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Pía Simonetti, Sandra Elizabeth Botté & Jorge Eduardo Marcovecchio

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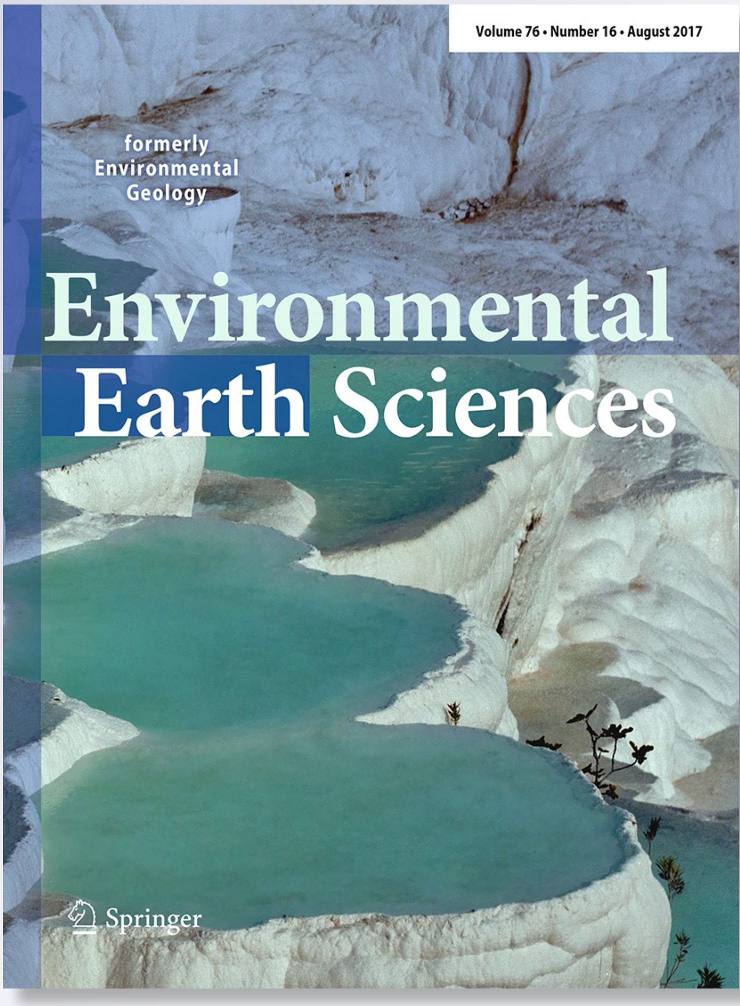

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ORIGINAL ARTICLE

Occurrence and spatial distribution of metals in intertidal sediments of a temperate estuarine system (Bahía Blanca, Argentina)

Pía Simonetti[1,2] · Sandra Elizabeth Botté[1,3] · Jorge Eduardo Marcovecchio[1,4,5]

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Abstract Intertidal sediments of the inner and middle zone from the Bahía Blanca estuary were sampled for geochemical and environmental assessment of metals (Cd, Cu, Pb, Zn, Mn, Ni, Cr and Fe). Results indicate that both the organic matter content and the sediment grain size plays an important role in controlling the differential concentrations of the metals found in sediments from both zones. For most of the elements (except Mn), sediment metal concentrations were greater in the middle zone, although the concentrations did not exceed the maximums for quality of marine sediments. In this sense, anthropogenic impact (i.e., sewage drain) appears to be a key factor in the distribution of metals within the estuarine system. Comparing the levels obtained with quality levels (LEL and SEL), except Cu that showed levels slightly above the LEL, the rest of the concentrations of metals were lower to those levels. The low metal concentrations obtained within this highly impacted estuarine system suggest that the great volume of water that flooding the extensive flats in each tidal cycle has much importance. Although the potential risks of metals to the estuarine environment were low, taking into account the toxicity of some of these metals, continuity of monitoring is highly recommended.

Keywords Bahía Blanca estuary · Intertidal sediments · Metals · Flooding · Anthropogenic impact

✉ Pía Simonetti
simonetti@criba.edu.ar

Sandra Elizabeth Botté
sbotte@iado-conicet.gob.ar

Jorge Eduardo Marcovecchio
jorgemar@iado-conicet.gob.ar

[1] Área de Oceanografía Química, Instituto Argentino de Oceanografía (IADO), CCT-CONICET, Camino La Carrindanga, km 7.5, B8000FWB Bahía Blanca, Pcia. de Bs. As., Argentina

[2] Área de Oceanografía Biológica, Instituto Argentino de Oceanografía (IADO), CCT-CONICET, Camino La Carrindanga, km 7.5, B8000FWB Bahía Blanca, Pcia. de Bs. As., Argentina

[3] Dpto. de Biología, Bioquímica y Farmacia, Universidad Nacional del Sur (UNS), San Juan 670, B8000ICN Bahía Blanca, Pcia. de Bs. As., Argentina

[4] Universidad Tecnológica Nacional-Fac. Regional Bahía Blanca (UTN- FRBB), 11 de Abril 461, B8000LMI Bahía Blanca, Pcia. de Bs. As., Argentina

[5] Universidad FASTA, Gascón 3145, B7600FNK Mar del Plata, Pcia. de Bs. As., Argentina

Introduction

The social and economic development of estuaries brings about the generation of several chemical pollutants through various sources such as industrial and agricultural activities, mining and domestic wastes, among others (Ridgway and Shimmield 2002; Ip et al. 2007; Hu et al. 2013; Zhao et al. 2013). In this context, estuarine sediments constitute the most important sink of pollutants in aquatic ecosystems. Metals deserve special attention because of its high toxicity, environmental persistence and potential bioaccumulation and biomagnification through food chains (Rainbow 2007; Pradit et al. 2010; Xu et al. 2016). The metal concentrations found in the sediment may vary as a function of the physicochemical variables such as pH, salinity, redox potential, organic matter content and sediment grain size (Eggleton and Thomas 2004; Du Laing et al. 2009; Acosta et al. 2011; Zhao et al. 2013). Benthic organisms also influence this variation mainly due to

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bioturbation, where feeding, movement and burrow formation introduce oxygenated water to deeper anoxic sediments (Eggleton and Thomas 2004). The content of organic matter in sediments, especially in estuarine and coastal areas, is recognized as an important tangler of various types of contaminants, including metals. Additionally, grain size distribution in sediments significantly influences metal concentrations and their bioavailability. Some studies have shown that highest concentrations of metals are associated with fine grained sediment particles, since higher specific surface area of clay–silt particles increases the association of metals with these particles (Ip et al. 2007; Chakraborty et al. 2015). Particle size and sediment type exert a strong influence upon contaminant binding ability. The presence of high concentrations of organic matter and ion exchange materials, such as clays, will greatly affect the ability of sediments to retain metal ions via adsorption, chelation and ion exchange mechanisms (Williams et al. 1994). Thus, this matrix acts not only as a sink but also as a source for metals to the environment. In this sense, the estuarine sediments become a fundamental tool to assess the health status of the studied environment.

The Bahía Blanca estuary is under constant and increasing anthropogenic pressure because several urban settlements (380,000 habitants) including industrial developments and harbors, produce an impact on the environment through the discharge of sewages to the estuary without suitable treatment (Ferrer et al. 2000; Andrade et al. 2002; Biancalana et al. 2012). The main urban sources of point pollution in this estuarine system are located in the Bahía Blanca district, being the sewage treatment plant of Bahía Blanca city and the sewer of Ingeniero White town the principal ones. On the other hand, the industrial discharges concern mainly the harbor area of Bahía Blanca including the petrochemical center (Limbozzi and Leitao 2008). Agricultural activities also impact this environment (Perillo et al. 2001; Botté et al. 2007).

The aim of this study was to determine the total concentration and spatial distribution of metals in surface intertidal sediments of the Bahía Blanca estuary. Although not always content of heavy metals in sediments reflects the amount available for biota because water is also a source, in this work we focus on the potential ecological risk of metal pollution in estuarine sediments.

Materials and methods

Study area

The Bahia Blanca estuary (38°45′–39°40′S and 61°45′–62°30′W) is a mesotidal coastal plain estuary extended over 2300 km^2, and formed by several tidal channels, extensive tidal flats with patches of low salt marshes and islands (Piccolo et al. 2008; Pratolongo et al. 2013). Tides are the main energy source of the system; the mean tidal amplitude ranges from 2.2 to 3.5 m and the spring tidal amplitude ranges from 3 to 4 m (Perillo and Piccolo 1991).

On the northern shore several ports (two are commercial ones), cities (i.e., Bahía Blanca, Punta Alta) and industries (oil, chemical, and plastic factories among others) are settled. The two main freshwater tributaries that enter the estuary from the northern shore are the Sauce Chico River (drainage area of 1588 km^2, 1.9 $m^3\ s^{-1}$) and Napostá Grande Creek (drainage area of 1450 km^2, 0.8 $m^3\ s^{-1}$) (Pérez and Perillo 2002; Piccolo et al. 2008). Two minor tributaries, Saladillo de García and Canal Maldonado, also drain into the estuary from the north. However, the sewage discharges from the cities of Bahía Blanca, Punta Alta, and Ingeniero White are responsible for the generation of the largest input of freshwater, nutrients, and contaminants (Spetter et al. 2015).

Two sites were selected within the Bahía Blanca estuary (Fig. 1). One of them, Cuatreros Port (CP), is located in the inner part of the estuary, within the area influenced by General Cerri town. This area is under the impact of the two branches of the Sauce Chico River and the Pejerrey canal, with a fluctuating flow, which drain big extensions of agricultural fields (Perillo et al. 2001; Limbozzi and Leitao 2008). The other sampling site, Rosales Port (RP), is located in de middle part of the estuary within the area influenced by the city of Punta Alta ($\sim$60,000 inhabitants). The site is within the area affected by the Punta Alta sewage discharge, which discharges into the estuary with no treatment. The main activities of RP are mooring buoys. Two buoys for mooring tankers, Punta Ancla and Punta Cigüeña, allow loading and unloading of liquid fuels and operation of large tankers due to the channel depth. In the port area there is a petrochemical plant that produces high and low density polyethylene. In the past 6 years, the movement of oil in this area increased almost 26%, from 9,568,200 to 12,008,486 tons (Management Consortium of the Port of Bahia Blanca 2016). This accounts for the importance of it within the port system in the Province of Buenos Aires.

Sampling

Samples ($n = 3$ for each site) of intertidal superficial sediment for determination of grain size, organic matter and metals concentration were seasonally collected from April 2014 to September 2015 with a PVC cores (100 mm i.d.; 150 mm long). Afterward, they were kept in polyethylene bags, carried to the laboratory in refrigerated boxes, and stored at 4 °C for less than 48 h. Sampling was performed during low tide in morning hours.

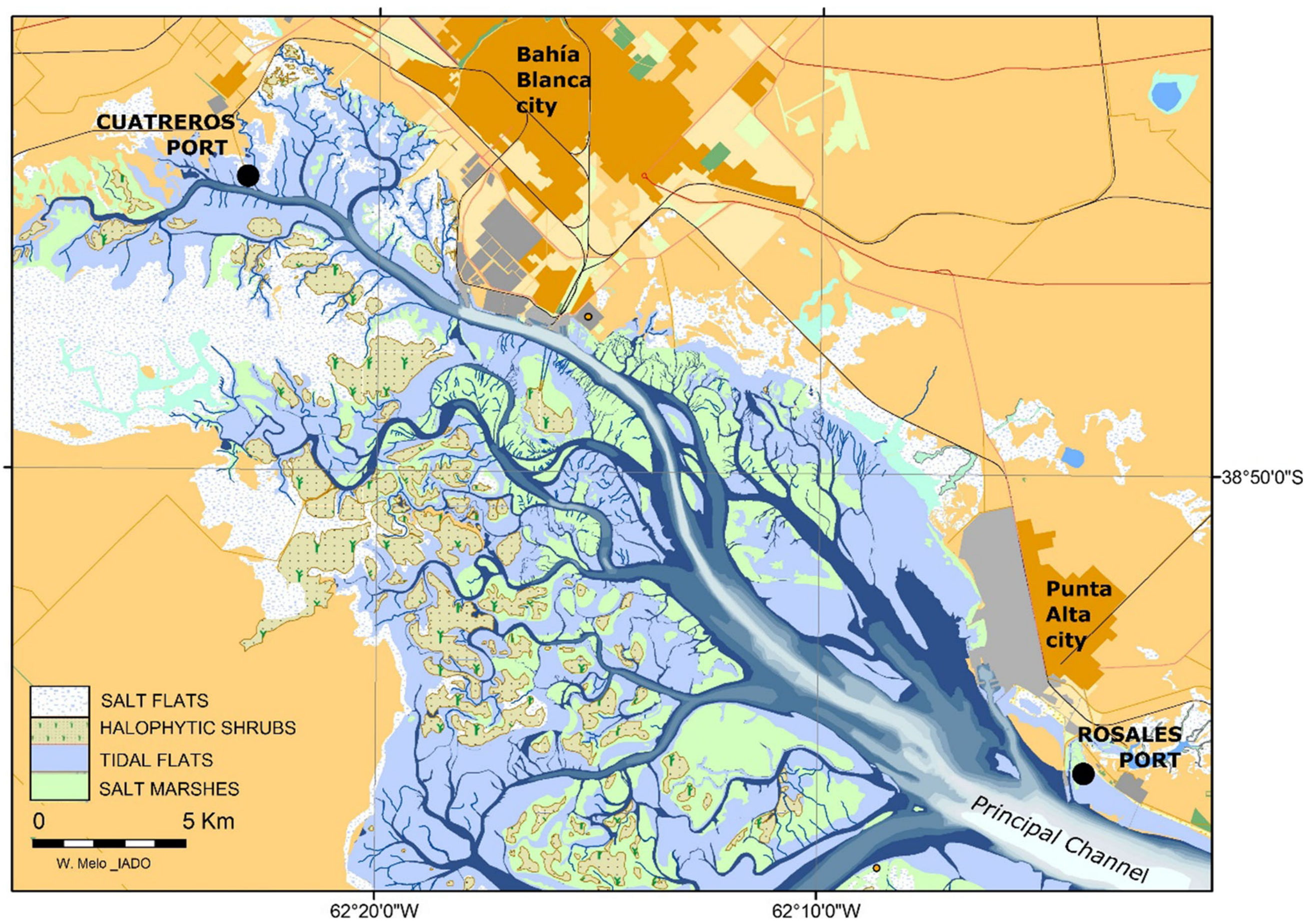

Fig. 1 Map of the study area. Black points represent the sampling areas in the Bahía Blanca estuary

The water physicochemical variables as temperature, pH and conductivity were recorded in each sampling station at 1 m depth with a multisensor HORIBA U-10. Salinity was calculated from conductivity.

Laboratory procedures

In the laboratory, sediment subsamples were taken in order to determine grain size composition, organic matter and metal contents in the <63 μm fraction (fine sediment). The subsamples to determine metal concentrations were oven dried at 60 ± 5 °C for 4 days. Large debris and fragments of biota were removed before grinding in a porcelain mortar. Afterward they were sifted through stainless steel meshes until fine particles (<63 μm) were obtained. All homogenized subsamples were stored in plastic desiccators until their analytical treatment. The subsamples for organic matter were oven dried at 60 ± 5 °C until constant weight. Organic matter content (%OM) was calculated from weight loss on ignition after drying samples at 450 ± 50 °C for 1 h in a muffle furnace (Dean 1974). Granulometry of each sample was measured with a Malvern Mastersizer 2000 laser diffractometer to obtain the percentages of clay (<4 μm), silt (4–63 μm) and sand (>63 μm) fractions.

Concentrations of (Cd, Cu, Cr, Ni, Pb, Zn, Mn and Fe) in the <63 μm grain size fraction were analyzed according to the methodology of Botté et al. (2010). About 500 mg of dry sediment samples were mineralized with a 1:5 HNO_3/$HClO_4$ mixture in a thermostatic bath at 110 ± 10 °C up to a minimum volume. Then the extracts (1 mL) were made up to 10 mL with 0.7% HNO_3. All equipment used was previously cleaned with diluted nitric acid (0.5% v/v) to prevent contamination.

An inductively coupled plasma-optical emission spectroscopy (ICPOES Optima 2100 DV Perkin Elmer) was used for determining all metal concentrations. The detection limit of the method (MDL) was calculated as the standard deviation (SD) of 10 blank replicates (Federal Register 1984). The MDLs (μg/g), were as follows: Cd 0.034, Cu 0.738, Pb 0.882, Zn 0.665, Mn 7.722, Ni 1.644, Cr 1.329 and Fe 16.47.

Analytical quality was checked against international certified reference materials (pond sediment flour R.M. No. 82) provided by The National Institute for Environmental

Studies (NIES) from Tsukuba University (Japan). For all the analyzed metals, recovery percentages match with official NIES and UNEP calibration exercises (Table 1).

Statistic analysis

Differences between sites were statistically checked by Student *t* test, combining all the data for the whole study period (i.e., ignoring seasonal/temporal differences). Appropriate statistical software was used (IBM SPSS Statistics 22.0 and Infostat version 2016—Grupo InfoStat, FCA, Universidad Nacional de Córdoba, Argentina), following Zar (1996). The acceptable level of statistical significance was 5%.

Results

Temperature, pH and salinity in superficial water

Water temperature in CP and RP varied from 9.6 to 22.5 °C, with lower values in August and September and higher ones in the early fall (Fig. 2a). This variation was similar for both sites, showing no significant statistical differences between them ($p = 0.61$).

Water pH in CP remained almost constant during the entire sampling period (8.1 ± 0.12). Although the values of water pH in RP were, on average, similar to those of CP, a greater variability was observed for RP (8.3 ± 0.43), finding a jump of one point between the lowest (7.9) and the highest (8.9) water pH value (Fig. 2b). Nevertheless, no significant statistical differences were found between sites ($p = 0.15$).

Salinity in CP and RP varied from 25.65 to 37.20, with highest values in April, February and September (Fig. 2c). Again, no significant statistical differences were found between sites ($p = 0.21$).

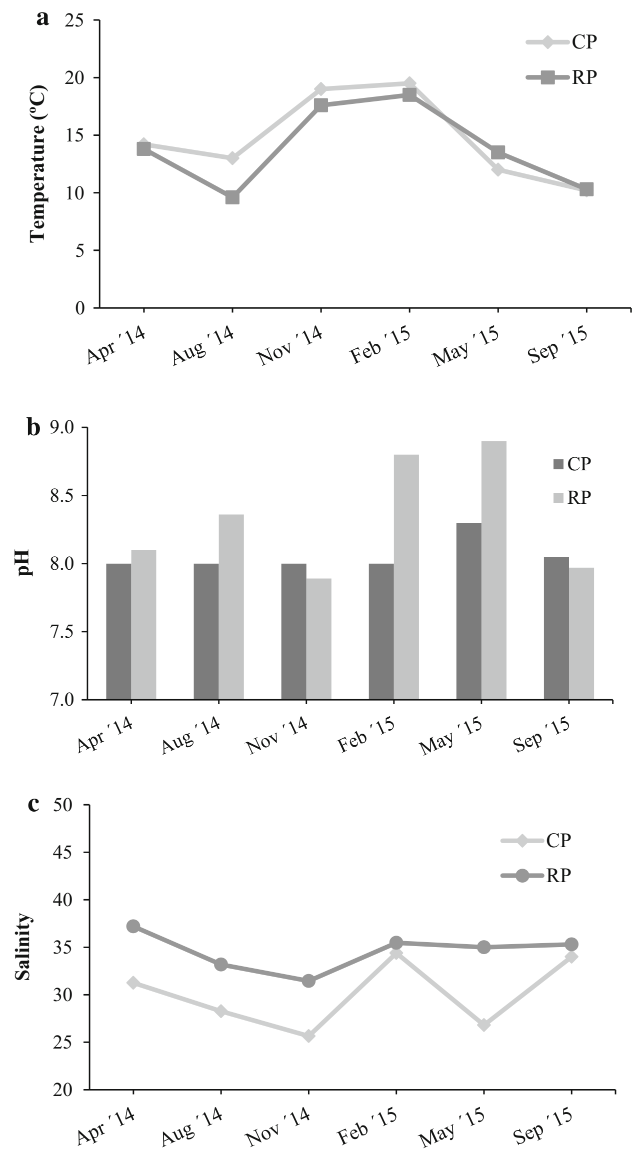

Fig. 2 Variation of temperature (**a**), pH (**b**) and salinity (**c**) in water from both sampling sites (*CR* Cuatreros Port, *RP* Rosales Port)

Table 1 Recovery values of the various metals from reference materials [pond sediment flour (R.M. No. 82)]

	Metal	Value obtained in our lab (μg/g dry weight)	Certified value (μg/g dry weight)	Recovery (%)
Pond sediment flour (R.M. No. 82)	Cu	22.63	31.6	71.6
	Pb	77.10	73	105.6
	Zn	248.35	231	107.5
	Mn	547.35	665	82.3
	Ni	33.1	31.5	105.1
	Cr	43.02	47	91.5
	Fe	23,330	30,700	76.0

Organic matter content and grain size

The sediment composition showed differences in the clay, silt and sand fractions between the two sites (Fig. 3a). In CP, the clay, silt and sand fractions ranged from 22.93 to 32.12, 53.34 to 62.94 and 5.13 to 23.73%, respectively, with an average of 26.90, 56.99 and 16.11%. In RP, the ranges were 30.19–38.51, 58.30–66.67 and 3.14–6.92% with an average of 33.58, 61.89 and 4.54%, respectively. Analyzing the percentage of fine grain (% <63 µm, clay and silt together) statistical significant differences were found for both sites ($p = 0.003$), showing a greater percentage of fine grain in RP than in CP (96.2 vs 83.89% respectively; Fig. 3a, b).

The %OM was, in all sampling dates, higher in RP than in CP (Fig. 3b). This coincides with the statistical analysis since significant differences were found between sites ($p = 0.04$). The average %OM for CP and RP was 4.29 ± 1.15 and 5.14 ± 1.32%, respectively ($n = 18$ for each site), with ranges between 2.52 to 6.07% for CP and 3.10 to 7.23% for RP.

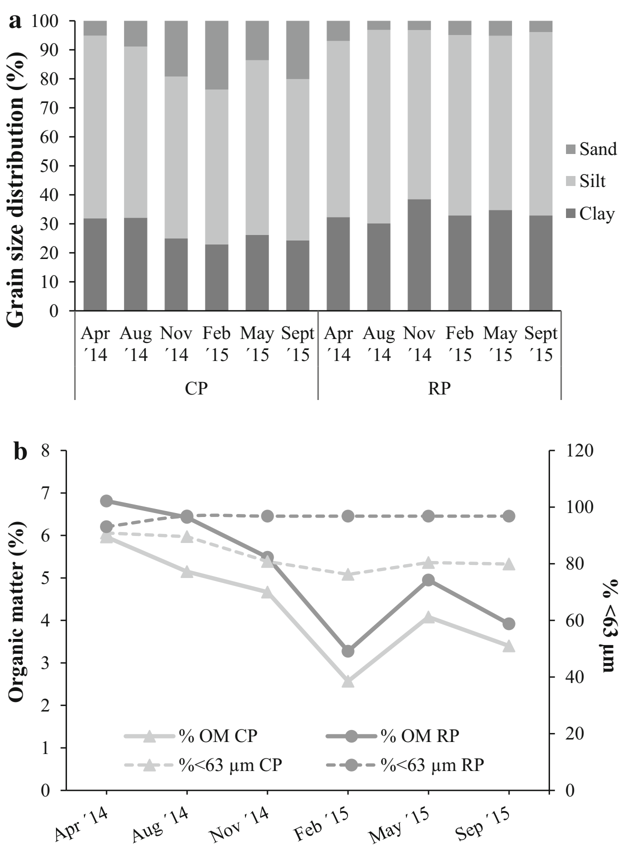

Fig. 3 **a** Grain size distribution and **b** percentage of organic matter (full line) and fine grain (<63 µm; dotted line) in the two sites throughout the sampling period (*CP* Cuatreros Port, *RP* Rosales Port)

Heavy metals in sediments

The mean, standard deviation and range of concentrations of Cd, Cu, Pb, Zn, Mn, Ni, Cr and Fe in the intertidal superficial sediments of CP and RP are summarized in Table 2. Cd was the only metal with concentrations below the detection limit (CP only). Meanwhile, Cd concentrations found in RP were not too high, showing the maximum value in August 2014 (0.11 µg/g dry wt., Table 2). The rest of the metals showed concentrations above the detection limit in all the sampling period. Except for Mn, all the metals had significantly higher concentrations in RP than in CP ($p < 0.05$; Fig. 4). The average concentrations of heavy metals in sediments at both sites showed the following order: Fe > Mn > Zn > Cu > Cr > Ni > Pb > Cd.

In order to determine the possible correlation between all metals as well as between metals and the different variables analyzed, a statistical analysis of all the data for each site was performed. The correlation coefficient matrices are shown in Table 3. In both places, a positive and significant correlation was found between various metals; however, the number of correlations was higher in CP than in RP. Regarding the correlation between metals and the analyzed variables, they were detected only in CP, with a negative and significant correlation between pH and Zn, Cr and Fe and pH and %OM.

Discussion

Physicochemical variables as temperature, pH and salinity can all contribute to mobility, bioavailability and potential toxicity of metals (Du Laing et al. 2007, 2008; Acosta et al. 2011). In this study, water temperature, water pH and water salinity showed no significant differences between the two sites. Water temperature in both locations followed values of air temperature registered by Vitale (pers. Communication) and Accuweather.com (Fig. 5). A strong regulation of the water temperature by the air temperature was previously described for the estuary (Freije et al. 2008).

Water pH values were homogenous and varied between 7.9 and 8.9. These values are in coincidence with those previously reported (Popovich et al. 2008; Fernández Severini et al. 2009; PMI Report 2014). However, given this jump of one point in the pH value in RP, it is convenient to continue evaluating this parameter taking into account a possible alkalinization of these estuarine waters. Salinity was the third variable measured. Although no significant differences between the studied sites were found, a greater variation was found for salinity values of CP (Standard deviations: 3.72 in CP vs 2.00 in RP). This greater variability in salinity values in the innermost zone of the estuary was described years before (Freije et al.

Table 2 Summary of heavy metal concentrations (μg/g dry wt.) in fine sediment from both sampling sites (mean ± SD, n = 18; minimum and maximum values)

	Metal							
	Cd	Cu	Pb	Zn	Mn	Ni	Cr	Fe
Cuatreros Port								
Mean ± SD	–	12.56 ± 1.61	7.51 ± 2.17	35.13 ± 9.36	353.33 ± 82.11	8.98 ± 2.09	12.51 ± 3.14	21,058.89 ± 2136.56
Min–max	<MDL–0.041	8.86–15.51	2.98–12.34	13.61–48.72	224.45–516.10	5.18–11.37	5.18–16.37	18,020–24,110
Rosales Port								
Mean ± SD	0.074 ± 0.007	31.32 ± 6.40	9.97 ± 2.49	78.82 ± 20.72	303.98 ± 46.02	10.33 ± 1.32	14.82 ± 3.25	23,124.72 ± 2773.03
Min–max	0.04–0.11	19.36–43.69	6.80–11.85	46.54–111.35	220–383.65	8.20–12.22	9.18–19.48	18,235–26,845

1981; Freije and Marcovecchio 2004). These authors highlighted a strong dependence between the values of salinity and precipitations. Also, the physical and geomorphological characteristics of the inner zone have an influence in this variability (Píccolo and Perillo 1990; Perillo et al. 2001; Freije and Marcovecchio 2004).

When assessing the amount of metals in the sediment, it is essential to know the % of fine grain that composes each sampling site, since it is precisely in this fraction where the aforementioned elements are mainly retained. Fine particles, such as clay and colloidal materials, are generally surface-active and contain organic matter and Fe/Mn oxide surface coatings, and they can play an important role in controlling deposition of trace metals to sediments from an estuary to a coastal area (Ip et al. 2007). The presence of metals is directly related to the organic matter in sediments, and it substantially affects the fate of metals in this matrix. Organic matter in sediments is derived from many sources, including dead plants and animals, fecal matter, domestic sewage and flocculated colloidal organic matter (Dewitt et al. 1992). According to the results obtained in this study, CP showed significantly lower % of fine grain and % of organic matter than RP (82.98 vs 96.2 and 4.29 vs 5.14%, respectively). The greatest content of organic matter in RP is not only related with the greater clay and silt content found in this site, but also due to the influence of urban sewage discharge which is relatively near the sampling area. A third factor that might be influencing is vegetation. According to Negrin et al. (2011, 2013), the presence of *Sarcocornia perennis* plays a key role in organic matter distribution. There is a marked difference in the abundance of vegetation between both studied sites, being notably superior in RP, thus contributing a greater content of organic matter to the system.

Selected metals (Cd, Cu, Pb, Zn, Mn, Ni, Cr and Fe) were found in almost all samples of surface sediments of the intertidal from the Bahia Blanca estuary. In Table 4, average metal concentrations found in this study were compared with previous data on the estuary, with values from other estuaries as well as with Sediment Quality Guidelines values described by Persaud et al. (1993): Lowest effect level (LEL) and severe effect level (SEL). LEL represents the level of contamination which has no effect on most of the sediment-dwelling organisms. SEL represents levels of contamination from which the sediment is considered heavily polluted and likely to adversely affect sediment-dwelling organisms.

Comparing with the concentrations previously found in the estuary (Table 4), we detected that the levels of Cd and Ni were lower than those from previous years. On the other hand, concentrations of Pb, Zn, Mn and Fe were within the concentrations previously described within estuary. Finally, Cu and Cr concentrations were greater than those

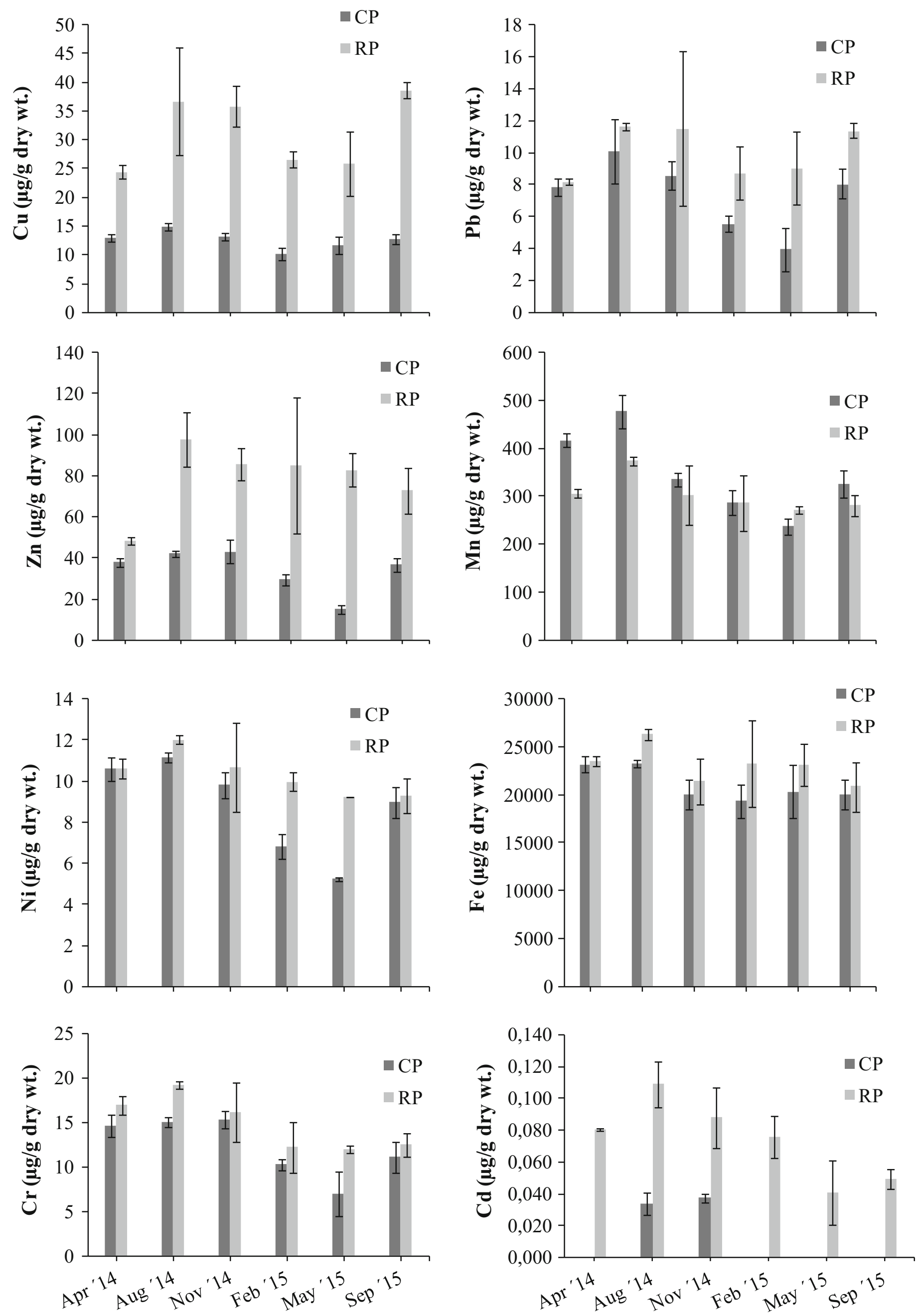

Fig. 4 Mean metal concentrations (µg/g dry wt.) in intertidal superficial sediments from Cuatreros Port (CP) and Rosales Port (RP) throughout the sampling period

found in previous years. In the case of Cd, CP showed concentrations below the detection limit in most samples. Meanwhile, in RP, Cd concentrations were slightly above the detection limit in all samples. According to Cifuentes et al. (2012), a single discharge could not be identified as the only source of contamination or the determining factor for the presence of Cd. Diffuse discharges from the former waste dump together with point source sewage discharges were identified as the most significant ones. A possible source could be through the atmospheric deposition, but so far there are no studies proving the entry through atmosphere. A second possibility could be from agricultural sources because of the utilization of phosphate fertilizers containing Cd between other metals. Except Mn, the rest of the metals showed levels significantly greater in RP than in CP in the whole sampling period. A possible explanation could be the contribution of this metal through the river system. This is evident from decades of study where the greatest average values always corresponded to the innermost section of the estuary, i.e., CP (Botté 2005). Sewage discharges coming from the city may contain various contaminants, among them, all the studied metals

Table 3 Correlation matrix (Pearson correlations) for heavy metals in sediments and physicochemical variables from both sites (bold indicate significant correlation, $p < 0.005$)

	Cu	Pb	Zn	Mn	Ni	Cr	Fe	%OM	pH	Temperature	Salinity
Cuatreros Port											
Cu	1										
Pb	**0.835**	1									
Zn	0.637	**0.944**	1								
Mn	0.794	**0.874**	0.771	1							
Ni	0.793	**0.958**	**0.933**	**0.924**	1						
Cr	0.672	**0.895**	**0.943**	**0.832**	**0.948**	1					
Fe	0.710	0.559	0.394	**0.863**	0.691	0.568	1				
%OM	0.711	0.506	0.412	0.691	0.669	0.640	**0.858**	1			
pH	−0.245	−0.704	**−0.854**	−0.662	−0.747	**−0.834**	−0.296	−0.213	1		
Temperature	−0.253	0.034	0.279	0.176	0.248	0.457	0.162	0.312	−0.599	1	
Salinity	−0.284	−0.005	0.110	0.185	0.168	0.062	0.205	−0.002	−0.344	0.402	1
Rosales Port											
Cu	1										
Pb	**0.978**	1									
Zn	0.459	0.568	1								
Mn	0.390	0.449	0.376	1							
Ni	0.265	0.339	0.286	**0.953**	1						
Cr	0.269	0.339	0.060	**0.899**	**0.948**	1					
Fe	−0.180	−0.101	0.314	0.772	0.710	0.600	1				
%OM	−0.045	0.039	−0.253	0.627	0.682	**0.854**	0.503	1			
pH	−0.576	−0.514	0.354	−0.183	−0.249	−0.437	0.422	−0.351	1		
Temperature	−0.444	−0.404	−0.013	−0.437	−0.179	−0.299	−0.321	−0.342	0.163	1	
Salinity	−0.643	−0.773	−0.737	−0.369	−0.406	−0.335	0.027	−0.082	0.251	−0.123	1

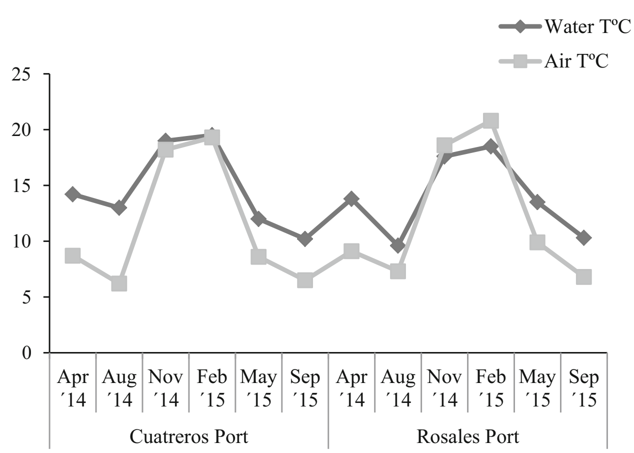

Fig. 5 Water and air temperature in both sampling sites of the Bahía Blanca estuary throughout the sampling period

derived from the different human activities that enter through runoff from precipitations, households and small businesses and industries. In the case of Cu, possible sources could be the use and application, in the cities mentioned and nearby, of fungicides, wood preservatives, pipes, pigments, antifouling paints among others. On the other hand, the sources of Cr into the system could be chemicals, cement, brake pads car, tanneries, steelmaking, chrome plating, manufacture of dyes and pigments, preserving wood, and water treatment of cooling towers. In smaller amounts, it is used in drilling muds, textiles, and toner for copiers. Taking into account both quality levels (i.e., LEL and SEL), with the exception of Cu, which showed concentrations slightly above the LEL, the concentrations found for the other metals, namely Cd, Pb, Mn, Zn, Cr, Ni and Fe, were lower than those levels. Besides, the average concentrations of all metals recorded in this study were, in general, comparable with those described for other estuaries considered non-polluted (Table 4). In this sense, toxicity to benthic organisms appears to be low. According to Persaud et al. (1993), contamination in sediments that exceeds the LEL may require further testing and a management plan. Although Cu was the only metal with concentrations slightly above the LEL, it would be desirable to carry out monitoring of the study area to evaluate the levels of all these metals over time.

Table 4 Summary of mean metal concentrations (µg/g dw, Fe in mg/g dw) in <63 µm fraction of the sediments from the intertidal of Bahía Blanca estuary and comparison with concentrations found in literature

Location	Cd	Cu	Pb	Zn	Mn	Ni	Cr	Fe	References
Bahía Blanca estuary[a]	<MDL–0.11	21.94 ± 10.76	8.68 ± 2.33	56.41 ± 26.97	325.42 ± 67.65	9.54 ± 1.89	13.51 ± 3.33	22.09 ± 2.04	This study
Bahía Blanca estuary[b]	1.35	16.99	18.36	63.03	384	15.72	11.64	25.84	Botté (2005)
Bahía Blanca estuary[c]	0.56–3.31	6.45–19.26	6.28–30.28	24.22–62.20	133–336	5.30–16.53	7.54–31.66	7.54–33.50	Botté et al. (2009)
Bahía Blanca estuary[c]	1.70–1.90	13.60–14.80	4.50–6.30	27–35	–	6–7.50	10–11.50	20.5–21.5	Martínez et al. (2012)
Bahía Blanca estuary[d]	0.90–2.20	7.70–15.50	5.70–8.90	3.50–42	–	3.50–7	4.50–23	10.8–25	
Yangtze estuary, China	0.26	30.7	27.3	94.3	–	31.8	78.9	–	Zhang et al. (2009)
Guadiana estuary, Spain	0.20 ± 0.02	50 ± 1.76	32.9 ± 1.17	168 ± 7.10	–	27.8 ± 0.75	19.2 ± 0.46	–	Delgado et al. (2010)
Changhua River estuary, China	0.09	15	27	73.7	–	23	53.1	31.84	Hu et al. (2013)
Cavado estuary, Portugal	0.37	113	40.9	170	449	16.4	34.7	10.4	Gredilla et al. (2015)
Santos São Vicente estuary, Brazil	–	8.87 ± 6.42	11.41 ± 7.57	47.68 ± 28.38	258.90 ± 182.21	7.41 ± 4.28	18.21 ± 9.70	18.90 ± 9.86	Kim et al. (2016)
LEL	0.6	16	31	120	460	16	26	2%	Persaud et al. (1993)
SEL	10	110	250	820	110	75	110	4%	

[a] Average of Cuatreros Port and Rosales Port

[b] Average of Cuatreros Port, Maldonado and Galvan Port

[c] Data from Cuatreros Port

[d] Data from Rosales Port

Previous studies on intertidal sediments from the Bahía Blanca estuary recording significant differences between metals concentrations on inner and outer sediments, indicating that a strong dilution effect was occurring within the system and pointed out that the tidal energy influence along time (twice a day) clearly redistribute the introduced metals, modifying the background level and also homogenizing the estuary sediment concentrations (Marcovecchio et al. 2008). The low metal concentrations obtained within this highly impacted estuarine system suggest that the great volume of water that flooding the extensive flats in each tidal cycle has a very important role. This dilution effect of huge volumes of water has also been described for other estuaries in the world, for instance the Yangtze estuary (Zhang et al. 2001; Chen et al. 2004).

Finally, except Cu and Fe, most of the studied metals in CP were significantly correlated each other, suggesting a common origin of these metals in sediments. This was not the same for RP where only few metals correlated each other. The lack of a positive correlation could be indicating the entry of the metals into the system in more current geological times, probably derived from human activity, which is large and with a high degree of dispersion (i.e., numerous sources).

Conclusions

- Studied metals were recorded in most of analyzed samples in both sites; however, their levels were not extremely high suggesting they could be very close to background ones.
- Both organic matter and % fine grain size within the studied sediments demonstrated to significantly govern metals contents within this matrix.
- Anthropogenic impact (i.e., sewage discharges, port activities) appeared to be determinant factors in the distribution and circulation of metals within the system.
- The degree of accumulation of evaluated metals does not overcome the maximums for quality of marine sediments. Some metals are environmentally significant; therefore, they must be monitored continuously to detect in time any probable alteration in the biota.
- The low metal concentrations obtained within this highly impacted estuarine system suggest that of great volume of water that flooding the extensive flats in each tidal cycle has much importance.
- The advantages reached from the analysis of metals in the finest grain size fraction of sediments are fully highlighted, and its incorporation into future monitoring programs within this environment is encouraged.

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