

## Geochemical Control of Heavy Metal Concentrations and Distribution Within Bahía Blanca Estuary (Argentina)

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**Abstract** Chromium and lead concentrations and distribution have been fully studied within Bahía Blanca estuary inner area, which is strongly influenced by urban and industrial stress. Not only metals dissolved in estuarine water but also those included in sediments and suspended particulate matters (SPM) were measured. In all cases, internationally standardized protocols were applied to metal measurements, including analytical quality check test through analysis of certified reference materials. Total metal contents from surface sediments and SPM were compared with those from a historical database of the area, as well as with values representing the natural geochemical baseline within the system. Results showed that heavy metal pollution is mainly localized in the areas close to both industrial effluents discharge system and urban sewage outfall discharge. Data from sequential extractions indicate that metals from anthropogenic sources (i.e., Pb) are

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potentially more mobile than those inherited from geological parent material (i.e., Cr). The influences of other potential sources of metals (i.e., streams, runoff) were also considered. SPM was clearly identified as the main carrier of the studied heavy metals within the system, and its significance to metals input into sediments and/or biota was verified. Finally, the normalization of measured metal concentrations against background reference elements (i.e., Al or Fe) has allowed to identify that most of the measured Cr was lithogenic, while a significant percentage of Pb was from anthropogenic origin within Bahía Blanca estuary.

**Keywords** Heavy metal pollution · Estuaries · Geochemical regulation · Dissolved and particulate metals · Geochemical fractionation

## 1 Introduction

Estuaries have been recognized as dynamic, complex and unique systems, which are included among the most productive marine ecosystems in the world (Chapman and Wang 2001). The pollution problem within estuaries can be characterized through extremely complicated interactions between their dynamic physical, chemical, biological and geological conditions, hindering the efforts to assess the impact of anthropogenic activities on estuarine quality (Dauvin 2008). In addition, estuarine characteristics also determine the corresponding pollutants behavior; thus, depending on the nature of the contaminant and the estuarine condition, two different features are possible during the mixing: (1) either the contaminant is removed from the water to settle in the sediments (sediments as a sink), or (2) contaminants are added to the water as they rise from the sediments (sediments as a source) (Ertfemeijer and Lewis 2006).

Furthermore, it is necessary to keep in mind that the natural occurrence of metals complicates the assessment of contaminated marine sediments because quantifiable levels of metals do not allow to automatically inferring anthropogenic enrichment (Osher et al. 2006; Doong et al. 2008). In this sense, the occurrence of a linear relationship between inert elements (named conservative or normalized elements, such as iron and aluminum) and the fine particle-size fractions (silt + clay) of the samples was opportunely reported (Dauvin 2008), all of which allow normalization to be substituted for the granulometric variability of sediments (Chapman and Wang 2001). Considering that iron and aluminum are abundant in the Earth's crust, given the naturally occurring high levels of these elements, they are scarcely influenced by anthropogenic input; this fact has supported their use as conservative tracers, and to successfully normalize metal contents in order to assess possible anthropogenic contributions (Idris et al. 2007; Sutherland et al. 2007; Zhou et al. 2007).

Other point that deserves to be carefully considered is the potential transference route of materials into the sea, considering estuarine systems have been recognized as major transport paths for metals of natural and anthropogenic origins from the continent to the coastal waters (Masson et al. 2006). In this sense, the suspended particulate matter (SPM) has been identified as the main carrier of heavy metals within estuarine systems (Bibby and Webster-Brown 2006) and in many cases has demonstrated to play a significant role in the transference processes of metals to the organisms (Fang et al. 2006).

The aim of the present study deals with the determination of levels and distribution trends of chromium and lead within Bahía Blanca estuary, focusing on both the dissolved and particulate forms, as well as on the potentiality of transference of these metals to the

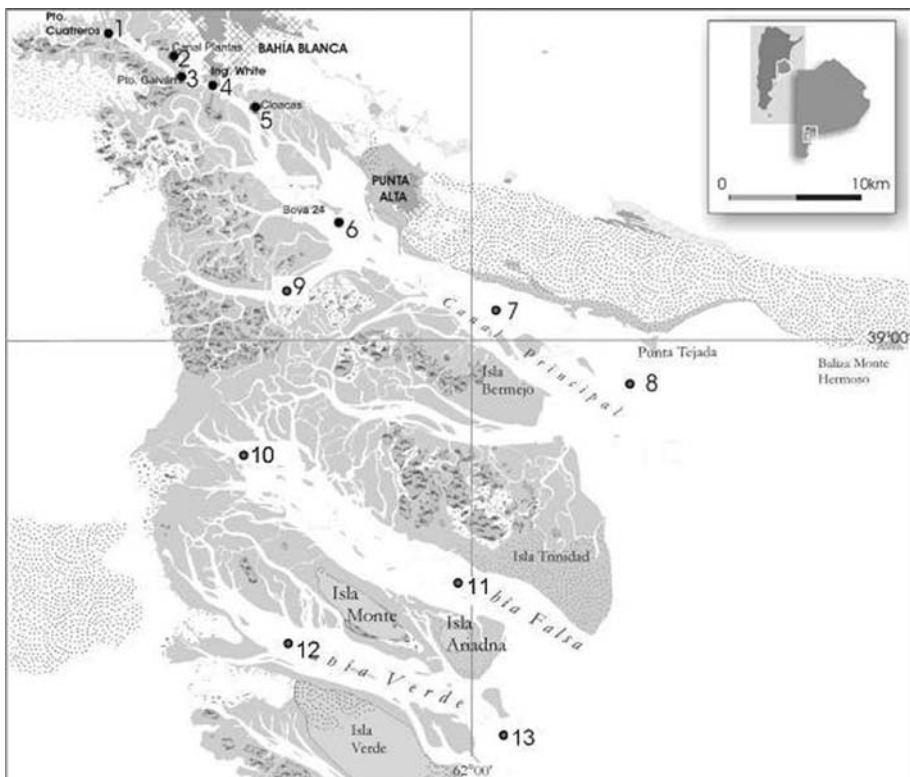
organisms of the estuary. Finally, the role of geochemical processes as regulators of metals' distribution and bioavailability are fully considered.

## 2 Materials and Methods

### 2.1 Description of the Study Area

Bahía Blanca estuary (Fig. 1) is formed by a series of NW–SE tidal channels separated by extensive intertidal flats, low marshes and islands (Perillo and Piccolo 1991). The principal channel, which includes our study area, covers a total length of 80 km and a width varying from about 3–4 km at the mouth (22 m depth) to 200 m at the head (3 m depth).

The principal energy input to Bahía Blanca estuary comes from a standing semidiurnal tidal wave (Piccolo et al. 2008). Strong NW and N winds dominate the typical weather pattern of the region, with a mean velocity of  $24 \text{ km h}^{-1}$  and gusts past  $100 \text{ km h}^{-1}$  (C.de Steffens and C.de Ferreras 2004). Freshwater input is low on the northern coast from the Sauce Chico River (drainage area of  $1,600 \text{ km}^2$ ) in the inner area and from the Napostá Grande Stream (drainage area of  $1,237 \text{ km}^2$ ) in the mid-zone of the estuary (Fig. 1), both with an annual mean run-off of  $1.72 \text{ m}^3 \text{ s}^{-1}$  (with a maximum flowrate of  $18.32 \text{ m}^3 \text{ s}^{-1}$ ) and  $1.05 \text{ m}^3 \text{ s}^{-1}$  (with a peak of  $167.1 \text{ m}^3 \text{ s}^{-1}$ ), respectively. The water column is



**Fig. 1** Location of sampling stations within Bahía Blanca estuary

vertically homogeneous all throughout the estuary, although it may be partially mixed in the inner zone depending on freshwater runoff conditions (Piccolo et al. 2008). In addition, the inner zone is highly turbid as a result of the combined effect of winds and tide currents containing large amounts of suspended matter (Piccolo and Perillo 1990; Gelós et al. 2004).

Dissolved oxygen values are usually close to saturation level values as a result of the high dynamics of the system, which stimulates both oxidation and re-mineralization of organic matter within the system. It is common to register supersaturating oxygen levels of up to 130% during the typical winter/early spring phytoplankton bloom within the estuary (Freije and Marcovecchio 2004). Nutrient concentrations are also high except during the bloom period when they undergo a notorious decrease as a result of phytoplankton consumption (Freije and Marcovecchio 2004; Popovich et al. 2008).

Various ports, towns (with over 300,000 inhabitants) and industries are located at the northern boundaries of the estuary. 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. Significant volumes of raw sewage are discharged daily into the study area (Andrade 2001; Ferrer 2001). This estuary is extensively used by fishing boats, oil tankers and cargo vessels and requires regular dredging. In this sense, this coastal marine system receives contaminant inputs from municipal waste-waters, direct industrial discharges, harbor-related operations and run-off waters that carry materials from land development areas as well as aerial fallout from atmospheric pollutants.

The corresponding sampling stations have been established along the estuary (Fig. 1), and they include different areas influenced by the above-mentioned potential sources of pollution.

## 2.2 Sampling and Analytical Methods

Samples of surface sediments, SPM, estuarine water and zooplankton from the study area were analyzed to determine their chromium and lead contents.

Surface sediment samples were obtained at the indicated sampling stations (Fig. 1) using a stainless steel sediment sampler; they were kept in plastic bags and stored in portable ice chests on board until treated in the laboratory. First, sediment samples were oven-dried at low temperature ( $50 \pm 5^\circ\text{C}$ ) up to constant weight. Afterward, two sub-samples were separated: (1) One of them was sieved through stainless steel mesh in order to separate sediment with grain size  $<63 \mu\text{m}$ ; this fraction was stored in acid-cleaned glass bottles in desiccators, prior to analytical treatment. (2) The other sub-sample was homogenized in a porcelain mortar and also stored in acid-cleaned glass bottles in desiccators, prior to analytical treatment; moreover, sediment samples for both organic matter determination and geological characterization were removed from this second sub-sample.

Surface water samples were collected at  $\sim 1\text{-m}$  depth in 1.5-l polyethylene-terefalate (PET) bottles; they were immediately transported to the laboratory and filtered through acid-treated Millipore HA filters ( $0.45 \mu\text{m}$  mesh) so as to determine dissolved metals and to obtain the corresponding SPM samples. In all cases, water samples have been obtained between tide extremes (from the high tide to the low one). The filtered samples were acidified at pH 2, using 1.5 ml of HCl analytical quality, in order to be stored in darkness at  $4^\circ\text{C}$  up to the analytical treatment phase at the laboratory. On the other hand, filters with

the SPM samples were oven-dried at low temperature ( $50 \pm 5^\circ\text{C}$ ) up to constant weight until analytical treatment. Prior to their use and following internationally recommended protocols (AWWA-WPCF), every piece of material employed for the sampling, filtration and sample storage process was carefully cleaned with diluted nitric acid (0.7%,  $\text{HNO}_3$  suprapur, Merk).

Cr and Pb concentrations in sediments (both in total sediment and  $<63\text{-}\mu\text{m}$  grain size fraction) and SPM samples were determined according to the method described by Marcovecchio and Ferrer (2005), including acid mineralization under controlled temperature and measurement through atomic absorption spectroscopy (AAS) with air-acetylene flame. In addition, geochemical fractioning of the  $<63\text{-}\mu\text{m}$  sediment fraction by a sequential extraction method was applied, according to the description of Marcovecchio and Ferrer (2005) based on description of Megalatti et al. (1983) and Lacerda et al. (1988). This methodology has provided information on the metal content of five geochemical fractions: (1)  $F_1$  exchangeable-adsorbed metals; (2)  $F_2$  oxidisable metal complexes; (3)  $F_3$  metals in carbonates; (4)  $F_4$  metals in reducible compounds and (5)  $F_5$  residual metals. Moreover, dissolved Cr and Pb concentrations were determined following Botté et al. (2008) guidelines, including chelation with ammonium pyrrolidine-dithiocarbamate (APDC), extraction with methyl isobutyl ketone (MIBK), and measurement through AAS with air-acetylene flame. In all cases, a Perkin–Elmer 2380 AAS has been used for the corresponding measurements.

Analytical grade reagents were utilized not only for sediment mineralization but also for blanks and calibration curve standards built up. In all cases, bi-distilled water was used to prepare the corresponding solutions.

The limit of detection of the applied analytical techniques were:  $0.07 \mu\text{g g}^{-1}$  for Pb in sediments and SPM;  $0.38 \mu\text{g l}^{-1}$  for dissolved Pb;  $0.03 \mu\text{g g}^{-1}$  for Cr in sediments and SPM and  $0.89 \mu\text{g l}^{-1}$  for dissolved Cr.

Analytical quality was checked against international reference materials (*pond sediment flour* R.M.No. 82- and *estuarine water* -R.M.No. 39-) provided by The National Institute for Environmental Studies (NIES) from Tsukuba University (Japan), and *seawater* -RM 425/A- from the United Nations Environment Programme (UNEP). For all the analysed metals, recovery percentages concurred with official NIES and UNEP calibration exercises (Table 1).

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). Moreover, factorial analysis was performed to reduce the number of variables recorded and to detect structure in the relationships between physico-chemical parameters and account for the variation present in the data set matrix. Factors were calculated from the correlation matrix and treated by Varimax rotation in order to maximize the load of each variable on one factor. Factors were extracted by principal components. All statistical tests were performed using the Statistica software package (version 7.1). Significance was set at  $P < 0.05$ .

**Table 1** Percentage of recovery (ranges) in the analysis of certified reference materials (NIES and UNEP) to assess analytical quality

Analyzed metals	Percentage of recovery		
	Pond sediment	Estuarine water	Seawater
Lead	93.6–99.3	92.9–96.5	92.2–97.5
Chromium	95.2–99.1	91.6–97.1	91.0–97.7

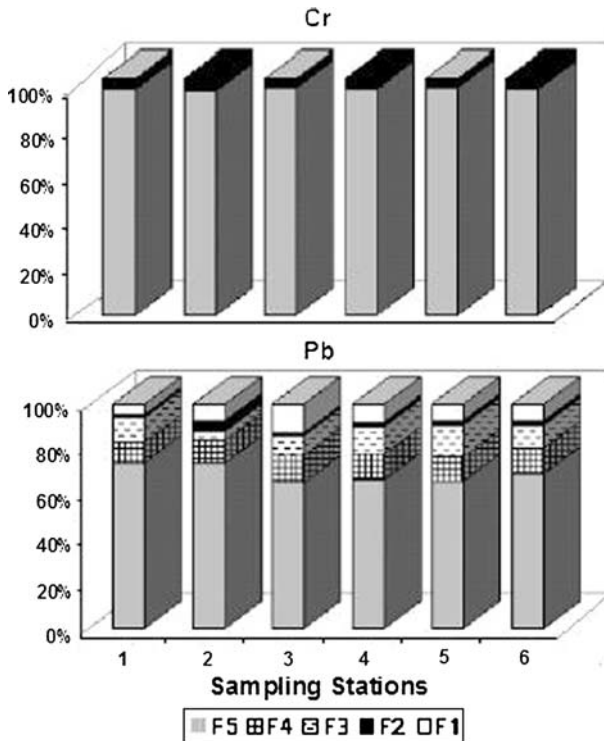
### 3 Results

Lead and chromium concentrations—both dissolved in estuarine water and particularly within surface sediments—were determined in Bahía Blanca estuary samples (Table 2). Moreover, the observed spatial distribution of the recorded Pb and Cr dissolved values along the estuary (Fig. 2) allows to identify two different data groups of metal concentrations that show significant differences ( $P < 0.01$ ) among them. The first one, including dissolved metal values recorded at the sampling stations located in the first 20 km from the estuary's head, reached up to  $2 \mu\text{g Cr l}^{-1}$  and  $4 \mu\text{g Pb l}^{-1}$  (Figs. 1 and 2, respectively). The second one group, including values recorded at the sampling stations between 25 km and the estuary's mouth) denoted dissolved Cr up to  $0.5 \mu\text{g l}^{-1}$  and dissolved Pb up to  $2.1 \mu\text{g l}^{-1}$  (Figs. 1 and 2).

Simultaneously, the distribution of both chromium and lead concentrations within surface sediments from Bahía Blanca estuary was also considered (Figs. 1 and 2). The resulting distribution trend fully agreed with that one identified for dissolved metals levels, even though the corresponding concentrations were significantly different ( $P < 0.01$ ) (Fig. 2). As it was previously commented, two groups of metals were identified in the sediment data: (i) Those corresponding to the first 20 km of the inner estuary showed high values, reaching up to  $\sim 9.3 \mu\text{g Cr g}^{-1} \text{ dw}$ , (r.v.:  $6.4 \pm 1.5$ – $9.2 \pm 1.6 \mu\text{g Cr g}^{-1} \text{ dw}$ ); and, up to  $\sim 20 \mu\text{g Pb g}^{-1} \text{ dw}$ , (r.v.:  $14.4 \pm 2.3$ – $19.8 \pm 2.2 \mu\text{g Pb g}^{-1} \text{ dw}$ ). (ii) Those recorded from  $\sim 25$  km from the estuary's head to its mouth proved to be significantly lower than the ones of the first group ( $P < 0.01$ ; Fig. 2), with values varying between  $2.1 \pm 0.6$  and  $3.6 \pm 1.4 \mu\text{g Cr g}^{-1} \text{ dw}$ , and from  $4.9 \pm 1.3$  to  $8.9 \pm 2.1 \mu\text{g Pb g}^{-1} \text{ dw}$ . Such identified spatial distribution, which fully agrees with that previously described for the dissolved phase, has also linked metal concentrations within sediments with the recognized potential sources, describing the highest values close to the industrial discharge area, the main ports within the estuary and the area of discharge of Bahía Blanca city sewage system (Figs. 1 and 2).

**Table 2** Lead and chromium concentrations within Bahía Blanca estuarine sediments ( $\mu\text{g g}^{-1} \text{ dw}$ ) and estuarine water ( $\mu\text{g l}^{-1}$ )

Sampling stations	Cr			Pb		
	Total sediment	<63 $\mu\text{m}$	Dissolved	Total sediment	<63 $\mu\text{m}$	Dissolved
Station #1	$7.9 \pm 1.9$	$35.8 \pm 5.4$	$1.9 \pm 0.6$	$15.7 \pm 2.9$	$31.1 \pm 2.4$	$3.1 \pm 0.9$
Station #2	$8.4 \pm 1.5$	$39.9 \pm 5.8$	$1.7 \pm 0.3$	$17.8 \pm 2.9$	$34.8 \pm 6.3$	$2.9 \pm 0.4$
Station #3	$8.7 \pm 1.5$	$31.6 \pm 6.4$	$1.2 \pm 0.5$	$19.8 \pm 2.2$	$28.3 \pm 4.1$	$2.6 \pm 0.9$
Station #4	$9.2 \pm 1.6$	$27.2 \pm 5.2$	$2.3 \pm 0.9$	$18.4 \pm 2.7$	$32.2 \pm 5.2$	$3.7 \pm 1.1$
Station #5	$6.4 \pm 1.5$	$39.4 \pm 4.6$	$0.6 \pm 0.3$	$14.4 \pm 2.3$	$35.3 \pm 4.3$	$2.1 \pm 0.7$
Station #6	$3.6 \pm 1.4$	$25.1 \pm 3.7$	$0.4 \pm 0.1$	$8.5 \pm 2.1$	$25.7 \pm 6.3$	$2.3 \pm 0.9$
Station #7	$3.2 \pm 1.1$	$20.4 \pm 3.6$	$0.4 \pm 0.3$	$6.2 \pm 1.6$	$17.6 \pm 3.8$	$2.1 \pm 0.5$
Station #8	$2.9 \pm 0.8$	$11.3 \pm 2.7$	$0.1 \pm 0.3$	$7.1 \pm 2.0$	$8.3 \pm 1.9$	$1.8 \pm 0.6$
Station #9	$3.4 \pm 1.2$	$23.7 \pm 4.7$	$0.3 \pm 0.1$	$8.9 \pm 2.1$	$24.4 \pm 5.2$	$0.8 \pm 0.2$
Station #10	$3.3 \pm 1.4$	$20.5 \pm 4.3$	$0.3 \pm 0.4$	$7.2 \pm 1.8$	$21.1 \pm 4.7$	$0.9 \pm 0.4$
Station #11	$2.5 \pm 0.5$	$9.6 \pm 1.2$	$0.1 \pm 0.1$	$5.1 \pm 1.7$	$7.4 \pm 1.4$	$0.4 \pm 0.3$
Station #12	$2.1 \pm 0.4$	$14.3 \pm 3.6$	$0.4 \pm 0.2$	$5.4 \pm 1.9$	$12.3 \pm 3.1$	$0.8 \pm 0.3$
Station #13	$2.3 \pm 0.5$	$6.1 \pm 1.1$	$0.1 \pm 0.2$	$4.9 \pm 1.3$	$4.2 \pm 0.9$	$0.7 \pm 0.4$



**Fig. 2** Cr and Pb geochemical partitioning (%) in <63- $\mu\text{m}$  grain-size sediment fraction

Chromium concentrations in sediments have varied between  $2.1 \pm 0.4 \mu\text{g g}^{-1} \text{ dw}$ , and  $9.2 \pm 1.6 \mu\text{g g}^{-1} \text{ dw}$ , while lead values varied from  $4.9 \pm 1.3$  up to  $19.8 \pm 2.2 \mu\text{g g}^{-1} \text{ dw}$  (Table 2). As it was mentioned before in reference to dissolved fractions and metals in the SPM, a clear spatial distribution trend was identified within sediment metals concentration. So, the highest concentrations of both Cr and Pb were described in sediments from the inner area of the estuary, where the potential sources are located; on the other hand, a significant decrease towards the external area was observed (Fig. 2).

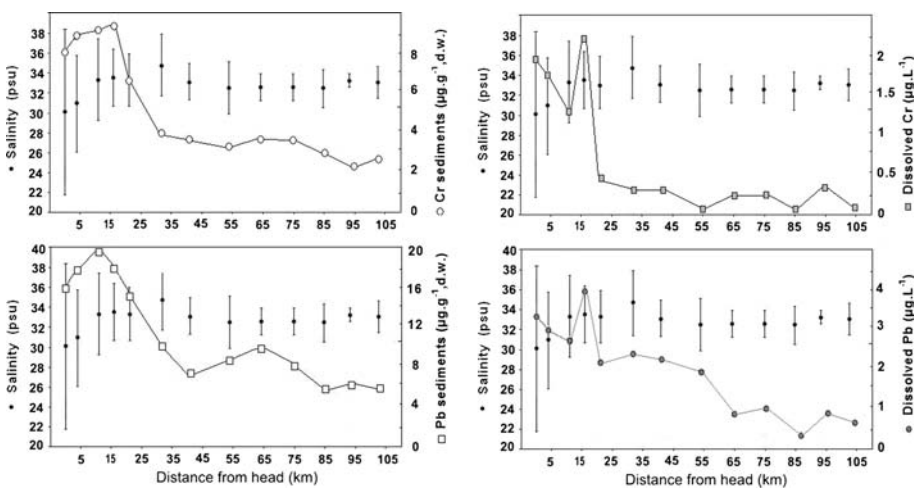
On the other hand, significantly higher Cr and Pb concentrations were determined within the corresponding finest grain-size sediments (<63 $\mu\text{m}$ ) in the studied area, reporting values varying from  $6.1 \pm 1.1$  to  $39.9 \pm 5.8 \mu\text{g Cr g}^{-1} \text{ dw}$ , as well as from  $4.2 \pm 0.9$  to  $35.3 \pm 4.3 \mu\text{g Pb g}^{-1} \text{ dw}$  (Table 2).

Finally, the geochemical fractioning of the studied metals were also considered in the inner stations of the estuary within the <63  $\mu\text{m}$  sediment fraction; it allowed to identify the main geochemical association of both metals within the sediments (Fig. 3), also including the metal potentially bioavailable fraction (PBF) (Marcovecchio et al. 1998). Again, two different distribution trends were identified: (i) Cr partitioning distribution showed that  $96.1 \pm 1.3$ – $97.5 \pm 0.6\%$  was recorded in the  $F_5$  (residual fraction), and  $2.5 \pm 0.6$ – $3.9 \pm 1.3\%$  in the  $F_2$  (oxidisable fraction). None of the other analysed geochemical fractions ( $F_4$ ,  $F_3$ ,  $F_1$ ) presented detectable values (Fig. 3). Analysis of the spatial distribution denoted no significant differences between Cr levels at all stations ( $P < 0.01$ ).



Moreover, chromium PBF was always lower than 3%, which indicates scarce probabilities that this element can be assimilated by organisms within the estuary. (ii) On the other hand, the assessment of lead geochemical fractioning showed that  $62.2 \pm 0.8$ – $76.6 \pm 0.7\%$  was recorded in the  $F_5$  (residual);  $8.7 \pm 0.6$ – $14.9 \pm 1.5\%$  in the  $F_4$  (reducible);  $3.8 \pm 0.4$ – $13.4 \pm 1.2\%$  in the  $F_3$  (carbonates);  $1.4 \pm 0.1$ – $6.5 \pm 0.4\%$  in the  $F_2$  (oxidisable); and,  $3.1 \pm 0.3$ – $13.2 \pm 1.5\%$  was in the  $F_1$  (exchangeable) (Fig. 3). When spatial distribution of Pb linked with geochemical sediment fractions, it was observed that the lowest percentage of Pb- $F_1$  ( $3.1 \pm 0.3\%$ ) was recorded at Station #6 (towards the outer area of the estuary) while the highest percentage ( $13.2 \pm 1.5\%$ ) was at Station #4 (close to Ing. White port); the same trend was recorded for Pb- $F_2$  ( $1.4 \pm 0.1\%$  and  $6.5 \pm 0.4\%$ ) as well as for Pb- $F_4$  ( $8.7 \pm 0.6\%$  and  $14.9 \pm 1.5\%$ ), but with the highest values recorded at Station #5 and Station #2, respectively. Unlike these, the lowest percentage of Pb- $F_3$  ( $3.8 \pm 0.4\%$ ) was recorded at Station #5 and the corresponding highest one ( $13.4 \pm 1.2\%$ ) at Station #3, while the lowest Pb- $F_5$  ( $62.2 \pm 0.8\%$ ) was found at Station #4 and the highest one ( $76.6 \pm 0.7\%$ ) at Station #6. In the case of Pb 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.

The factorial analysis of the physico-chemical parameters recorded revealed that 77.15% of the total variance could be explained by three factors (Table 3). The first factor accounts for 34.62% of the variance including Cr and Pb in sediments (both total sediment and  $<63 \mu\text{m}$  fraction) and pH, and consequently associated with deposition processes. This factor explains more than a quarter of the total variation, meaning that it is a dominant factor. Factor 2 is correlated with Cr and Pb dissolved and in the SPM, as well as pH, explaining 27.68% of the variance, representing transference processes among both compartments. The third factor (14.85% of total variance) presented positively correlation with Cr and Pb in SPM and salinity, which could be related to metals transport within the estuarine mixing zone (Table 3).



**Fig. 3** Salinity (psu), Pb and Cr dissolved ( $\mu\text{g l}^{-1}$ ) and in sediments ( $\mu\text{g g}^{-1} \text{ dw}$ ) along Bahía Blanca estuary



**Table 3** Rotated varimax factors loaded for environmental variables, eigenvalues and explained variance for each factor extracted

Variables	Factor 1	Factor 2	Factor 3
Dissolved Cr	0.120436	<b>0.631508</b>	0.005579
Dissolved Pb	0.098972	<b>0.683954</b>	-0.002253
Cr in sediment	<b>0.918334</b>	0.012326	-0.081105
Pb in sediment	<b>0.888522</b>	0.094867	-0.040944
Cr in <63 $\mu\text{m}$	<b>0.903024</b>	0.034568	0.029636
Pb in <63 $\mu\text{m}$	<b>0.921728</b>	0.094615	0.095347
Cr in SPM	0.132336	<b>0.681536</b>	<b>0.461235</b>
Pb in SPM	0.105698	<b>0.705574</b>	<b>0.483329</b>
pH	<b>0.561532</b>	<b>0.463375</b>	0.093624
Salinity	-0.076833	0.172966	<b>0.893749</b>
DO (%sat)	-0.053496	0.068433	0.050726
Eigenvalue	4.520253	3.613722	1.938923
% Total variance	34.622854	27.679285	14.851171
Cumulative variance	34.622854	62.203129	77.153309

Extraction: principal components. Marked loadings are >0.45

#### 4 Discussion

Even though the recorded values of both lead and chromium dissolved in estuarine waters were very low and close to the corresponding analytical detection limits of the applied methodology (Table 2), they had been liable to be measured along the whole study. This fact indicates that a permanent input of these dissolved metals occurs within the estuary. Bearing in mind that this chemical form of metals can remain only for a short time after being transferred into suspended particulate matter (SPM), sediments or biota (Alquezar et al. 2007; Doig and Liber 2007), it can then be assumed that a continuous (or *quasi-continuous*) source of Pb and Cr exists within this environment.

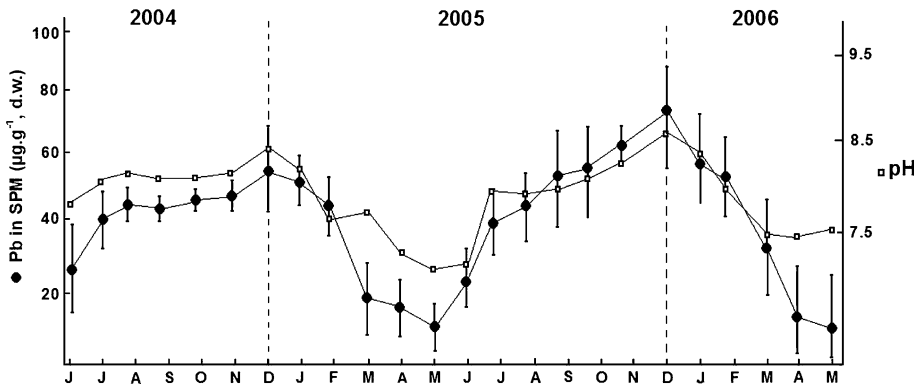
These spatial distributions identified for both the dissolved Pb and Cr fractions within Bahía Blanca estuary were strongly linked with several of the potential sources closely located to this system. Thus, the area that included the highest concentrations of both dissolved metals (i.e., Sampling Stations #2, #3, #4 and #5) fully agreed with the location of the industrial discharges (S.S. #2), the main ports (S.S. #3 and #4) or the discharge of Bahía Blanca city sewage system (S.S. #5) (Figs. 1, 3). This kind of spatial distribution of dissolved metals closely restricted to the main sources or input points within the studied environment was in accordance with other former descriptions for different estuaries or coastal systems, like the Huelva river estuary, in Spain (Sainz et al. 2004); the Seine river estuary, in France (Dauvin 2008); or coastal areas from the Gulf of Cadiz, in Spain (Gonzalez et al. 2007), among others. Several previous studies have pointed out that metals may be complexed with organic ligands in surface waters, and theoretical models for chemical speciation indicated that in aqueous solutions would also be complexed first with  $\text{Cl}^-$ , which is a dominant ion among salinity contributors (Wang and Liu 2003).

Such identified spatial distribution, which fully agrees with that previously described for the dissolved phase, has also linked metal concentrations within sediments with the recognized potential sources, describing the highest values close to the industrial discharge area, the main ports within the estuary and the area of discharge of Bahía Blanca city sewage system (Figs. 1, 3). This coincidence between both distribution trends allowed assuming the occurrence of the same metals' sources for both phases within the system, as

well as the regulation mechanisms that may control metals' transference between water and solid compartments (sediment and SPM). However, though the close agreement between both distribution trends can be observed in Fig. 3 (Cr and Pb dissolved and in sediments), differences between them can be also recognized. So, in several areas of this graphic, significant increases of metal contents in sediments coincided with decreases in corresponding dissolved levels and vice versa; such changes were also connected with changes in salinity values: increased in the first case and decreased in the other one (Fig. 3). In previous reports on this environment, it has been demonstrated that metal levels did not vary during the tidal cycle, neither dissolved (Botté et al. 2008) nor particulate ones (Marcovecchio et al. 2008). The variation of salinity was highlighted as one of the regulator mechanisms of transference between both phases (Chapman and Wang 2001). It is one controlling factor for the distribution of contaminants in estuaries through (1) desorption, due to increasing complexation with seawater anions and/or increasing competition for particle adsorption sites with seawater cations, and (2) coagulation, flocculation and precipitation processes (Dauvin 2008). This fact strongly supports the occurrence of the highest Cr and Pb concentrations within the inner area of the estuary not only due to the location of the main identified metals sources but also because the maximum variation of salinity has been recorded there (Fig. 3). So, it would be inferred that dissolved Pb and Cr were strongly associated with small particles and colloids, and the salt-induced coagulation of these particles was an important mechanism for the removal of dissolved metal fraction during water mixing within the estuary (Wang and Liu 2003). Results denoted that although both Cr and Pb are soluble elements at middle and high salinities and show desorption behavior, removal singularly occurred in the low-salinity zone and may be induced by flocculation and/or adsorption reactions. It is important to emphasize that the studied metals easily remained in the dissolved phase when the system presented a more oxidative condition, which is in accordance with the comment made by Adamo et al. (2005) for Naples coastal system.

In the present study, the concentration of dissolved oxygen (DO) within estuarine water was also considered, keeping in mind that this is a shallow estuary, and the water movement (through tide, waves and freshwater discharges) usually removes the surface sediment generating a high amount of suspended particles (Perillo and Piccolo 1991; Perillo et al. 2001). In this sense, significant changes in DO concentration determine changes in the redox condition within surface sediments. Likewise, the resuspension of sediments and/or deflocculation of particles may also affect the behavior of dissolved metals, and even disturb the coagulation process, especially at shallow and tidal-dominated estuaries, as well as in those ones that have high concentration of suspended matter, both conditions which characterize Bahía Blanca estuary (Perillo et al. 2001). In addition, the present results showed that both dissolved metals clearly displayed non-conservative behavior, which is common with most other estuaries (Chapman and Wang 2001).

Furthermore, the studied metals proved to be also strongly accumulated within the suspended particulate matter (SPM), where the recorded concentrations were much higher than both dissolved and sediment ones (Fig. 4). As an example, SPM Pb concentrations have reached up to  $\sim 75 \mu\text{g g}^{-1}$ , which was almost four times higher than values measured in sediments of this system. This fact fully coincided with previous reports by other authors, like Censi et al. (2006) on the north-western Gulf of Thailand, among others. SPM includes the finest grain sediment, usually clays and slime; consequently, these kind of particles—with a large surface:volume relationship—present great ability to trap substances or elements through sorption processes (Pasternack and Brown 2006). Several authors have proposed that SPM is the main metal carrier within estuarine environments



**Fig. 4** SPM Pb concentration ( $\mu\text{g g}^{-1}$  dw) and pH distribution during the study period

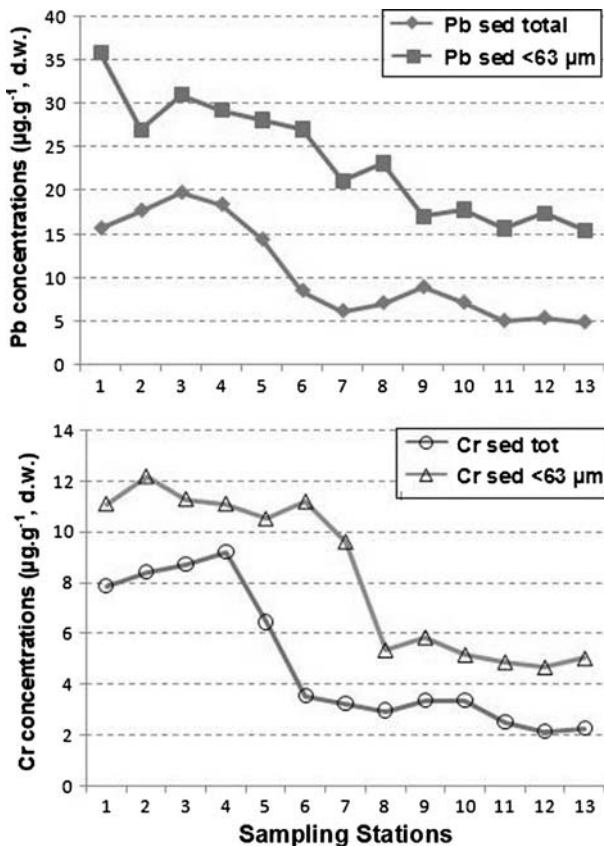
(i.e., Tattersall et al. 2003; Bibby and Webster-Brown 2006), representing the main transference step between water and sediments or organisms (Chapman and Wang 2001; Alquezar et al. 2007). Metals bonded to suspended particles can either remain there or be removed according to physical–chemical conditions within the corresponding environment. During this study, a strong relationship between Pb adsorbed to SPM and the pH was observed, thus describing a significant metal removal at a decreasing pH and the opposite process at an increasing one (Fig. 4). In this case, the recorded variations of pH can be related to natural biological processes, with significant decreases during the main annual phytoplankton bloom (later autumn–early winter) and increases during summer (Popovich et al. 2008). Even though other studies (i.e., Shi et al. 1998; Lu and Allen 2001) have shown a decrease in metal adsorption to SPM with increasing SPM concentration in the water column, commonly attributed to the “particle concentration effect” (Benoit and Rozan 1999), this kind of process was not observed during the present study.

Chromium concentrations in sediments have varied between  $2.1 \pm 0.4 \mu\text{g g}^{-1}$  dw and  $9.2 \pm 1.6 \mu\text{g g}^{-1}$  dw, while lead values varied from  $4.9 \pm 1.3$  up to  $19.8 \pm 2.2 \mu\text{g g}^{-1}$  dw (Table 2). As it was mentioned earlier in reference to dissolved fractions and metals in the SPM, a clear spatial distribution trend was identified within sediment metals concentration. So, the highest concentrations of both Cr and Pb were described in sediments from the inner area of the estuary, where the potential sources are located; on the other hand, a significant decrease toward the external area was observed (Fig. 3). This kind of spatial distribution fully agreed with previous reports about different estuaries made by other authors, like Acevedo-Figueroa et al. (2006), when referring to sediments from estuarine lagoons from Puerto Rico, or Doong et al. (2008) in the Gao-Ping river estuary, Taiwan, among others. Moreover, the recorded differences between metal concentrations within these two areas were very important ( $p < 0.01$ ).

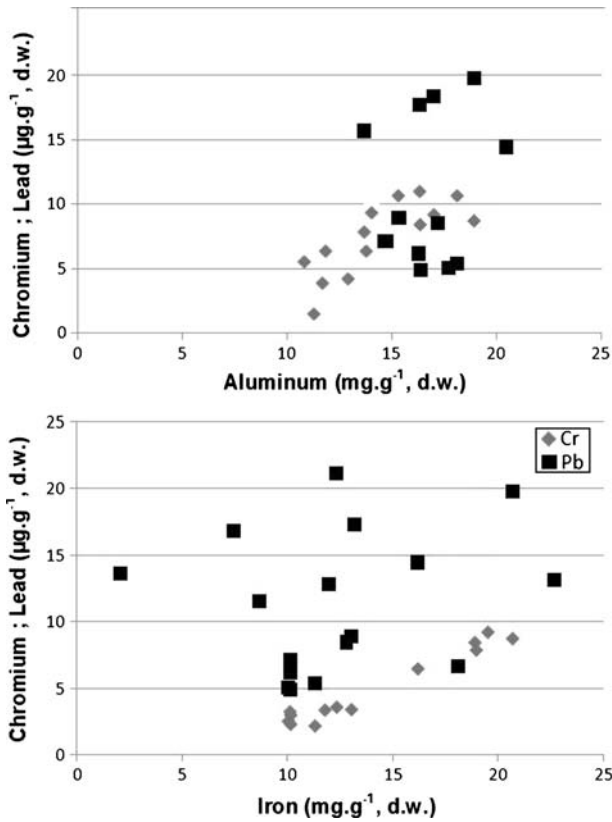
The significant association between trace metals and the finest grain-size sediment as observed within Bahía Blanca estuarine system has opportunely been reported by different authors (i.e., Zhang et al. 2002; Hansen et al. 2005), together with the corresponding *dilution effect* that can be defined by relating the metal levels in total sediments and that in the  $<63\text{-}\mu\text{m}$  one was explained considering the percentage of finest grain-size particles (63–92.6%) within Bahía Blanca estuary sediments (Gelós et al. 2004). A remarkable point was that even the magnitude of Cr and Pb within total sediment and  $<63\text{-}\mu\text{m}$  fractions were significantly different ( $p < 0.01$ ), they both presented clearly similar spatial distribution

trends, which allowed to sustain the occurrence of common metal sources (Fig. 5). Nevertheless, the same Fig. 5 shows particular biases between both distribution lines, which can be attributed either to spatial changes in the percentage of fine grain-size fraction (with the consequent modification of the dilution effect) or changes in the physical–chemical conditions (i.e., pH, redox condition); thus, it modifies the corresponding adsorption–desorption processes, leading to alternative increases or decreases in metal sediment contents or transferences to SPM or even to the dissolved phase (Chapman and Wang 2001; Dauvin 2008).

A complementary tool used in the present study was the geochemical normalization, which was extensively applied to assess anthropogenic contributions of metals in sediments, where the ratio of natural concentrations has been defined by a normalizing factor (i.e., a metal whose concentration is unaffected by human activities) (Acevedo-Figueroa et al. 2006). Usually, metal concentrations are normalized against some elements such as aluminum, iron or lithium that is both geochemically inactive and abundant in the fine grain material (Hwang et al. 2006; Sutherland et al. 2007). In the present study, both geochemical normalizations against aluminum and iron were used (Fig. 6), providing similar results: (1) in both cases Cr showed a good association to Al and Fe ( $r = 0.693$  and



**Fig. 5** Cr and Pb distribution ( $\mu\text{g g}^{-1}$  dw) in total sediment and  $<63\text{-}\mu\text{m}$  grain-size fraction within Bahía Blanca estuary. %finest fraction within the studied metals: 63–92.6%



**Fig. 6** Geochemical normalization of Cr and Pb ( $\mu\text{g g}^{-1}$  dw) against Al and Fe ( $\text{mg g}^{-1}$  dw)

$r = 0.861$ , respectively), indicating that these metals have similar (or even the same) geochemical origin, and that there were no anthropogenic enrichment of Cr within the sediments of the studied area. (2) On the contrary, Pb presented an extremely low relationship with both Al and Fe ( $r = 0.263$  and  $r = 0.103$ , respectively), with a consequent large spread of distribution data, indicating different geochemical origin as well as a significant enrichment of anthropogenic Pb within the sediments of the study area. This kind of analysis was previously used by different authors in other estuaries (i.e., Acevedo-Figueroa et al. 2006; Gonzalez et al. 2007), it is regarded as a successful tool for environmental assessment.

Analysis of the spatial distribution of the Cr geochemical fractions within the finest grain-size sediments denoted no significant differences between levels at all stations ( $p < 0.01$ ) (Fig. 2). Moreover, chromium potentially bioavailable fraction (PBF) was always lower than 3%, which indicates scarce probabilities that this element can be assimilated by organisms within the estuary. When spatial distribution of Pb linked with geochemical sediment fractions, it was observed that the lowest percentage of **Pb-F<sub>1</sub>** ( $3.1 \pm 0.3\%$ ) was recorded at Station #6 (towards the outer area of the estuary), while the highest percentage ( $13.2 \pm 1.5\%$ ) was at Station #4 (close to Ing. White port); the same trend was recorded for **Pb-F<sub>2</sub>** ( $1.4 \pm 0.1$  and  $6.5 \pm 0.4\%$ ) as well as for **Pb-F<sub>4</sub>** ( $8.7 \pm 0.6$  and  $14.9 \pm 1.5\%$ ), but with the highest values recorded at Station #5 and Station #2,

respectively. Unlike these, the lowest percentage of **Pb-F<sub>3</sub>** ( $3.8 \pm 0.4\%$ ) was recorded at Station #5 and the corresponding highest one ( $13.4 \pm 1.2\%$ ) at Station #3, while the lowest **Pb-F<sub>5</sub>** ( $62.2 \pm 0.8\%$ ) was found at Station #4 and the highest one ( $76.6 \pm 0.7\%$ ) at Station #6. In the case of Pb, 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. The occurrence of those extremely mobile fractions (i.e., **F<sub>1</sub>** and **F<sub>2</sub>**) clearly indicated Pb enrichment on the studied sediments, as it was opportunely reported by other authors (i.e., Turner 2000; Adamo et al. 2005).

## 5 Conclusions

The obtained results within the present study have allowed sustaining the following concluding comments:

1. Extreme removal of dissolved Cr and Pb occurred at lowest salinity ranges, with concentrations dropping from 2.3 to 0.1  $\mu\text{g Cr l}^{-1}$  and from 3.7 to 0.4  $\mu\text{g Pb l}^{-1}$  at higher ones.
2. SPM showed the highest ability to trap metals at this estuary, as well as to be the main metal carrier within the system. Besides, the corresponding transference processes (i.e., adsorption from dissolved phase or flocculation into sediment) seemed to be strongly related to the corresponding water pH.
3. <63- $\mu\text{m}$  sediment fraction was identified as the main reservoir of metals within Bahía Blanca estuary.
4. The geochemical normalization demonstrated to be a very useful tool to assess anthropogenic contribution of metals in sediments from the studied estuary.
5. The partitioning of heavy metals through sequential-extractive techniques was also used in this study in order to acquire information on the heavy metal origin and form of occurrence, as well as to identify the proportion of metals, which are chemically mobile and bio-available.
6. Results obtained through techniques indicated in *items* 4 and 5 showed that: Cr was primarily associated with minerals within the sediments, while Pb was clearly enriched within sediments, and anthropic activities appeared to be its main source.
7. Most of the transference processes of the studied metals have been geochemically regulated, and the main identified regulators were salinity, pH, redox potential (or even dissolved oxygen) and grain size of the sediment particles.

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