarine sediments was studied. The results are presented in percentage of metal concentration in each analyzed geochemical fraction.

Cadmium geochemical partitioning exhibited the follow trend: 25.73 ± 2.99 to $66.60 \pm 2.23\%$ was recorded in the F_5 (residual metals); 7.96 ± 0.76 to $19.40 \pm 0.80\%$ in the F_4 (metals in reducible compounds); 4.53 ± 0.35 to $14.83 \pm 1.01\%$ in the F_3 (metals in carbonates); 4.97 ± 0.25 to $17.07 \pm 0.74\%$ in the F_2 (oxidisable metal complexes); while, 8.67 ± 0.75 to $22.97 \pm 1.51\%$ was in the F_1 (exchangeable adsorbed metals) (Figure 3a). When the spatial distribution of Cd linked with sediment geochemical fractions was studied, it was observed that the lowest percentage of Cd- F_1 ($8.67 \pm 0.75\%$) was recorded at Station #1 (outer area of the estuary) while the highest ($22.97 \pm 1.51\%$) was at Station #3 (close to the Ing.White port). The same trend was recorded for Cd- F_2 ($4.97 \pm 0.25\%$ and $17.07 \pm 0.74\%$ respectively) as well as for Cd- F_3 ($4.53 \pm 0.35\%$ and $14.83 \pm 1.01\%$ respectively). Unlike these, the lowest Cd- F_4 percentage was recorded in the inner area of the estuary (Station #6, $7.96 \pm 0.76\%$) while the highest one was close to the Ing.White port (Station #3, $19.40 \pm 0.80\%$). Finally, the lowest level of Cd- F_5 was measured at Station #3 ($25.73 \pm 2.99\%$) and the highest at Station #2 (close to Bahía Blanca city sewage outfall, $66.60 \pm 2.82\%$). In the case of cadmium, a percentage between 13% and 40% was recorded within the *potentially bioavailable fraction* (PBF = $F_1 + F_2$) (MARCOVECCHIO *et al.*, 1998), which indicated that a significant amount of Cd could be assimilated by the organisms within this environment.

Zinc geochemical partitioning followed the trend: 40.05 ± 0.44 to $66.95 \pm 3.01\%$ was recorded in the F_5 (residual); 18.79 ± 1.69 to $31.14 \pm 1.54\%$ in the F_4 (reducible); 3.68 ± 1.68 to $15.82 \pm 1.51\%$ in the F_3 (carbonates); 1.50 ± 0.36 to $6.56 \pm 0.43\%$ in the F_2 (oxidisable); while, 1.06 ± 0.18 to $18.78 \pm 0.46\%$ was in the F_1 (exchangeable) (Figure 3b). The analysis of spatial distribution of Zn geochemical partitioning has shown that for Zn- F_1 , Zn- F_2 and Zn- F_3 , Station #1 (at the outer area of the estuary) has presented quite high percentages ($18.78 \pm 0.46\%$, $6.56 \pm 0.43\%$ and $15.82 \pm 1.51\%$ respectively), and values were significantly lower (no more than $3.08 \pm 0.25\%$, $4.50 \pm 0.62\%$, and $6.12 \pm 0.40\%$ respectively) in all the inner areas. In the case of Zn- F_4 the lowest value ($18.79 \pm 1.69\%$) was recorded at Station #1 (in the outer area), while the highest ($31.14 \pm 1.54\%$) was measured at Station #2 (close to Bahía Blanca city sewage outfall discharge). Furthermore, Zn- F_5 has shown the minimum value

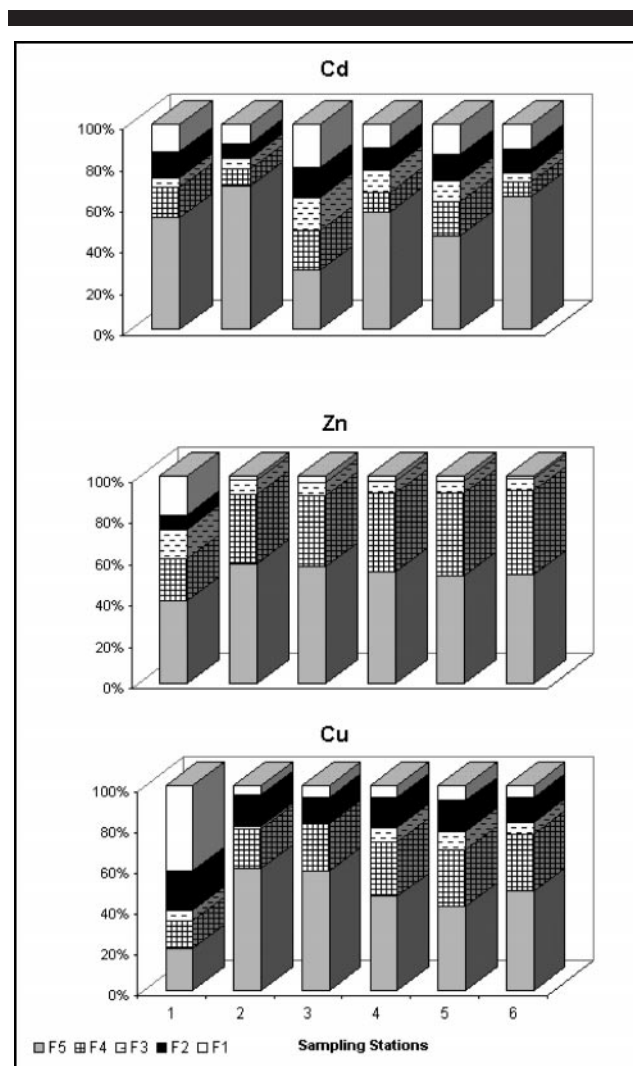


Figure 3. Geochemical partitioning (%) of heavy metals in Bahía Blanca finest sediment.

($40.05 \pm 0.44\%$) at Station #1 and the corresponding maximum ($66.95 \pm 3.01\%$) was recorded at Station #4 (close to Galván port). In the case of zinc the PBF varied between 3% and 25%, which indicated potential level of this element to be assimilated by organisms.

For copper geochemical fractioning 21.61 ± 1.36 to $53.01 \pm 1.90\%$ was measured in the F_5 (residual); 13.71 ± 0.22 to $26.68 \pm 1.71\%$ in the F_4 (reducible); 5.50 ± 0.61 to $9.54 \pm 0.77\%$ in the F_3 (carbonates); 12.68 ± 0.46 to $18.61 \pm 0.93\%$ in the F_2 (oxidisable); and, 3.80 ± 0.43 to $40.57 \pm 0.86\%$ was in the F_1 (exchangeable) (Figure 3c). The analysis of spatial distribution of Cu geochemical fractioning has shown that for Cu- F_1 and Cu- F_2 , Station #1 (at the outer area of the estuary) had the highest percentages ($40.57 \pm 0.86\%$ and $18.61 \pm 0.93\%$ respectively), while for the other geochemical fractions it had the lowest ones (*i.e.*, Cu- F_3 = $5.5 \pm 0.61\%$, Cu- F_4 = $13.71 \pm 0.22\%$, and Cu- F_5 = $21.61 \pm 1.36\%$). Moreover, the lowest Cu- F_1 value ($3.80 \pm 0.43\%$) was recorded at Station

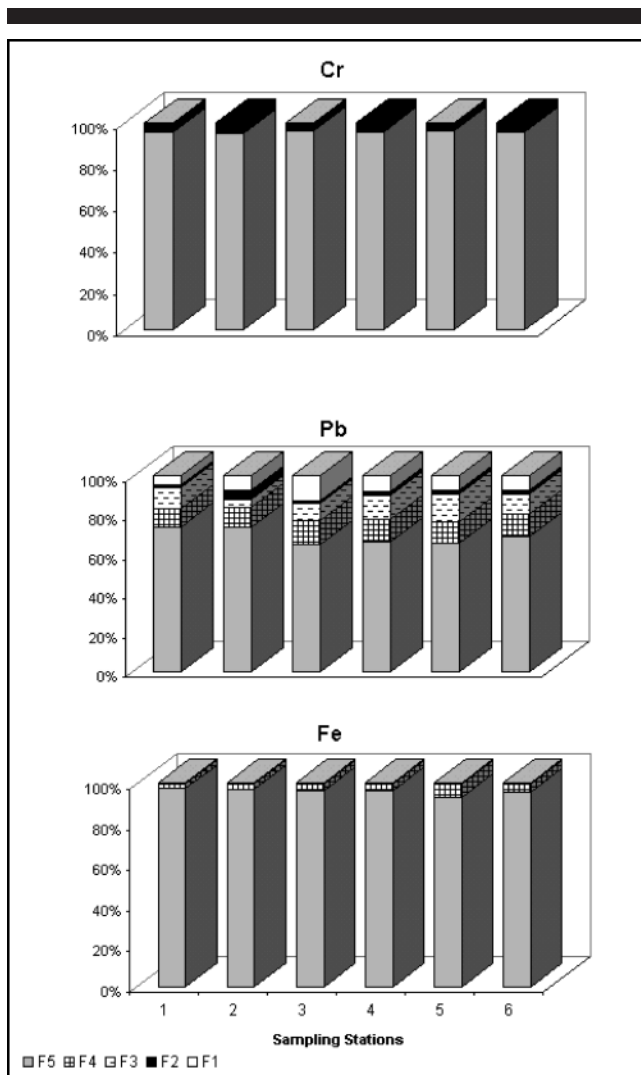


Figure 4. Geochemical partitioning (%) of heavy metals in Bahía Blanca finest sediment.

#4 (close to Galván port), and for Cu-F₂ it was $12.68 \pm 0.46\%$ at Station #3 close to Ing. White port). The highest percentage for Cu-F₃ ($9.54 \pm 0.77\%$) was recorded at Station #5, for Cu-F₄ ($26.08 \pm 1.71\%$) at Station #6, and for Cu-F₅ ($53.01 \pm 1.90\%$) at Station #2. The Cu geochemical fractioning values identified a PBF of between 19% and 59%, which indicated the potential level of this element which could be assimilated by organisms.

Chromium geochemical partitioning distribution showed that 96.14 ± 1.26 to $97.52 \pm 0.58\%$ was recorded in the F₅ (residual fraction), and 2.48 ± 0.58 to $3.86 \pm 1.26\%$ in the F₂ (oxidisable fraction). None of the other analyzed geochemical fractions (F₄, F₃ and F₁) had detectable values (Figure 4a). Analysis of the spatial distribution showed no significant differences between Cr levels at all stations. Moreover, chromium PBF was always lower than 3%, which indicates scarce probabilities that this element can be assimilated by organisms in the estuary.

The assessment of lead geochemical fractioning showed that 62.20 ± 0.85 to $76.57 \pm 0.67\%$ was recorded in the F₅ (residual); 8.66 ± 0.65 to $14.87 \pm 1.46\%$ in the F₄ (reducible); 3.80 ± 0.36 to $13.43 \pm 1.21\%$ in the F₃ (carbonates); 1.37 ± 0.15 to $6.50 \pm 0.44\%$ in the F₂ (oxidisable); and, 3.10 ± 0.30 to $13.17 \pm 1.47\%$ was in the F₁ (exchangeable) (Figure 4b). When Pb linked with sediment geochemical fractions spatial distribution was studied, it was observed that the lowest percentage of Pb-F₁ ($3.10 \pm 0.30\%$) was recorded at Station #1 (at the outer area of the estuary) while the highest ($13.17 \pm 1.47\%$) was at Station #3 (close to Ing. White port); the same trend was recorded for Pb-F₂ ($1.37 \pm 0.15\%$ and $6.50 \pm 0.44\%$) as well as for Pb-F₄ ($8.66 \pm 0.65\%$ and $14.87 \pm 1.46\%$), but with the highest values recorded at Station #2 and Station #5 respectively. Unlike these, the lowest percentage of Pb-F₃ ($3.80 \pm 0.36\%$) was recorded at Station #2 and the corresponding highest one ($13.43 \pm 1.21\%$) at Station #4, while the lowest Pb-F₅ ($62.20 \pm 0.85\%$) was found at Station #3 and the highest one ($76.57 \pm 0.67\%$) was at Station #1. In the case of lead a range between 4.5 and 15% of PBF was recorded, indicating the potential level of metal assimilation by organisms from the Bahía Blanca estuary.

Finally, the geochemical partitioning of iron showed 93.34 ± 0.09 to $96.87 \pm 0.52\%$ in the F₅ (residual fraction); 3.00 ± 0.55 to $6.26 \pm 0.12\%$ in the F₄ (reducible fraction); 0.06 ± 0.01 to $0.34 \pm 0.03\%$ in the F₃ (carbonate fraction); 0.01 ± 0.01 to $0.04 \pm 0.02\%$ in the F₂ (oxidisable fraction); and, 0.01 ± 0.01 to $0.04 \pm 0.01\%$ was in the F₁ (exchangeable fraction) (Figure 4c). The spatial distribution of iron geochemical partitioning showed that most of this element was recorded in two of the analyzed fractions: Fe-F₅ and Fe-F₄. The first one showed percentages between $93.34 \pm 0.09\%$ (Station #5) and $96.87 \pm 0.52\%$ (Station #1), while in the second one $3.0 \pm 0.55\%$ (Station #1) to $6.26 \pm 0.12\%$ (Station #5) was recorded. The values of the other geochemical fractions recorded (Fe-F₁, Fe-F₂ and Fe-F₃) were extremely low, and were non significant from an environmental viewpoint. In the same way, iron PBF was close to null throughout the area.

Heavy Metals—Organic Matter Relationship

A metals vs organic matter distribution pattern was evaluated within the studied sediments from the Bahía Blanca estuary. Several of the analyzed metals (*i.e.*, zinc, copper and chromium) showed a strong relationship with organic matter in sediments ($r = 0.7529$, $r = 0.7599$, and $r = 0.7278$, $p < 0.01$, respectively), which can contribute to the availability of these metals within the system (Figure 5).

In the case of iron a different trend was identified, showing a slight relationship with the organic matter content of sediments ($r = 0.6083$, $p < 0.01$), and less significant than those previously mentioned (Figure 5).

Finally, a third group of metals was identified (*i.e.*, cadmium and lead) which presented a very restricted relationship with OM content of sediments, with a non-significant level (Figure 5).

DISCUSSION

Selected heavy metals (Cd, Zn, Cu, Cr, Pb and Fe) were found in all sediment samples from the Bahía Blanca estuary.

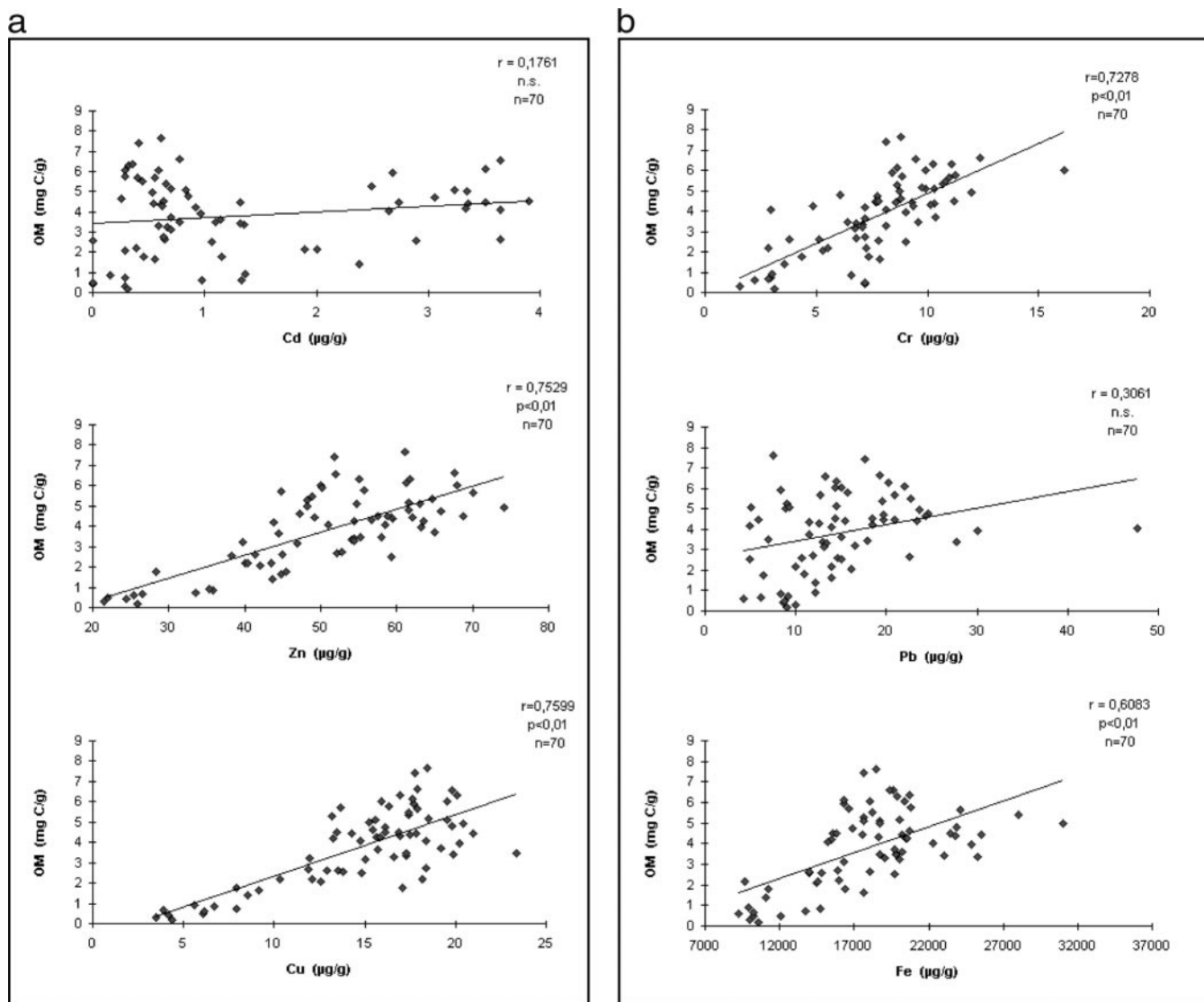


Figure 5. Heavy metals vs Organic matter relationship in Bahía Blanca sediments.

Their concentrations were variable, even though definite distribution trends have been identified. The total metal concentrations exhibited a general distribution pattern, with the lowest values at the outer area of the estuary and the highest in the inner one. The highest metal concentrations (*i.e.*, Cd, Zn, Cu, Pb and Fe) were always recorded in the central area of the studied zone (Stations #3 and #4), which agreed with the concentrations reported in the ports of Ing. White and Galván. Nevertheless, this information does not establish if metals entered into the estuary at these places or if they were redistributed through circulation and transport processes. In the particular case of Cr, its concentration distribution was homogeneous in the estuary, although the lowest values were always recorded in the outer area.

The levels of heavy metals in the present study were compared with those previously reported for the same environ-

ment, and values were in similar ranges for most of them. *I.e.*, Cu, Cr, Pb and Fe in Bahía Blanca sediments fully agreed with those reported by SERICANO and PUCCI (1982), VILLA and PUCCI (1987) and by PUCCI (1988). On the other hand, present concentrations of Cd and Zn in sediments of this estuary were higher than the values reported during the '80s, which have implies that an input of these metals is actually affecting the environment. This is an important, considering that Cd is highly toxic even at low concentrations. When Bahía Blanca sediment metal concentrations were compared with data by other authors for different estuaries or coastal areas it was observed that—except for Cd and Pb concentrations—levels as recorded were lower than those recognized as characteristic in polluted environments. Data by PANUTRAKUL and BAEYENS (1991) about the Scheldt estuary, in Belgium; by DASSENAKIS *et al.* (1996) in bays and gulfs in

Greece; or, by HAYES *et al.* (1998) for Botany Bay, Australia, all reported similar trends to those included here. Ahumada's 1992 report on the San Vicente Bay, in Chile, was likewise considered since the author's characterization of Cd and Pb as enriched sediments coincides with metal levels similar to those found in the Bahía Blanca estuary.

On the other hand, two different patterns have been identified through the geochemical fractioning study of Bahía Blanca sediments:

(i) The first group, *i.e.* Cr and Fe, was characterized with F_5 as the dominated fraction, representing metals in the mineral matrix of the sediment. According to SALOMONS (1995), high percentages of Me- F_5 indicate both low bioavailability and mobility within the studied system. These results agree with geochemical fraction distributions as reported by BAISCH *et al.* (1988) in coastal sediments from Brazil; PANUTRAKUL and BAEYENS (1991) in sediments from the Scheldt estuary, Belgium; AMÍN *et al.* (1997) in coastal sediments from Ushuaia, in the southeast Argentina; or, by MESTRINHO *et al.* (1999) in estuarine sediments from Bahia (Brazil).

(ii) The second group (Cd, Zn, Cu, Pb) was characterized by a significantly decreased Me- F_5 percentage, and the consequent increases in other geochemical fractions. In the case of Cu, a notable contribution was observed in Cu- F_1 which includes adsorbed exchangeable compounds, with a high potentiality of incorporation to biological systems (MARCOVECCHIO *et al.*, 1998). Similar results were previously reported by LACERDA *et al.* (1988b) as well as by BAISCH and WASSERMAN (1998), both assessing Cu occurrence in coastal sediments from Brazil. In the case of zinc, percentages of Zn- F_5 were also significantly decreased, but the most enriched geochemical fractions were F_1 (adsorbed exchangeable compounds) and F_4 (reducible compounds), a pattern which coincides with that previously described by RAURET *et al.* (1989) in sediments of Barcelona coast, Spain. High percentages of Cu and Zn linked to F_1 as recorded at Station #1, which is at the outer area of the estuary, is a typical process observed in marine sediments due to great ionic exchange ability of seawater (FÖRSTNER and STOFFERS, 1980; DASSENAKIS *et al.*, 1996). The geochemical fractioning distribution of Cd behaves differently, with a slight decrease of Cd- F_5 (in most cases percentages no lesser than 50%), but with one particular area (Station #3, close to Ing. White port) where Cd- F_5 were close to 10% and simultaneously Cd- F_1 has increased up to 23%. The same behaviour has been described by LACERDA *et al.* (1988b) as typical in strongly industrialized systems, as is the case in this area of Bahía Blanca estuary where there is a large industrial nucleus. Finally, most of the Pb contents were recorded within residual fraction (Pb- F_5), even percentages up to 60% were not surpassed, and Pb- F_1 were usually increased, while Pb- F_2 were slightly magnified. A similar pattern was described by PANUTRAKUL and BAEYENS (1991) in sediments from the Scheldt estuary, in Belgium. According to CALMANO and FÖRSTNER (1983), FÖRSTNER and WITTMAN (1983), SALOMONS and FÖRSTNER (1984) or BAISCH and WASSERMAN (1998) the assessment of geochemical partitioning is an excellent tool to identify the influence of human activities on trace metal distribution within natural systems. Increased values of Me- F_1 (adsorbed

exchangeable compounds) and Me- F_2 (oxidizable complexes), as recorded in the present study, are environmentally significant because they comprise the potentially bioavailable fraction, PBF, which indicates metals that can be assimilated by organisms (MARCOVECCHIO *et al.*, 1998). In the same way, increasing values of Me- F_3 (in carbonates) and Me- F_4 (reducible compounds) indicate greater mobility and reactivity within the system (BAISCH and WASSERMAN, 1998).

Organic matter content within estuarine sediments has largely been recognized as an efficient trapper of pollutants, including heavy metals (*i.e.*, LIN MAOFU *et al.*, 1986; PRAGATHEESWARAN *et al.*, 1986; CAMPBELL *et al.*, 1988; SALOMONS, 1995). Distribution of OM in Bahía Blanca sediments has shown the lowest values on the external area (*i.e.*, Station #1) and the highest close to the ports (*i.e.*, Stations #3 and #4). There is a similarity between this OM distribution and that previously described for heavy metals. Furthermore, positive correlations found between OM and studied metals have indicated high affinity among them (LANGSTON, 1982; COQUERY and WELBOURN, 1995); this was observed for Zn, Cu, Cr and Fe, and can be interpreted through their ability to produce strong complexes with humic substances within natural waters (NRIAGU, 1979). In contrast, Cd and Pb have presented no significant relationships with OM, presumably linked with a lower stability constant of Cd-humic compounds as well as the fact that Cd and Pb does not tend to form stable organic complexes (CAMPBELL *et al.*, 1988). Finally, it is important to remark that high OM contents determine a low bioavailability of metals within the system (COQUERY and WELBOURN, 1995; KOBLITZ *et al.*, 1997).

In conclusion, Bahía Blanca estuarine sediments have low to medium heavy metal concentrations. Their geochemical partitioning indicated that many bioavailable species occur within the system, including those of highly toxic elements such as cadmium. Correlations with OM have permitted to better perceive the metal distribution studied and to understand in many cases how metals were retained within the sediments. This scenario supports the idea that the Bahía Blanca estuary is a system impacted by anthropic activities, and it is recommended that a permanent monitoring programme be established to assess confined pollution problems.

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