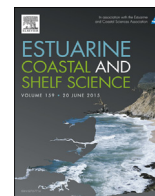




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## Dissolved and particulate metals dynamics in a human impacted estuary from the SW Atlantic

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### ABSTRACT

In order to evaluate metal behavior in urban stressed estuaries, the distribution of major elements (Fe and Mn) and trace elements (Cd and Cu) between suspended particulate matter (SPM) and subsuperficial seawater in the Bahía Blanca Estuary, Argentina, was studied. Four different impacted areas were selected to study the spatial and temporal distribution of these metals in an estuary in continuous industrial development and where an environmental law was implemented to supervise industrial discharges in waters. Sampling was performed within intertidal areas. Physicochemical conditions usually influence the partitioning of metals between the dissolved and particulate fraction thus, salinity, pH, turbidity, temperature and dissolved oxygen were also measured.

Dissolved metals were analyzed with atomic absorption spectrophotometry (AAS) and the particulate fraction with inductively coupled plasma optical emission spectrometry (ICP OES). Metals concentration ranges, within the dissolved fraction ( $\mu\text{g/L}$ ), were from below the method detection limit for all the elements to 4.7 in the case of Cd, 6.0 for Cu and 62 for Fe. Minimum and maximum values in the particulate fraction ( $\mu\text{g/g}$ , d.w.) were from below the method detection limit to 11 for Cd; from 24 to 220 for Cu and from 630 to 1500 for Mn. For Fe, concentrations ranged from 2.2 to 9.6 (%). The general order of the dissolved/particulate partition coefficients ( $\text{Log}_{10}\text{Kds}$ ) for the studied metals, considering mean values, were: Fe (7.0) > Cu (4.2) > Cd (3.3).

The metals values as well as the physicochemical parameters showed temporal variations and many correlations were found among them.  $\text{Log}_{10}\text{Kd}$  Fe values were the highest, highlighting its strong affinity for particles. Metals concentrations were sometimes higher than those from other polluted areas as well as from previous studies from the same estuary, which highlights the potential impact of these elements in the study area.

The concentrations of particulate metals achieved in the present work were in some cases of higher ranges than the previous from the same estuary and/or from other polluted estuarine environments. Thus, the environmental law that regulates the discharge of industrial waters appeared not to have a specific impact on the metals concentrations found. Moreover, human activities that surround the estuary and are in continue development should be considered as they might constitute a source of metals for the estuarine system.

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### 1. Introduction

A wide majority of countries have a large percentage of their population (80–100%) living within 100 km of the coastline. Human burden on the coasts enhance pressure on these ecosystems through habitat conversion, infrastructure for manufacturing, transportation, energy processing, waste products disposal, among others (Martínez et al., 2007). Inputs of contaminants onto these

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environments have been intensified in the last years (Duarte and Caçador, 2012). Within coastal environments, the estuaries are recognized as dynamic and unique systems and of great economic importance. In addition, they are considered as filters of several inorganic and organic contaminants transported through rivers, streams, subterranean drainage and effluents, between others (Duarte and Caçador, 2012; Fu et al., 2013). Thus, estuaries play a key role in the transference of contaminants to the open sea, being these elements transformed, dissolved or/and sunk there (e.g. Lim et al., 2012), interacting with the biota and, discouraging human development along the coasts.

Among contaminants, metals are of particular concern as a result of their environmental persistence, biogeochemical recycling and human risk. Mobility and partitioning of metals within estuaries are dependent on several factors, e.g. pH, salinity, redox conditions, background levels, resuspension of sediment (due to dredging, tidal action, winds and storms), flocculation and coagulation of colloidal material and adsorption onto suspended particles (e.g., Zwolsman and Van Eck, 1999; Oursel et al., 2014). Metal partitioning is also highly influenced by the equilibrium of the metal between dissolved fraction and surface of suspended particles (Alquezar et al., 2007; Doig and Liber, 2007). Partition coefficients ( $K_d$ s) have proved to be a convenient parameter to quantify and rank the relative strength of the association between individual contaminants and SPM. There are important differences, however, in the actual values of  $K_d$  between geographical areas which is related with the nature of the particle surface and physicochemical conditions (Owens et al., 1996).

There are many researches on metals in estuarine environments of the world, most of them studying their occurrence and distribution in the sediment fraction; However, to the best of our knowledge, in the last decade no more than 18 articles have dealt with heavy metals in the dissolved and particulate seawater fractions together (e.g., Audry et al., 2007; Jonas et al., 2010; Fu et al., 2013). Hence, it is worth evaluating metal concentrations in seawater as it is a particularly difficult matrix to study and since it is useful to make comparison with estuaries from other geographical areas of the world.

The Bahía Blanca estuary (BBE), a coastal environment in Argentina, is of great economical and biological value. Important industries, cities and harbors are in continuous developing. However, few articles studied metal concentrations (i.e. Cd, Cu, Fe and Mn) in the waters of this system, working with either one or all the metals in the dissolved (Ferrer et al., 2000; Botté et al., 2007, 2008) or the particulate fraction (Fernández Severini et al., 2013). Both compartments together were evaluated four times (Andrade et al., 2000; Ferrer et al., 2003; Botté, 2005; Fernández Severini et al., 2009) and only in one case (Fernández Severini et al., 2009) the interaction between metals was analyzed, with samples taken from the subtidal area. In the present work, sampling was performed within intertidal areas, known as important sites within an estuary (Wood and Widdows, 2002; Feng et al., 2004; Botté et al., 2007), which could be used as proxies for monitoring metal concentrations in a more immediate way.

The present work is the first record of these four metals distribution together, in the particulate and dissolved fraction, after the enforcement of an environmental law supervising industrial discharges in this estuarine waters (Law: 12257, 2007). It is also a contribution to the knowledge of metal concentrations in an estuary with a continuous industrial development. By 2002, the industrial area surrounding the petrochemical center embraced only 9 industries while nowadays includes more than 135 industries, within an area of 136 ha (Sznaiberg, 2012). Physicochemical parameters were also evaluated to determine possible influences on metal partitioning. In addition, the study includes the first registers

for two sampling sites, with recognizable “biological pollution” originated by sewage discharges on these ecosystems (Pierini et al., 2012; Spetter et al., 2015).

## 2. Materials and methods

### 2.1. Study area

The BBE (Fig. 1) is the second largest estuary of Argentina, South America, located in the south-east coast of the country, between 38°45' and 35°10'S and 61°45' and 62°30'W. It is a mesotidal estuary, which drains an area of 2300 km<sup>2</sup> of a very complex system of channels. It is northwestern–southeastern directed, with the Canal Principal (60 km long) as the main navigation channel (Perillo and Piccolo, 1999). The BBE has a semidiurnal tidal regime with a mean amplitude that varies between 3.5 and 2.2 m at the head and mouth of the estuary, respectively (Perillo and Piccolo, 1991). Winds are mainly from northwest and north with a medium velocity of 24 km per hour (Piccolo, 2008). The inner zone has been regarded as turbid with an annual mean of particulate suspended matter of 78 mg/L (Guinder et al., 2009). Sediments are mainly represented by silts and clays, while towards the mouth, the estuary becomes characterized by sandy sediments (Gelos et al., 2004). The BBE has few minor freshwater contributors, producing localized spots of lower salinity but with marine conditions prevailing. The Sauce Chico river, with a mean discharge of 150,000 m<sup>3</sup>/day and the Naposta Grande stream, with a mean of 91,000 m<sup>3</sup>/day, are the major contributors to the freshwater superficial drainage net (Limbozzi and Leitao, 2008). Additionally, the BBE receives other freshwater inputs through continental runoff, sewage discharges and harbor-related operations (Botté et al., 2010).

Two cities are established adjacent to the estuary, Bahía Blanca (350,000 inhabitants) and Punta Alta (60,000 inhabitants), generating urban sewage discharges of almost 84,000 m<sup>3</sup>/day that reaches the estuary without appropriate treatment (CTE, 2003). One of the most important deep-water port systems of Argentina is located on the northern coast of the BBE, contributing with the mobilization of thousands of tons of sediment from deepening and maintenance activities of the navigation channels. Industries from a petrochemical center are located in the harbor area, which main ports are Puerto Galván and Ingeniero White. The latter comprises a dock for coastal fishing boats and an area for loading grain (Limbozzi and Leitao, 2008). Water discharges of this harbor area have a mean of 22,000 m<sup>3</sup>/day (CTE, 2012), with some type of treatment before reaching the estuary. Spills originated from harbor actions in Puerto Rosales port, near Punta Alta city, also reach the estuary. Cattle and agricultural activities are well developed in the area, especially in the upper part of the Naposta Grande stream and the Sauce Chico river (Limbozzi and Leitao, 2008) adding different types of contaminants to the water courses. The BBE, hence, undergoes intense human-induced disturbances related to urban and industrial developments in the area (Botté et al., 2007; Fernández Severini et al., 2009).

### 2.2. Sampling sites

Four sites, from the head to the mouth of the estuary, were selected representing locations with presumable different anthropogenic impact (Fig. 1).

Almirante Brown (AB) is the closest to the head of the estuary, with the Maldonado stream coming from across Bahía Blanca city and draining next to the sampling site. It is located next to an urban effluent discharge that began to operate in 2008 with an estimated release of 4800 m<sup>3</sup>/day (Streitenberger and Baldini, 2010). This area was also an ancient municipal dump until 1992 but still receives

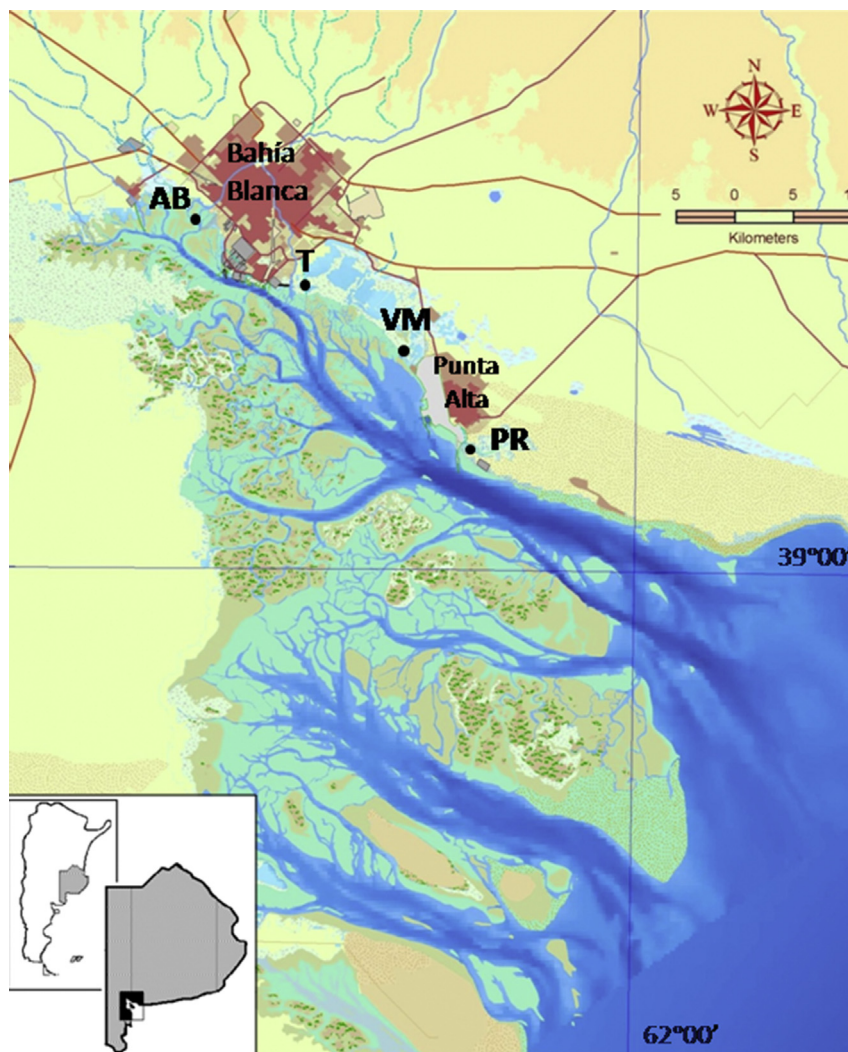


Fig. 1. Map of Bahía Blanca Estuary, Argentina, showing the study area and the four sites selected.

clandestine discharges and has a permanent lixiviation favored by constant flooding. Termoelectrica (T) is located near the industrial area, close to the petrochemical center and the main harbors. Villa del Mar (VM) is a coastal town located in the middle–outer reach of the BBE, usually used as a recreational area and for fishery. Puerto Rosales (PR) is the harbor adjacent to Punta Alta city and receives the influence of urban effluents with scarce treatment.

Samples were collected in a seasonal basis from spring 2011 to summer 2013, comprising six surveys (November 2011; February 2012; May 2012; August 2012; October 2012; February 2013). Seawater samples were obtained in the intertidal areas at high tide from a dock, using 1.5 L polyethylene-tereftalate (PET) bottles. They were submerged 0.5 m down at each site, rinsed three times before filling, double bagged and transported to the laboratory in refrigerated boxes. Physicochemical parameters (salinity, pH, turbidity, temperature and dissolved oxygen) were measured simultaneously with a multisensor Horiba U-10.

### 2.3. Laboratory analyses

At the laboratory, water samples were immediately filtered through 0.45  $\mu\text{m}$  mesh cellulose acetate Millipore HA filters (pre-weighed) in order to obtain particulate and dissolved fractions for metals determination. Filtered fractions were acidified to  $\text{pH} < 2$

with concentrated analytical quality HCl, placed in bottles, double bagged and stored at 4 °C in darkness until analysis. Particulate fractions in filters were dried in a stove at  $50 \pm 5$  °C until constant weight, weighted in an analytical balance (OHAUS, Adventurer) and stored in dry conditions. The content of SPM (mg) in each sample was calculated as follows: (weight of the filter with SPM) – (weight of the same filter before proceeding with filtration).

A preconcentration procedure was applied for dissolved metals (Cd, Cu, Fe) determination according to Botté et al. (2007), based on the report by Koirtyohann and Wen (1973). A sample of 500 mL (by duplicate) was put into separatory funnels, with a previous addition of ammonium hydroxide buffer to adjust  $\text{pH}$  to  $4.00 \pm 0.02$ . The sample was then mixed with 10 mL APDC (ammonium pyrrolidine dithiocarbamate) as chelating agent and 20 mL MIBK (methyl isobutyl ketone) as organic surfactant. It was shaken for 30 min, leaving to stand for at least 16 h, after which the upper organic phase was separated in a beaker of 100 mL. The volume was reduced to less than 8 mL on a heating plate and the final extract carried up to 10 mL with MIBK saturated in water. Metals concentrations were measured using an AAS (Perkin–Elmer AA-2380) with air/acetylene flame. Dissolved manganese was not analyzed, since this element forms unstable complexes working at  $\text{pH} 4$ . The Mn complexes deteriorate rapidly at room temperature, resulting in a lower response of the instrument (APHA, 1998). After phase



separation, the lower aqueous phase was used to prepare metal-free seawater, which was obtained by subjecting the aqueous phase to three consecutive extractions. The metal-free seawater was used to prepare the reactive blanks and the corresponding standards.

Particulate metals (Cd, Cu, Fe and Mn) determination was performed based on Botté et al. (2010) with a further modification annexed to the procedure. The filters were put in test tubes and were subjected to an acid digestion with 6 mL of HNO<sub>3</sub>:HClO<sub>4</sub> (5:1) in a glycerin bath at 110 ± 10 °C for 72 h or until the volume was reduced to less than 1 mL. The acidic extracts were transferred to centrifuge tubes and 0.7% HNO<sub>3</sub> was added up to 10 mL of final solution. Metals were measured with an ICP OES Perkin Elmer Optima 2100 DV with axial view for Cd, Cu and Fe and radial view for Mn.

#### 2.4. Cleaning procedures

All material used during sampling and in the laboratory was cleaned according to internationally recommended protocols (APHA, 1998). The conditioning procedure included washing the material with non ionic detergent, rinsing them three times with tap water and then three times with deionized water. The material was then soaked for 24 h in a diluted acid nitric solution (5% HNO<sub>3</sub>) and finally rinsed three times with deionized water. The 0.45 µm mesh filters were also conditioned in 0.7% HNO<sub>3</sub> for 48 h, rinsed with deionized water and dried to constant weight in individual Petri dishes in a laboratory stove at 50 ± 5 °C during 56 h.

#### 2.5. Data processing and statistical analyses

Salinity values were measured using the Practical Salinity Scale. One-way analysis of variance (ANOVA) was performed to assess differences in physicochemical parameters and metal concentrations between sampling sites using the data for the whole study period. Based on the results of these analyses, the differences between sampling dates were evaluated using ANOVA and Scheffé contrast. If necessary, data was previously transformed to meet the required assumptions of homogeneity and normality for the parametric tests. When the data did not meet the assumptions, a non-parametric test was used (Kruskal–Wallis). Coefficients of variation (CV) were used to estimate the variability of the physicochemical parameters.

Partition coefficients (Log<sub>10</sub>K<sub>d</sub>) are used as a common approach for better understanding the circulation of metals between the different compartments. They were determined according to Tang et al. (2002) with the following formula (expressed on a logarithmic scale):

$$K_d = \frac{[M_{PART}]}{[M_{DISS}]} \quad (1)$$

Where  $M_{PART}$  is the metal concentration in the particles (µg/Kg) and  $M_{DISS}$  is the metal concentration in the filter-passing fraction (µg/L).

Heavy metals might be originated from similar sources and/or have similar reactivity towards physicochemical parameters. Therefore, significant relationships were evaluated with Pearson correlation.

The analytical method detection limit (MDL) for each dissolved metal (µg/L) was: 0.18 for Cd; 0.44 for Cu; 3.1 for Fe. The MDL for each particulate metal (µg/g) was: 0.99 for Cd; 3.5 for Cu; 12 for Fe; 2.9 for Mn. Metals concentrations reported as below MDL were substituted by one half the MDL for statistical analyses (Jones and Clarke, 2005) and no analyses were performed when 40% or more of the concentrations of the metal evaluated were below the MDL (Federal Register, 1984). All statistical analyses were carried out using STATISTICA 7.0 (StatSoft, Inc.), following Zar (1996). The

acceptable level of statistical significance was minor than the 5%. Data presented in the figures were not transformed. Error values, either in figures, tables or in text, represent standard deviation.

### 3. Results

#### 3.1. Physicochemical parameters

Profiles of the physicochemical parameters analyzed showed no significant differences between sampling sites ( $p > 0.16$ ).

Mean salinity was  $36 \pm 1.8$ , ranging from 33 to 40 with a small CV (4%). The distribution pattern of salinity fluctuated seasonally ( $p < 0.010$ ), with autumn 2012 and both summers achieving the highest concentrations (Fig. 2A).

Mean pH was  $8.1 \pm 0.36$ , ranging from 7.4 to 9.1 with a small CV (4.6%). Even though a general trend of decreasing concentrations towards the last three samplings could be appreciated, significant differences ( $p = 0.015$ ) only showed that summer 2013 recorded the lowest values ( $p < 0.050$ ) (Fig. 2B).

Mean turbidity was  $140 \pm 120$  NTU, fluctuating from 36 to 490 NTU with a CV of 86%. SPM concentrations varied between 26 and 230 mg/L with a mean of  $89 \pm 66$  mg/L and a high CV (74%). Even though no significant differences between sampling dates or sites were recorded for either of the parameters ( $p > 0.12$ ) (Fig. 2C and 2D), spring 2011 exhibited, in average, the lowest concentrations.

Temperature varied between 7.7 and 26 °C with a mean of  $17 \pm 5.0$  °C and a CV of 29%. Significant temporal differences were found ( $p < 0.010$ ), as expected, with winter 2012 recording the lowest values ( $p < 0.050$ ) (Fig. 2E).

Dissolved oxygen concentrations ranged from 6.1 to 9.3 mg/L, with a mean of  $7.6 \pm 0.85$  mg/L and a small CV (11%). Even though no significant differences were observed ( $p = 0.25$ ) (Fig. 2F), dissolved oxygen values reached a maximum in winter 2012 and a minimum in summer 2012.

#### 3.2. Dissolved and particulate metals

All metals showed a uniform distribution of the dissolved and particulate fraction in the different sampling sites, thus, no significant differences were achieved ( $p > 0.44$ ).

Levels of dissolved Cd ranged from below MDL to 4.7 µg/L with a mean of  $1.8 \pm 1.5$  µg/L (Table 1). There were significant differences between sampling dates ( $p < 0.010$ ), with autumn 2012 showing higher values than spring 2011 ( $p < 0.050$ ) (Fig. 3A). Particulate Cd varied from below MDL to 11 µg/g with an average of  $2.3 \pm 2.7$  µg/g (Table 1). There were no significant differences between sampling dates in particulate Cd concentrations ( $p = 0.31$ ), although the highest values were registered in winter 2012 due to high concentrations in the inner zone (T and AB) (Fig. 3B).

Dissolved Cu concentrations varied from below MDL to 6.0 µg/L, with a mean of  $3.3 \pm 1.6$  µg/L (Table 1). Particulate Cu ranged between 24 and 220 µg/g with a mean of  $47 \pm 39$  µg/g (Table 1). Even though no significant differences were found either in the dissolved or particulate fraction along the sampling period ( $p = 0.075$  both) both fractions exhibited an opposite behavior in spring 2011 (Fig. 3C, 3D).

Dissolved Fe ranged from below MDL to 62 µg/L, with a mean of  $8.8 \pm 12$  µg/L (Table 1). There were significant differences between sampling dates in dissolved Fe values ( $p < 0.010$ ). Summer and winter 2012 values were higher than those found in spring 2011 and summer 2013 ( $p < 0.050$ ) (Fig. 3E). Also autumn 2012 showed increased values. Particulate Fe ranged from 2.2 to 9.6 µg/g, with a mean of  $5.6 \pm 1.7$  µg/g (Table 1) and varied over time. Although there were no significant differences between sampling dates ( $p = 0.060$ ), spring 2011 exhibited the lowest concentrations (Fig. 3F).

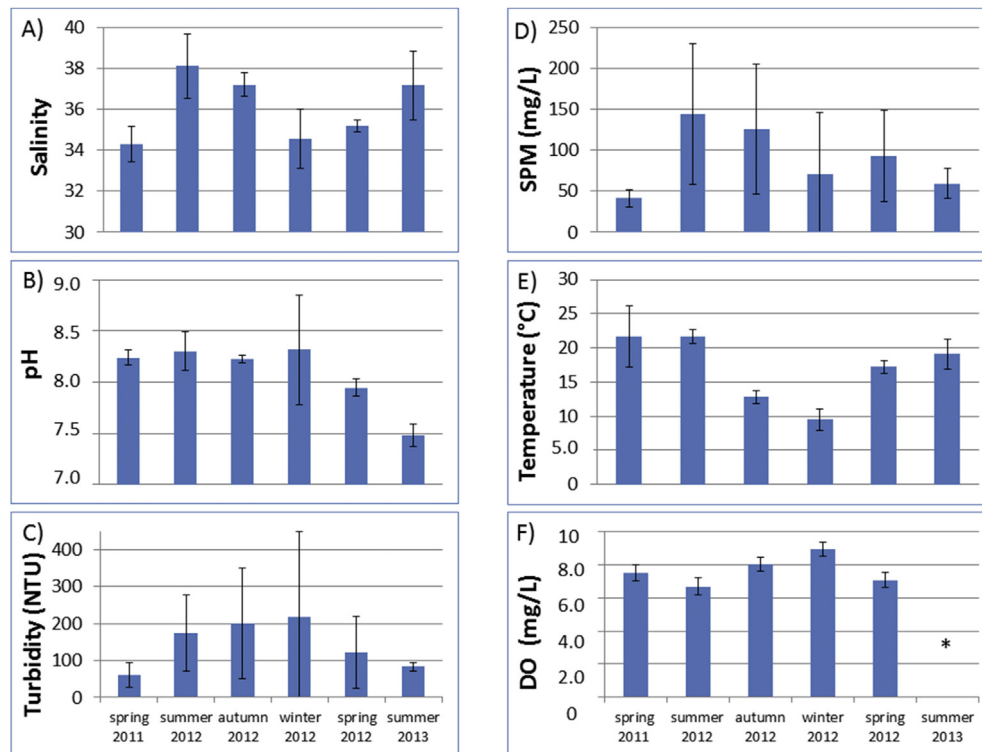


Fig. 2. Average values  $\pm$  Standard deviation of physicochemical parameters at each sampling season. \*: Data missing due to equipment failure.

Dissolved Mn was not analyzed, since the element forms unstable complexes working at the pH of the protocols. Particulate Mn varied from 970 to 1500  $\mu\text{g/g}$  with a mean of  $1000 \pm 210 \mu\text{g/g}$  (Table 1). Although no significant temporal pattern distribution was

observed ( $p = 0.075$ ), summer 2013 showed lower concentrations in comparison with the other sampling dates (Fig. 3G).

The dissolved/particulate fractionation of metals during the sampling period showed relatively constant  $\text{Log}_{10}\text{Kd}$  values

Table 1

Dissolved ( $\mu\text{g/L}$ ) and particulate ( $\mu\text{g/g}$ ) metals concentration and  $\text{Kd}$  values (L/Kg) from the Bahía Blanca estuary. Notes: PR: Puerto Rosales; VM: Villa del Mar; T: Termoelectrica; AB: Almirante Brown; <MDL: below method detection limit; SD: Standard deviation.

| Sampling sites | Sampling dates | Dissolved metals ( $\mu\text{g/L}$ ) |               |               | Particulate metals     |                        |                |                        | $\text{Log}_{10}\text{Kd}$ (L/Kg) |                |                |
|----------------|----------------|--------------------------------------|---------------|---------------|------------------------|------------------------|----------------|------------------------|-----------------------------------|----------------|----------------|
|                |                | Cd                                   | Cu            | Fe            | Cd ( $\mu\text{g/g}$ ) | Cu ( $\mu\text{g/g}$ ) | Fe (%)         | Mn ( $\mu\text{g/g}$ ) | Cd                                | Cu             | Fe             |
| PR             | Spring 2011    | <MDL                                 | <MDL          | <MDL          | 1.4                    | 40                     | 5.2            | 1200                   | 4.2                               | 5.3            | 7.5            |
|                | Summer 2012    | 3.1                                  | 4.1           | 22            | <MDL                   | 42                     | 7.5            | 1300                   | 2.2                               | 4.0            | 6.5            |
|                | Autumn 2012    | 3.2                                  | 4.0           | 7.5           | 2.9                    | 241                    | 4.5            | 920                    | 3.0                               | 4.0            | 6.8            |
|                | Winter 2012    | 0.90                                 | 2.7           | 11            | 1.4                    | 30                     | 3.3            | 720                    | 3.2                               | 4.1            | 6.5            |
|                | Spring 2012    | 2.0                                  | 3.2           | 9.5           | 1.5                    | 55                     | 6.1            | 1000                   | 2.9                               | 4.2            | 6.8            |
|                | Summer 2013    | 4.7                                  | 6.0           | 4.1           | 1.6                    | 38                     | 4.8            | 820                    | 2.5                               | 3.8            | 7.1            |
|                | Mean $\pm$ SD  | $2.3 \pm 1.7$                        | $3.3 \pm 1.9$ | $9.3 \pm 7.2$ | $1.5 \pm 0.76$         | $41 \pm 8.2$           | $5.2 \pm 1.4$  | $1000 \pm 220$         | $3.0 \pm 0.68$                    | $4.2 \pm 0.52$ | $6.9 \pm 0.38$ |
| VM             | Spring 2011    | <MDL                                 | <MDL          | <MDL          | 1.4                    | 220                    | 2.2            | 670                    | 4.2                               | 6.0            | 7.1            |
|                | Summer 2012    | 4.0                                  | 4.3           | 14            | 1.4                    | 26                     | 4.3            | 1100                   | 2.5                               | 3.8            | 6.5            |
|                | Autumn 2012    | 3.2                                  | 4.2           | 5.5           | <MDL                   | 36                     | 8.6            | 1300                   | 2.2                               | 3.9            | 7.2            |
|                | Winter 2012    | 1.0                                  | 1.7           | 9.7           | <MDL                   | 36                     | 8.2            | 1100                   | 2.7                               | 4.3            | 6.9            |
|                | Spring 2012    | 2.6                                  | 5.1           | 3.4           | 1.7                    | 57                     | 5.6            | 880                    | 2.8                               | 4.0            | 7.2            |
|                | Summer 2013    | 2.6                                  | 2.9           | <MDL          | 1.2                    | 24                     | 4.1            | 630                    | 2.7                               | 3.9            | 7.4            |
|                | Mean $\pm$ SD  | $2.3 \pm 1.4$                        | $3.1 \pm 1.8$ | $5.9 \pm 4.8$ | $1.1 \pm 0.51$         | $67 \pm 78$            | $5.5 \pm 2.5$  | $940 \pm 260$          | $2.9 \pm 0.69$                    | $4.3 \pm 0.83$ | $7.1 \pm 0.31$ |
| T              | Spring 2011    | <MDL                                 | <MDL          | <MDL          | 4.4                    | 28                     | 5.2            | 1100                   | 4.6                               | 4.4            | 7.5            |
|                | Summer 2012    | 2.6                                  | 4.4           | 7.5           | 4.4                    | 43                     | 6.8            | 1200                   | 2.3                               | 3.8            | 7.0            |
|                | Autumn 2012    | 2.9                                  | 3.2           | 9.9           | <MDL                   | 48                     | 9.6            | 1500                   | 2.2                               | 4.0            | 6.7            |
|                | Winter 2012    | <MDL                                 | 5.1           | 6.4           | 11                     | 51                     | 3.7            | 940                    | 5.0                               | 3.9            | 5.9            |
|                | Spring 2012    | <MDL                                 | 2.5           | <MDL          | <MDL                   | 51                     | 6.3            | 1000                   | 4.1                               | 4.0            | 6.8            |
|                | Summer 2013    | 2.1                                  | 4.1           | <MDL          | 1.1                    | 34                     | 4.7            | 760                    | 3.6                               | 4.0            | 7.5            |
|                | Mean $\pm$ SD  | $1.3 \pm 1.4$                        | $3.3 \pm 1.7$ | $4.7 \pm 3.7$ | $3.6 \pm 3.9$          | $43 \pm 9.3$           | $6.1 \pm 2.1$  | $1100 \pm 250$         | $3.6 \pm 1.2$                     | $4.0 \pm 0.21$ | $6.9 \pm 0.60$ |
| AB             | Spring 2011    | <MDL                                 | 1.2           | <MDL          | 3.4                    | 33                     | 5.2            | 1100                   | 4.7                               | 5.1            | 7.5            |
|                | Summer 2012    | 2.6                                  | 5.0           | 7.2           | <MDL                   | 35                     | 7.5            | 1000                   | 3.2                               | 4.0            | 7.0            |
|                | Autumn 2012    | 3.5                                  | 3.9           | 11.2          | <MDL                   | 39                     | 6.0            | 830                    | 2.2                               | 4.2            | 7.0            |
|                | Winter 2012    | <MDL                                 | 3.4           | 62            | 9.7                    | 29                     | 5.1            | 1200                   | 5.1                               | 4.0            | 6.8            |
|                | Spring 2012    | <MDL                                 | 4.8           | 8.9           | 1.1                    | 44                     | 5.6            | 980                    | 3.7                               | 4.3            | 7.6            |
|                | Summer 2013    | 0.41                                 | 3.5           | <MDL          | 1.6                    | 36                     | 5.3            | 860                    | 2.7                               | 3.9            | 7.5            |
|                | Mean $\pm$ SD  | $1.1 \pm 1.5$                        | $3.6 \pm 1.4$ | $15 \pm 23$   | $2.8 \pm 3.6$          | $36 \pm 5.0$           | $5.8 \pm 0.91$ | $1000 \pm 140$         | $3.6 \pm 1.1$                     | $4.3 \pm 0.44$ | $7.2 \pm 0.35$ |

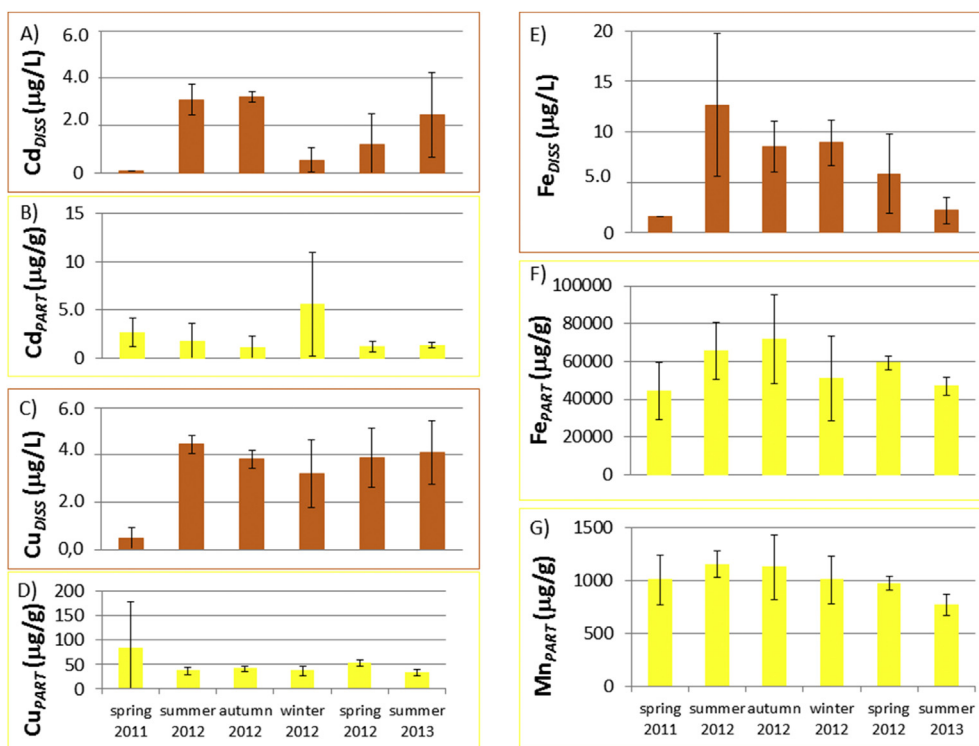


Fig. 3. Average values  $\pm$  Standard deviation of dissolved and particulate metals at each sampling season.

throughout the whole BBE (Table 1). The general order of the  $\text{Log}_{10}K_d$  for the studied metals, considering mean values, were: Fe (7) > Cu (4.2) > Cd (3.3).

### 3.3. Correlation analyses

The correlation analyses between the physicochemical parameters and the concentrations of dissolved and particulate metals were, in most cases, not significant ( $p < 0.050$ ) (Table 2). Among statistical significant correlations, those with values of correlation higher than 65% were taken into account. A high negative significant correlation was found between SPM and particulate Cd ( $r^2: -0.70$ ). SPM and turbidity showed a positive significant correlation between each other ( $r^2: 0.88$ ) and both parameters with particulate Fe ( $r^2: 0.90$  and  $0.79$ , respectively). Dissolved Cd correlated positively with salinity ( $r^2: 0.72$ ). Finally, a positive significant correlation was found between particulate Fe and Mn ( $r^2: 0.67$ ).

## 4. Discussion

### 4.1. Physicochemical parameters

The salinity gradient of the Bahía Blanca Estuary is considerably milder than other temperate estuaries due to the reduced river runoff (Guinder et al., 2012 and references therein). That being said, salinity in this study varied even in a narrower range (CV 4%), in comparison with most previous studies from the BBE: 16 to 41 (1974–2002) (Freije and Marcovecchio, 2004), 10 to 38 (2001–2002) (Botté et al., 2007). A general tendency towards higher values could be observed in this study in comparison with previous ones. The differences between present work and previous studies could be associated with the punctual sites monitored and/or the meteorological conditions. Historical mean precipitation in the BBE is 637.4 mm (INTA, 2012) whereas in the study period was 560.6 mm (INTA, 2012). The high

salinity levels found in both summer and autumn 2012 could also be influenced by meteorological conditions, since reduced precipitations were achieved in these seasons, being almost half the values than those reported in spring 2011 (INTA, 2012).

The general trend of decreasing values in pH concentrations found in the study, could be further associated to the environmental changes described for the BBE as part of the global change effects on biogeochemical processes in estuaries (Kopprio et al., 2015). Additionally, the increasing concentration of  $\text{CO}_2$  gases as a consequence of the greenhouse effect might also lead to increasing  $\text{CO}_2$  concentration in the seawater and thus a decrease in pH (Piccolo, 2013).

Turbidity and SPM concentrations in this study were high as expected for the BBE, characterized by high values due to resuspension of fine sediments (silt and clay) and strong winds and tides, identified as the main inputs of energy (Cuadrado et al., 2005). Winds are persistent all year round, with a significant number of days a year (196) with strong winds (Piccolo, 2008). The Canal Principal is regularly dredged, thus increasing the resuspension of particulate matter (Marcovecchio and Freije, 2004). Both parameters also presented a significant positive association, showing a similar temporal distribution pattern.

Temperature values achieved were in agreement with data from the period 1996–2006 (Ferrer et al., 2000; Botté et al., 2007; Fernández Severini et al., 2009; Marcovecchio et al., 2010). The temperatures found could be influencing the high dissolved oxygen concentrations in winter 2012 due to the higher oxygen solubility at low temperatures. In addition, during the typical winter/early spring phytoplankton bloom within the estuary, as a result of photosynthesis, oxygen levels are usually increased (Freije and Marcovecchio, 2004). Results also evidenced no oxygen deficiency, contrary to what was observed in previous studies (Botté et al., 2007), since values for hypoxia of less than 3 mg/L (Tyson and Pearson, 1991) were not recorded during the studied period.

**Table 2**

Pearson correlation analyses between metals concentrations and physicochemical parameters. Notes: bold red numbers are statistical significant correlations; bold red numbers marked with a\* are strong statistical significant correlations.

|                    | Cd <sub>PART</sub> | Cd <sub>DISS</sub> | Cu <sub>PART</sub> | Cu <sub>DISS</sub> | Fe <sub>PART</sub> | Fe <sub>DISS</sub> | Mn <sub>PART</sub> | SPM          | Turbidity | pH    | Salinity | Dissolved Oxygen |
|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------|-----------|-------|----------|------------------|
| Cd <sub>PART</sub> | 1.0                |                    |                    |                    |                    |                    |                    |              |           |       |          |                  |
| Cd <sub>DISS</sub> | -0.34              | 1.0                |                    |                    |                    |                    |                    |              |           |       |          |                  |
| Cu <sub>PART</sub> | -0.024             | -0.11              | 1.0                |                    |                    |                    |                    |              |           |       |          |                  |
| Cu <sub>DISS</sub> | 0.042              | <b>0.54</b>        | 0.15               | 1.0                |                    |                    |                    |              |           |       |          |                  |
| Fe <sub>PART</sub> | <b>-0.52</b>       | 0.25               | 0.26               | 0.11               | 1.0                |                    |                    |              |           |       |          |                  |
| Fe <sub>DISS</sub> | -0.20              | 0.40               | -0.020             | 0.29               | 0.24               | 1.0                |                    |              |           |       |          |                  |
| Mn <sub>PART</sub> | -0.090             | 0.039              | 0.038              | -0.037             | <b>0.67*</b>       | 0.32               | 1.0                |              |           |       |          |                  |
| SPM                | <b>-0.70*</b>      | 0.38               | 0.13               | 0.24               | <b>0.90*</b>       | 0.18               | 0.46               | 1.0          |           |       |          |                  |
| Turbidity          | -0.58              | 0.17               | 0.084              | 0.20               | <b>0.79*</b>       | 0.15               | 0.43               | <b>0.88*</b> | 1.0       |       |          |                  |
| pH                 | 0.093              | 0.098              | 0.21               | -0.083             | -0.090             | 0.28               | 0.34               | -0.17        | -0.17     | 1.0   |          |                  |
| Salinity           | -0.39              | <b>0.72*</b>       | -0.21              | 0.36               | 0.36               | 0.066              | -0.053             | 0.46         | 0.37      | -0.12 | 1.0      |                  |
| Dissolved oxygen   | 0.039              | 0.018              | <b>-0.63</b>       | -0.27              | -0.29              | -0.040             | 0.032              | -0.27        | -0.22     | 0.22  | -0.094   | 1.0              |

#### 4.2. Dissolved and particulate metals

It was found that metal distribution between sites was quite similar, whereas some differences were observed between seasons. Metals in the particulate fraction exhibited always higher values than in the dissolved fraction. Particulate concentrations tend to fluctuate probably due to a combination of suspended particulate interactions, namely remineralization of organic matter, and sedimentation (Colbert and McManus, 2005). Bioturbation or other physical disturbances/resuspension of bottom sediments might also release dissolved metals to porewater and then to the water column and would rapidly be a part of the particulate fraction. Dredging activities also contribute to the increase in the particulate levels. After becoming associated with suspended particulate matter, metals might be buried again in the sediments and recycled within the coastal/estuarine circulation pattern for considerable periods of time. These processes, common in estuaries, could be responsible of metals distributions and concentrations in the BBE even though potential anthropogenic sources cannot be ruled out either.

##### 4.2.1. Cadmium

Dissolved Cd distribution throughout the sampling period could be related to the Cd-chloro-complexes, due to the positive correlation between dissolved Cd and salinity. The Cd-chloro-complexes have high stability and solubility (Du Laing et al., 2009) possibly producing Cd mobilizations from the particulate fraction into the solution (Kraepiel et al., 1997). Additionally, an increase in salinity increments the concentrations of major cations (e.g. Na, K, Ca, and Mg) that then compete with Cd for the sorption sites (Tam and Wong, 1999). Studies in estuaries such as the Scheldt estuary in Belgium and The Netherlands (Gerringa et al., 2001), the Wanquan and the Wenchang/Wenjiao River estuary in China (Fu et al., 2013) and the Changjiang Estuary in China (Wang and Liu, 2003) showed increasing Cd desorption from the particulate fraction with high salinities.

The overall inverse relationship of particulate metal values with SPM called “particle concentration effect” (PCE) (Turner and Willmard, 2002), that is attributed to heterogeneity effects of particle size and composition (including the presence of colloidal organic matter), was apparent for Cd. The contrasting behaviors can be accounted on the basis of a high affinity between Cd and particulate organic matter (Valenta et al., 1986).

The levels of dissolved and particulate Cd in this study were higher than the ones reported previously in the BBE. Values up to 2.5 µg/L in intertidal areas (Botté et al., 2007) and 4.1 µg/L from subtidal sampling sites (Andrade et al., 2000) and of 1.4 µg/g (Ferrer et al., 2000) and 10 µg/g (Andrade et al., 2000) in subtidal zones were found. The exception was one study that, even though was unable to detect dissolved Cd concentrations, found higher particulate levels in subtidal zones from the inner part of the estuary (up to 29 µg/g) (Fernández Severini et al., 2009). The cause of this kind of discrepancies in values of the same estuarine system could be due to the differences when sampling (subtidal vs intertidal sampling sites). Nevertheless, the two highest concentration of particulate Cd found in this study were also found in the two sampling sites closer to the head of the estuary, in agreement with Fernández Severini et al. (2009). This suggests that, in the BBE, non-point inputs of Cd with variations in time might occur.

In comparison with other high anthropogenic impacted systems (Table 3), like the estuary of Tinto and Odiel rivers (Vicente-Martorell et al., 2009), world-known polluted with Cd, Cu and Mn (Sainz et al., 2004 and references therein), this study found interesting similarities. Mean concentrations of dissolved Cd in the present study were similar to those found in other estuaries whereas for particulate Cd were higher in comparison with the same estuarine systems. It is worth mentioning that in these areas subtidal samples were taken. Regarding potential hazardous impact, even though mean dissolved Cd levels were below the maximum of 5.0 µg/L recommended by the Environmental Quality Standard (EQS, for estuarine waters) (Cole et al., 1999), at some specific sampling dates and sites the recorded values were close (e.g. 4.7 µg/L). Hence, Cd concentrations should be carefully monitored in the BBE in order to avoid dangerous increments in the next years, especially from the intertidal area.

##### 4.2.2. Copper

Particulate Cu values in the present study were higher than most previous data reported for the BBE, but dissolved values were usually lower. Data from the subtidal area reported dissolved concentrations from 0.50 to 2.4 µg/L and from below MDL to 54 µg/g of dissolved and particulate Cu, respectively (Fernández Severini et al., 2009). Ferrer et al. (2003) also found mean dissolved values of 4.7 ± 2.3 µg/L and particulate Cu of 36 ± 9.8 µg/g and Botté (2005), with data from the intertidal areas, found dissolved concentrations



**Table 3**  
Dissolved ( $\mu\text{g/L}$ ) and particulate ( $\mu\text{g/g}$ ) metals concentration in human impacted estuaries and coastal zones. References data are given as range data or mean value  $\pm$  standard deviation; nd: non-detectable; F: data taken from figures.

| Sampling area              | Dissolved metals ( $\mu\text{g/L}$ ) |                         |           | Particulate metals     |                        |              |                        | References                     |
|----------------------------|--------------------------------------|-------------------------|-----------|------------------------|------------------------|--------------|------------------------|--------------------------------|
|                            | Cd                                   | Cu                      | Fe        | Cd ( $\mu\text{g/g}$ ) | Cu ( $\mu\text{g/g}$ ) | Fe (%)       | Mn ( $\mu\text{g/g}$ ) |                                |
| Port Jackson estuary       |                                      |                         |           |                        | 20–130 (F)             | 0.60–1.6 (F) | 300–2000 (F)           | Hatje et al., 2001             |
| Conwy estuary              |                                      | 0.1–2.5 (F)             | nd-80 (F) | 5.0 (F)                | 20–380 (F)             |              | 600–1600 (F)           | Zhou et al., 2003              |
| Odiel river                | 1.8 $\pm$ 0.78                       | 20 $\pm$ 7.6            |           | 1.9 $\pm$ 3.1          | 30 $\pm$ 9.6           |              |                        | Vicente-Martorell et al., 2009 |
| Tinto river                | 2.2 $\pm$ 0.96                       | 23 $\pm$ 16             |           | 1.5 $\pm$ 1.7          | 33 $\pm$ 14            |              |                        | Vicente-Martorell et al., 2009 |
| Severn Estuary             |                                      | 2–9.5 (F)               |           |                        | 25 $\pm$ 23            |              |                        | Jonas and Millward, 2010       |
| Portuguese Coast           | 0.0011–0.10                          | 0.057–2.9               |           | 0.11–1.7               | 3.2–63                 |              |                        | Santos-Echandia et al., 2012   |
| Coastal system of Malassia | nd-5.7                               | 5.2–530                 | 83–980    |                        |                        |              |                        | Looi et al., 2013              |
| Bahía Blanca estuary       | n.d-4.7 (1.8 $\pm$ 1.5)              | n.d-6.0 (3.3 $\pm$ 1.6) | n.d-62    | n.d-11 (2.3 $\pm$ 2.7) | 24–220 (47 $\pm$ 39)   | 2.2–9.6      | 970–1500               | This study                     |
| EQS guidelines             | 5                                    | 5                       | 1000      |                        |                        |              |                        | Cole et al., 1999              |

ranging from 0.65 to 13  $\mu\text{g/L}$  and particulate ones of up to 36  $\mu\text{g/g}$ . The higher particulate Cu concentrations achieved in the intertidal areas, especially from this study, in comparison with subtidal ones, highlight the importance of the former and bring attention towards a trend of increasing values in the last years. Intertidal flats might then be functioning as a source of metals to the water column, being then the contaminants redistributed through the dynamics of this shallow system.

In comparison with other estuaries (Table 3), average values of particulate Cu were higher than many polluted estuaries such as the estuary of Tinto and Odiel rivers in Spain and the Severn estuary in Great Britain. Given the strong affinity of Cu to organic matter (e.g. Benedetti et al., 1995; Jonas and Millward, 2010), the high concentration of particulate Cu in the BBE could be related to the usually high particulate organic matter concentration in this system (e.g., Freije et al., 2008). Even though some punctual dissolved values (see Table 1) were observed to exceed the maximum concentration established by the EQS, they were usually below the estuarine systems concentrations abovementioned.

#### 4.2.3. Iron

For particulate active elements like Fe, the geochemical behavior in estuaries is strongly affected by SPM. Large scale removal of dissolved Fe resulting from the aggregation of colloidal Fe has typically been observed in estuarine studies (e.g. Figueres et al., 1978). In the present work, a high positive correlation is established between particulate Fe and SPM. This highlights the strong affinity of Fe for particles (e.g. Fu et al., 2013). High SPM and turbidity are favored by dredging activities, as mentioned before, since when polluted areas are dredged, heavy metals adsorbed to sediments and buried are remobilized (Mateus et al., 2008). It is worth mentioning that increased sedimentary Fe values have been registered in the last years (Serra, A.V., unpublished data) in comparison with previous data (Botté, 2005; Marcovecchio and Ferrer, 2005).

Fe determinations in the BBE were scarce, with dissolved values of up to 38  $\mu\text{g/L}$  (Botté, 2005), which were higher than the ones in the present study. Maximum particulate concentrations were of almost 3.0% (Botté, 2005; Delucchi et al., 2008), these being half the particulate Fe concentrations found in the present work. These differences might indicate a change in the partitioning dynamics of this metal with time.

In comparison with other estuaries in the world, particulate Fe levels in the BBE were higher than those recorded in estuaries like the Port Jackson (Table 3), considered one of the most polluted systems in Australia (Hatje et al., 2001). As regards for the dissolved fraction, the levels found were lower than the concentrations found in both other estuarine systems and the maximum values recommended by the EQS.

#### 4.2.4. Manganese

The concentrations of particulate Mn achieved in this study might be related to the oxidation of Mn, probably being the main driving force which strongly influences the partitioning of Mn towards the particulate fraction. Mn is a redox sensitive element and as a result, is strongly affected in its distribution by the change in the oxidation state, due to changes in dissolved oxygen (Fang and Lin, 2002). When the environment is sufficiently well oxygenated, Mn (hydro) oxides are formed and the precipitation of Mn begins (Chaudry and Zwolsman, 2008).

Mn and Fe are strongly correlated, being this correlation the only one found between metals. They are hydroxides that play particularly important roles in cycling and transporting metals due to their large surface areas and high capacity to sorb and co-precipitate other metals (Liang et al., 2013). Moreover, sewage sludge, which affects BBE, contains high amounts of Fe and Mn oxides, (Parkpain et al., 2000).

In the only previous study with Mn concentrations in the BBE, reported values ranged between 93 and 410  $\mu\text{g/g}$  (Botté, 2005), denoting that concentrations from the present study were by far higher (up to 3 times). It is worth highlighting that during this previous study, as abovementioned, dissolved oxygen concentrations was also lower, thus influencing Mn distributions. Comparisons with data available from other estuarine systems (Table 3) (i.e. Conwy, Port Jackson), denote that present values were similar to those reported concentrations.

#### 4.2.5. Partitioning coefficients

The partition coefficients of the three metals studied did not vary much within the BBE system. The lack of variance suggests that partitioning of these elements does not undergo major modifications due to estuarine processes. Note that  $\text{Log}_{10}\text{Kd}$  is not a true equilibrium coefficient, but is an empirical term, which depends on factors such as pH, temperature, solution composition and concentration of colloids in the 'dissolved' fraction, metal speciation and heterogeneity in particle surfaces (Hatje et al., 2003).

The general order of the  $\text{Log}_{10}\text{Kd}$  for the studied metals, considering mean values, were: Fe > Cu > Cd. Fe values were higher than those observed for Cu and Cd, which highlights a stronger affinity for particles, as observed by other authors (e.g. Fu et al., 2013). This result was also supported by the positive correlation found between Fe and SPM as abovementioned. Fe has a geochemical behavior different to the other metals due to a tendency to selectively partition onto particles.  $\text{Log}_{10}\text{Kd}$  values for Cd were the lowest and could be explained by the negative correlation between Cd and SPM. Thus, the numerator in Eq. (1) decreases leading to lower values of  $\text{Log}_{10}\text{Kd}$ . Cd and Cu partitioning behavior



from this study were not similar to those previously found in the BBE (Fernández Severini et al., 2009). The Log<sub>10</sub>Kds found for Cu by Fernández Severini and coworkers were much lower, ranging from –0.35 to 2.8. As for Cd, no partitioning values were evaluated in their study since no dissolved concentrations were found.

The values of Log<sub>10</sub>Kd are comparable to the ones reported for other coastal systems of the world (Zhou et al., 2003; Vicente-Martorell et al., 2009; Fu et al., 2013), suggesting that partitioning of elements in the suspended matter is of major importance on the water-particle partitioning worldwide. One of the most polluted systems by metals in Europe, the estuary of Tinto and Odiel rivers, showed Log<sub>10</sub>Kd data ranging from 0.15 to 1.7 for Cd and 1.1–2.0 for Cu (Vicente-Martorell et al., 2009), meaning that the affinity of Cd and Cu for the particulate fraction is higher in the BBE. The Conwy estuary, the largest of the North Wales coast, has Log<sub>10</sub>Kds similar to this study, since they ranged from 5.5 to 6.7 for Fe and 4.5–6.5 for Cu (Zhou et al., 2003). The same was observed in the Wanquan River estuary and the Wenchang/Wenjiao River estuary in East-Hainan Island, since mean values were 6.0, 4.8 and 4.8 for Fe, Cu and Cd, respectively (Fu et al., 2013).

#### 4.3. Implications of metals in the nearshore ecosystem

Metals concentrations were related to the nearshore Bahía Blanca ecosystem, as it is one of the most productive marine systems in Argentina (Fernández Severini et al., 2013) and thus, the evaluation of risk for the ecosystem exposed to environmental stress is of vital importance.

Planktonic organisms have been thoroughly and systematically studied during the last 30 years (Gayoso, 1983, 1988; Popovich, 2004; Guinder et al., 2012) and have presumably generated the largest database regarding South America coastal systems. Even though these organisms tend to accumulate trace elements from ingested food and the dissolved phase (Reinfelder et al., 1998; Wang and Fisher, 1999), there were only two studies evaluating toxicity effects of Cd in diatoms (Andrade et al., 2000) and in copepods (Fernández Severini, 2008). Also, a third researcher focused on toxicity tests in biota, evaluating the LC<sub>50</sub> of Cd and Cu in larvae and young crabs at different times of exposure (Ferrer et al., 2000, 2003, 2006).

It is important to emphasize that even though LC<sub>50</sub> values from acute toxicity experiments of the abovementioned researches were higher than dissolved concentrations obtained in this study, those previous studies were conducted under experimental conditions and metal bioavailability is a function of not only the total metal concentrations but also their free ion activity, which is affected by factors such as salinity and complexation capacity (Blaudez et al., 2000; Philp, 2001).

## 5. Conclusion

In the Bahía Blanca estuary, the presence and distribution of metals between the dissolved and particulate fraction was assessed in seawater samples from the intertidal areas. The possible influence of coastal industrial developments and physicochemical parameters in metal partitioning, and the consequences of the enforcement of an environmental law supervising industrial discharges in estuarine waters were evaluated.

The intertidal areas studied showed to be quite homogeneous as regards metals distribution within the BBE, with variations between sites only detected in specific dates. This could either mean that different human activities (agriculture, industries and cities) exert the same pressure on metal contamination or that the differences are not detectable due to the action of physical forces (e.g.

tides, winds). These physical forces tend to produce mixtures of water to give a homogeneous system in the coastal area.

The concentrations of particulate metals achieved in the present work were of higher ranges than previous studies from the BBE. Thus, human activities that surround the estuary, streams, rivers and areas like saltmarshes and tidal flats outflowing within the estuary should be considered as they might constitute a significant source of metals for the estuarine system. Additionally, even though a law regulating industrial discharges was established, the values of some metals, instead of remaining equal or of lesser magnitude, were increased.

Cd, Cu and Fe particulate concentrations were higher compared to other polluted estuaries of the world. It is very important to emphasize that it represents a high risk for plants and animals, considering that these metals could be bioconcentrated or bioaccumulated by organisms (Botté et al., 2013), including the human population.

The dissolved/particulate fractionation of the given metals expressed in Log<sub>10</sub>Kd values showed neither temporal nor spatial variations. Fe and Cd had respectively the highest and the lowest Log<sub>10</sub>Kd values, indicating their differential affinities for particles. It is also worth mentioning that previous Log<sub>10</sub>Kd registered for Cu were lower thus, the variables influencing the differences in metal partitioning should be further studied.

This research demonstrated the importance to study seawater in intertidal areas. These areas would have a principal function as regulators of metals contamination between land and coastal marine systems. Nevertheless, for a better understanding of the mechanisms involved in metal partitioning and distribution, adsorption kinetics on organic matter and porewater determinations should be taken into account.

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