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ORIGINAL ARTICLE

# Metals in tidal flats colonized by microbial mats within a South-American estuary (Argentina)

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**Abstract** In this study, we measured the concentrations of metals (Cd, Cu, Pb, Ni, Cr, Zn, Hg, Mn, and Fe) and assessed the characteristics of tidal flats (grain size and organic matter content) in sediments and their overlying microbial mats fractions to evaluate the anthropogenic impact within the Bahía Blanca Estuary (BBE). Puerto Rosales (PR) and Almirante Brown (AB), located in the middle and inner zone of the estuary, respectively, were used as sampling sites. Sediments were composed mainly of silt–clay in AB, whereas first fine-grained particles were coarser in depth in PR. Regarding the concentration of metals in both fractions, we found differences between sites: There were higher concentrations of overall metals in AB relative to PR. In addition, higher concentrations of Cu were recorded in the first centimeters of AB tidal flats, whereas higher concentration of Cd were recorded in microbial mats of PR. Considering that the grain size was similar between sites, these results are consistent with the high concentration of organic matter found in AB, probably because this site is close to a former municipal dump and sewage discharges. Also, the higher Cd content found in PR site would highlight both the influence of untreated urban discharges and port anthropogenic activities. In conclusion, this study allowed identifying high values of some metals in the presence of microbial mats in the BBE, thus suggesting a possible interaction between both, at least for metals like Cu or Cd.

**Keywords** Marine pollution · Metals · Microbial mats · Sediments · Estuaries

## Introduction

Estuaries and coastal environments are historically chosen for urban, agro-industrial and recreational activities. Consequently, these environments receive large amounts of different types of contaminants. During the last few decades, the distribution of trace metals in estuaries has been studied extensively because metal contamination has become an environmental issue of international concern.

Metals are released into the environment by natural processes and anthropogenic activities such as wet and dry atmospheric deposition, stream and river inputs, dredging spoils, burning of fossil fuels, antifouling paints, direct discharges of industrial dumps, and sewage sludge (Kennish 1991; Valavanidis and Vlachogianni 2010). When metals are present at small concentrations, they do not represent toxicity for plants or animals (Ndimele and Jimoh 2011). However, at higher levels, metals can begin to be toxic to both the environment and their biotic constituents (de Smedt et al. 1998; Kehrig et al. 2003). Nevertheless, some metals, such as cadmium, lead, and mercury, can be toxic even at low concentrations (De Vries et al. 2007; Hasan et al. 2013; Binbin et al. 2014).

In estuarine environments, tidal flats represent a transition area from land to sea in which sediments may act both as sources as well as sinks for certain metals (Botté et al.

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2010; Louriño-Cabana et al. 2011; Hasan et al. 2013; Mil-Homens et al. 2013). Sediment habitats in intertidal and shallow subtidal marine ecosystems frequently support extensive areas covered by microbial mats, a multilayered sheet accumulation of microorganisms (mainly algae, pennate diatoms, and cyanobacteria) arranged in cohesive structures (Bender et al. 1995; Des Marais 1995). Modern microbial mats are remarkably cosmopolitan, and some of their most important representatives are encountered in practically every country of the world (Esteve et al. 1992). These assemblages form a matrix of cells, sediments, and extracellular polymeric substances (EPS) that create a complex microhabitat which influences sediment stabilization (Underwood and Paterson 2003; Cuadrado et al. 2013).

Microbial mat ecosystems support most of the major biogeochemical cycles within a vertical dimension of only a few millimeters from the surface (Paerl and Pinckney 1996). Fike et al. (2008) indicate a distinctive vertical distribution of trace metals related to a vertical zonation of physical–chemical gradients within the microbial mat. The ability of microbial communities to absorb metals—besides the EPS capacity to bind and fix sediments—contributes to decreasing metal toxicity in those environments (e.g., Wieland et al. 2003; Giloteaux et al. 2011; Maldonado et al. 2011; Burgos et al. 2013). The phototrophic organisms living in microbial mats secret negatively charged EPS which plays a significant role in biologically influenced mineralization. In addition, microorganisms can remove toxic metals from contaminated waters and waste streams by converting them to forms that are precipitated or volatilized from solutions (Lovely and Coates 1997). In fact, the ecological success of microbial mats and their broad array of microbial activities suggest that these microbial ecosystems might be useful for the bioremediation of environmental pollutants (Decho 2013; Giloteaux et al. 2011; Tice et al. 2011).

A special feature of the Bahía Blanca Estuary (BBE) is that tidal flats have been colonized by extensive microbial mats (Cuadrado and Pizani 2007; Cuadrado et al. 2011, 2012). Moreover, these tidal flats have been extensively studied to explore the relationship between microphytobenthos, sediment, and physical factors, such as radiance, temperature, sedimentation rate, and wave height (Cuadrado et al. 2012, 2013; Pan et al. 2013).

In the last 25 years, the BBE has suffered severe perturbations as a result of strong demographic expansions, and the rise of industrial activities as much in number as in production (e.g., oil refineries, petrochemical industries, plastic factories, leather and textile plants, and meat factories). Much of the waste derived from these activities end up into streams or directly into the estuary with scarce previous treatment, meaning that potentially contaminant substances could be affecting both sediments and biota in this environment (Ferrer 2001). Several studies have evaluated the concentration of metals in different matrixes within the BBE (e.g., Andrade et al. 1996; Marcovecchio and Ferrer 2005; Botté et al. 2007; Fernández Severini et al. 2009; Marcovecchio et al. 2010; La Colla et al. 2015). Sediments from tidal plains have, however, been much less studied (Hempel et al. 2008; Botté et al. 2010; Spetter et al. 2015).

In view of the economic importance of the coastal region and the adverse effects of metal pollution on living resources in BBE, this study aimed at evaluating: (1) the role of microbial mats as tramps of metals in two sites under different anthropogenic influence; and (2) the distribution of metals in a depth profile of sediments colonized by microbial mats.

## Materials and methods

### Study area and sampling sites

The Bahía Blanca Estuary is a temperate and turbid estuary, with a northwestern–southeastern direction (38°44′–39°27′S and 61°45′–62°30′W) and 80 km in length (Fig. 1). Water circulation is dominated by semidiurnal tidal waves whose mean tidal range is of around 2.3–3 m (Perillo and Piccolo 1991). This estuary has been classified as a mesotidal estuary, partially mixed with a strong tendency to be vertically homogeneous due to strong tidal currents (Perillo and Piccolo 1999). Strong NW and N winds dominate the typical weather pattern of the region, with a mean velocity of 24 km $h^{-1}$ and gusts past 100 km $h^{-1}$ (Capelli de Steffens and Campo de Ferreras 2004). The water column is vertically homogeneous throughout the estuary, although it may be partially mixed in the inner zone depending on freshwater runoff conditions (Piccolo et al. 2008). In the northern area, two main tributaries (the Sauce Chico River and Napostá Grande stream), input freshwater into system. The Sauce Chico River discharges at the estuarine head an annual media of 1.9 $m^3$ $s^{-1}$, whereas the Napostá Grande stream discharges in the mid-area of estuary around of 0.8 $m^3$ $s^{-1}$ of freshwater. Other minor affluents are Galván, Saladillo de García, and Maldonado streams, whose joint volumes do not reach that of the Napostá stream. Thus, the inner zone of the estuary is highly turbid as a result of the combined effect of winds and tide currents containing large amounts of suspended matter (Gelós et al. 2004).

Two different sites were selected for the purpose of this study (Fig. 1): Almirante Brown (AB) and Puerto Rosales (PR), located in the inner and middle estuary, respectively. The supratidal flats of both sites are colonized by

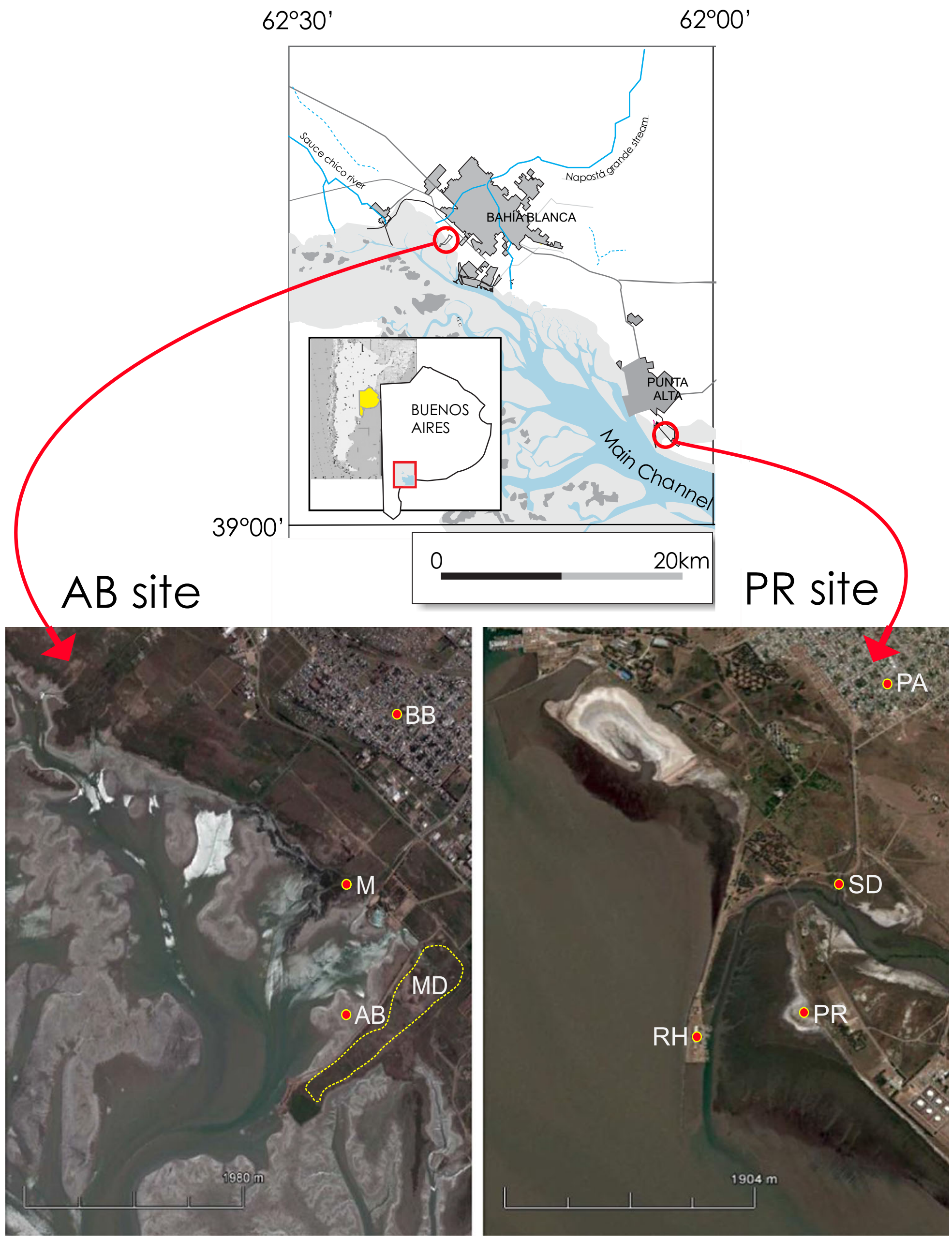


**Fig. 1** Location map showing the Bahía Blanca Estuary and sampling sites (marked with *red circles*), *PR* Puerto Rosales and *AB* Almirante Brown

microorganisms forming sedimentary structures that are microbially induced and named polygonal microbial mats (Fig. 2). These mats are flooded by seawater only during spring high tides or in storm events (Cuadrado et al. 2013) and may vary in physical characteristics as well as in the type of anthropogenic influence they are exposed to.

Almirante Brown (38°44′S; 62°19′W) is located at the inner zone of the BBE, where the main channel has a width of the order of 400 m. The muddy sediments of intertidal flats are inhabited by burrowing crabs (*Neohelice granulata*), whereas only the supratidal zone is vegetated by halophytic *Sarcocornia perennis* patches. Higher in the BBE, the municipal open dump operated for 25 years until 2010, and this place is still used clandestinely for similar purposes. The Maldonado stream runs through Bahia Blanca City and indirectly receives urban sewage as well substances (i.e., pesticides) derived from neighboring land areas of agricultural and livestock production (Freije and Marcovecchio 2004). Maldonado stream discharges in proximity of AB and thus influences our study area during ebb flooding.

Puerto Rosales (38°55′S; 62°03′W) is located in the medium zone of the BBE, close to the main channel. Extensive tidal flats (~1000 m wide) with low slopes (~0.4 gradient) are composed of sandy to muddy siliciclastic sediments which predominantly consist of quartz

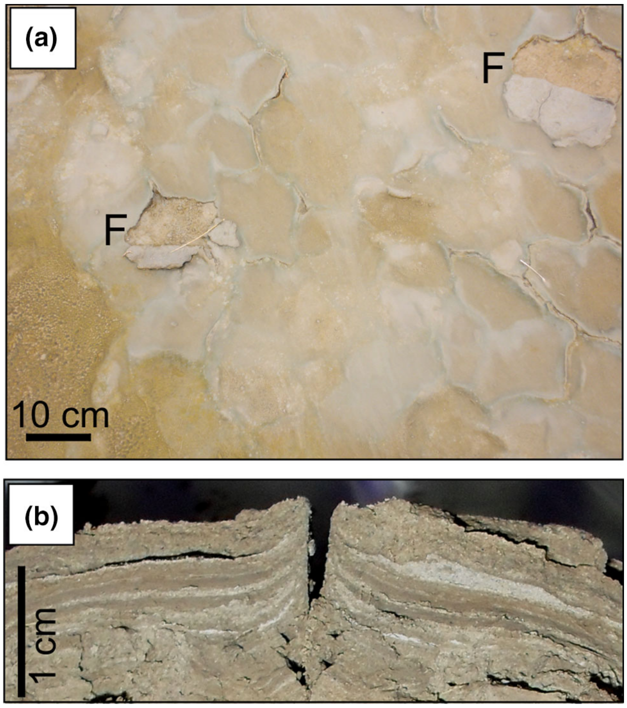


**Fig. 2** **a** Almirante Brown tidal flat colonized by microbial mats. The surface presents microbially sedimentary structures as desiccation cracks in a polygonal pattern. Edges of mat polygon are upwardly bended by desiccation. The sediment underneath the upper layer (H1) forming the H2 horizon is shown. Flip-overs (**a**, *F*) are formed over a preexisting crack margin in the microbial mat, generated after an increase in the water energy. **b** Cross section of a desiccation crack. Note the upward bend of the different layers. Lighter layers are sand representing past storm events in the environment

with minor amounts of feldspars (Cuadrado and Pizani 2007). The intertidal zone is vegetated by cordgrass *Spartina alterniflora* which promotes sedimentation in neighboring coastal areas, thus favoring the colonization of benthic microbial mats in protected supratidal zone (Cuadrado et al. 2011). The upper zone present patches of *S. perennis*. The sediments of this site are also disturbed by the crab *N. granulata*, which activities seem to be restricted to the vegetated substrates. The studied zone receives the sewage of Punta Alta city without treatment. Moreover, the Bahía Blanca-Coronel Rosales free trade zone (and associated intense port activity) and Oiltanking Ebytem SA are located in the area. This oil company operates a pipeline carrying crude oil by pumping, in addition to tanker cargoes at mono-buoys in deep water and offshore.

## Sampling and sample preparation

Sediment cores ($n = 3$ in each site) were collected in mudflats on July 2012. Samples were extracted during low tide, using a hand-driven PVC tube of 6.3 cm inner diameter. The samples were transported to the laboratory where they were immediately cut into three layers (called horizons): H1 (surface to 1 cm), H2 (1–5 cm), and H3 (5–7 cm). The horizon 1 corresponds to the newly laminated microbial community.

## Granulometry

For particle size determination, a subsample of 10 g from each horizon was treated with hydrogen peroxide 65% to remove the organic matter content (wet oxidation). After 48 h at 25 °C, the samples were placed on a heating plate (50 ± 5 °C), to achieve more complete removal of fine organic matter. Grain size was determined using a Malvern Masterziser 2000 based on the principle of laser diffraction.

## Organic matter content

The organic matter (OM) content (%) was calculated from loss of ignition (LOI) in subsamples taken in each horizon. Each of them was dried in a stove at 50 ± 5 °C until constant weight and subsequently calcined in a muffle furnace at 450 °C during 4 h (Commendatore and Esteves 2004).

## Metal concentrations

To determine the concentration of metals, the sediment was cleaned free of clasts (large debris, fragments of biota and inorganic clasts), before drying at 25 °C to constant weight. All samples were crushed and homogenized using a porcelain mortar; then, they were passed through a stainless steel sieve to obtain the fine fraction (<63 μm). Sediment subsamples (0.5 ± 0.01 g) were mineralized with a mixture of $HNO_3$:$HClO_4$ (5:1) (Merck) at 110 ± 10 °C in a glycerin bath until complete mineralization. After cooling, 0.7% nitric acid was added to the residue up to 10 ml into centrifuge tubes prior to undergoing metal concentration analyses (Botté et al. 2010). The concentration of Cd, Cu, Zn, Cr, Pb, Ni, Fe, and Mn was measured using an inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 2100 DV).

Total Hg content in sediment subsamples was determined following the methodology described in De Marco et al. (2006). About 0.8 g of sediment was digested with a mixture of $HNO_3$/$H_2SO_4$ (1:4) followed by an oxidation with potassium permanganate. The addition of stannous chloride was used to obtain elemental mercury. The Hg content was measured by cold vapor flameless atomic absorption spectrophotometry (CV-FAAS, PerkinElmer 2380).

The detection limit of the method (MDL) was calculated as three times the standard deviation (SD) of 12 blank replicates with $\alpha = 0.01$. The MDL for each metal (μg $mL^{-1}$) was: Cd: 0.042, Cu: 0.0985, Pb: 0.0620, Zn: 0.1175, Mn: 1.7846, Ni: 0.0024, Cr: 0.0015, Fe: 2.6810,

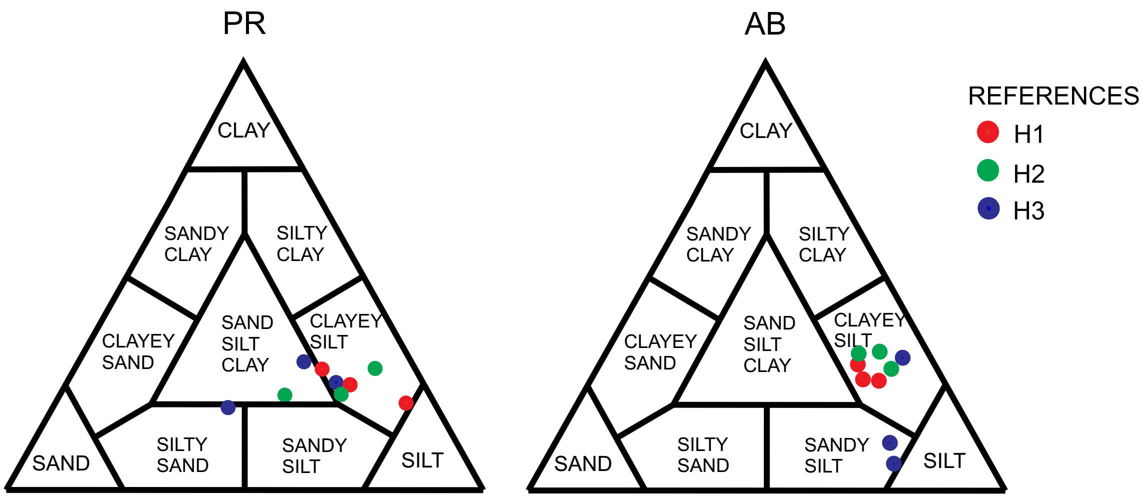


**Fig. 3** Sediment classification of *PR* Puerto Rosales and *AB* Almirante Brown sites (following Shepard 1954)

Hg: 0.023. All of the relative SDs of the replicate samples were <25%. For the analytical quality control (AQ), reagent blanks, certified reference materials (CRM; Pond Sediments, R.M. No. 2, NIES, Japan), and analytical-grade reagents (Merck or Carlo Erba) were used. The recovery percentages for all trace metals in CRM were higher than 75%.

All material used for metal measurement during sampling and in the laboratory was cleaned according to internationally recommended protocols (APHA 1998). This involved washing the material with nonionic detergent and subsequent rinsing it with tap water. After rinsing with deionized water, the material was soaked for 24 h in a solution of dilute nitric acid (5% $HNO_3$). Finally, the material was rinsed again with deionized water three times more.

### Statistical analyses

To detect differences in the concentrations of metals and organic matter, we used a two-way ANOVA with location (PR and AB) and depth (H1, H2 and H3) as factors. Tukey HSD post hoc tests were performed whenever the null hypothesis was rejected at a significance level of 0.05. All analyses were performed in Statistica 7.0 Statistical software. Data presented in the figures were not transformed, and error values in figures, tables, and in text represent ± 1 standard deviation.

## Results

### Granulometry

To describe the approximate relationship between the sizes of different sediment particles in each sample, the Shepard's (1954) classification system was used (Fig. 3). The grain-sediment size in PR showed that the surface 1-cm layer was predominantly fine-grained, silt to clayey silt. Coarser grain was found in more depth, and silty sand was attained at 5 and 7 cm depths. In contrast, the grain size classification in AB revealed more homogeneity for surface sediments up to 5 cm deep, with more than 85% of clayey silt sediments (mode = 20 µm), whereas a sandy silt sediment was found in deeper horizons (>5 cm deep).

### Organic matter content

The percentage of OM varied between the two sampling sites, showing values from 0.68 to 2.07% in PR and from 2.96 to 5.60% in AB (Fig. 4). The OM average (each site, $n = 9$) was significantly higher (almost three times) in AB than in PR ($p = 0.025$). The distribution of OM in varying depths shows a significant interaction with site: In AB, the content of OM was higher in H1 than in H3 ($p = 0.0252$).

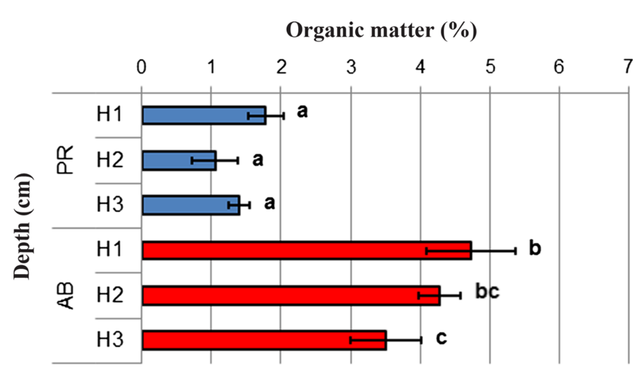


**Fig. 4** Average of organic matter content from *PR* Puerto Rosales and *AB* Almirante Brown throughout the sediment profile; values are means ± 1 SE ($n = 3$). *Different letters* indicate significant differences

### Metals content

The ranges of trace metals in the sediment cores and their overlying microbial mats for each site are summarized in Table 1. The average concentrations of most of the studied metals were higher in AB than in PR (Cu, Zn, Cr, Ni; all $p < 0.05$) (Table 2). Cd was the only element with a significantly higher concentration in PR ($p < 0.001$). For Fe, Mn, and Pb, we found no differences in concentrations between sites ($p = 0.3464$, $p = 0.5375$ and $p = 0.0963$, respectively).

The concentration of metals in the microbial mats and sediments shows different trends with depth at each site (Fig. 5). In PR, the average Cd concentration was significantly higher ($p < 0.01$) in H1 than in the horizons beneath. In turn, the Zn concentration in this site was significantly lower in H1 ($p < 0.05$) than in H2 or H3. Copper concentration in AB was significantly higher in the first 5 cm of depth (H1 and H2) than in H3 ($p < 0.05$). Moreover, there was a higher concentration of Cu in H2 than in H1 and H3 in PR ($p < 0.05$). The overall trend observed at each site was as follows: In AB, the highest metal concentrations were in H1 or H3, whereas in PR, highest concentrations occurred in the H2.

## Discussion

The fate of metals in the aquatic environment is influenced by several processes such as complexation to inorganic and organic ligands, sorption to metal oxides, clays, and particulate organic matter, bioaccumulation, and exchange between sediment and water (e.g., Ip et al. 2007; Botté et al. 2010; Mil-Homens et al. 2013).

According to our results, higher levels of organic matter in the AB site than in the PR site would be associated with a higher percentage of fine sediments recorded (see Fig. 3). The BBE is characterized by fine sediments in the studied sites, typically clayey silt (Cuadrado et al. 2012; Pan et al. 2013; Botté et al. 2010; Negrin et al. 2012). On the one hand, the natural source of organic matter includes phyto and zooplankton, fecal pellets, and exuvia, as well as the contribution made by saltmarshes plants (Thornton and McManus 1994; Schratzberger and Warwick 1998; Negrin et al. 2012). On the other hand, the external input of organic matter in these environments comes mainly from the urban activity of sewage treatment plants or domestic wastes, which probably raises its content in the intertidal and supratidal sediments (Fig. 4). Values around 2377 mgC $m^{-3}$ of particulate organic matter (POM) have been recorded during winter in waters that cover tidal flats of AB site (Monitoring Program of Bahia Blanca Estuary 2010), whereas a range of POM of 1130–3150 mgC $m^{-3}$ was detected in the area (Spetter et al. 2015).

Sediments constitute important repositories of contaminants in the environments. Metal ions bind easily to clayey silt particles because these particles have a high adsorption capacity (high volume-to-surface ratio). In turn, organic matter is positively correlated with the distribution of metals in coastal environments. Frequently, muddy sediments are enriched with organic matter, which affect not only the absorption of metals, but also the precipitation processes (Du Laing et al. 2002; Reddy and DeLaune 2008; Pande and Nayak 2013).

In the sites measured, we found that the concentration of metals differed both between areas and depths. In the inner zone of the estuary (AB site), most of the metals analyzed (Hg, Cr, Ni, Zn, Fe, Pb, and Cu) presented higher values respect to those measured in the medium zone (PR site). The highest organic matter content in the AB site, and the close relationship between concentration of organic matter and metals could explain the spatial variation of the studied metals in the present study.

Several studies have demonstrated the ability of microbial mats to accumulate metals, mainly in the finest sediment fraction, in both cultures (Maldonado et al. 2010; Puyen et al. 2012) as well as in situ samples (Webster-Brown and Webster 2007). The concentration of the different metals measured in the AB site showed a relatively homogeneous distribution in depth, except for Cu and Mn. Copper concentration was higher in the 5-cm layer, while Mn decreases toward surface, where the microbial mats are more developed. Seder-Colomina et al. (2013) found that copper is an essential metal that acts as a cofactor for different enzymes, including plastocyanin. Filamentous cyanobacteria dominate in abundance the

**Table 1** Concentration ranges (expressed in μg $g^{-1}$ dry weight) of metals in PR (Puerto Rosales) and AB (Almirante Brown) site ($N = 9$ in each site)

| Site | Metals | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cu | Pb | Zn | Mn | Cr | Ni | Fe | Cd | Hg |
| PR | 10.91–18.51 | 5.38–7.33 | 29.56–43.29 | 324.55–510.5 | 9.175–12.56 | 5.94–8.52 | 19,510–31,305 | nd–0.51 | nd–0.076 |
| AB | 15.04–21.49 | 6.16–9.48 | 38.18–48.6 | 323.4–492.9 | 10.77–14.45 | 7.32–9.74 | 23,290–29240 | nd–0.05 | 0.027–0.055 |

*nd* not detected

**Table 2** Summary of trace metal concentration (expressed in μg $g^{-1}$ dry weight) recorded in sediments of the BBE

| References | Year of sampling | Site | Cu | Pb | Zn | Mn | Cr | Ni | Fe | Cd | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Present study | 2012 | PR | 15.10 ± 2.86 | 6.32 ± 0.80 | 37.5 ± 4.48 | 409 ± 52.7 | 11.44 ± 0.99 | 7.39 ± 1.07 | 25,076 ± 3975 | 0.196 ± 0.232 | 0.040 ± 0.020 |
| | | AB | 19.07 ± 2.86 | 7.18 ± 1.09 | 43.88 ± 3.17 | 396 ± 61.1 | 12.67 ± 1.16 | 8.44 ± 0.70 | 26,351 ± 2383 | 0.020 ± 0.014 | 0.043 ± 0.010 |
| Spetter et al. (2015) | 2011 | PR | 11.66 ± 0.95 | 4.91 ± 0.30 | 34.70 ± 2.01 | – | 8.60 ± 0.46 | – | 19,500 ± 1084 | 0.073 ± 0.016 | – |
| Martinez et al. (2012) | 2010 | PR | 9.90 ± 4.317 | 6.29 ± 1.56 | 16.49 ± 13.60 | – | 8.28 ± 5.86 | 4.58 ± 1.76 | 15,269 ± 6571 | 1.236 ± 0.486 | – |
| | | PC | 12.62 ± 2.576 | 5.22 ± 1.20 | 26.63 ± 9.06 | – | 8.96 ± 1.86 | 6.77 ± 0.87 | 19,875 ± 2032 | 1.739 ± 0.208 | – |
| Botté et al. (2010) and Botté (2005) | 2000/2002 | PC | 14.62 ± 1.06 | 15.5 ± 1.37 | 49.09 ± 6.10 | 272 ± 93.1 | 9.81 ± 1.58 | 13.72 ± 1.84 | 24,980 ± 1970 | 0.87 ± 0.08 | 0.07 ± 0.08 |
| | | M | 11.11 ± 1.56 | 13.80 ± 1.78 | 41.78 ± 6.35 | 142 ± 44.11 | 8.58 ± 1.45 | 9.63 ± 1.67 | 18,750 ± 1910 | 0.80 ± 0.10 | 0.07 ± 0.08 |
| | | PG | 14.78 ± 0.91 | 15.15 ± 1.10 | 46.07 ± 6.78 | 225 ± 67 | 10.16 ± 2.12 | 13.09 ± 1.89 | 23,830 ± 1720 | 0.98 ± 0.11 | 0.09 ± 0.13 |
| Grecco et al. (2006) | 2002 | 3000 years | 5.2 | 4.8 | 23 | 150 | 4.4 | 8.0 | 26,000 | 0.60 | – |

References data are given as mean value ± 1 SD

*PR* Puerto Rosales, *AB* Almirante Brown, *PC* Puerto Cuatreros, *M* Maldonado, *PG* Puerto Galván

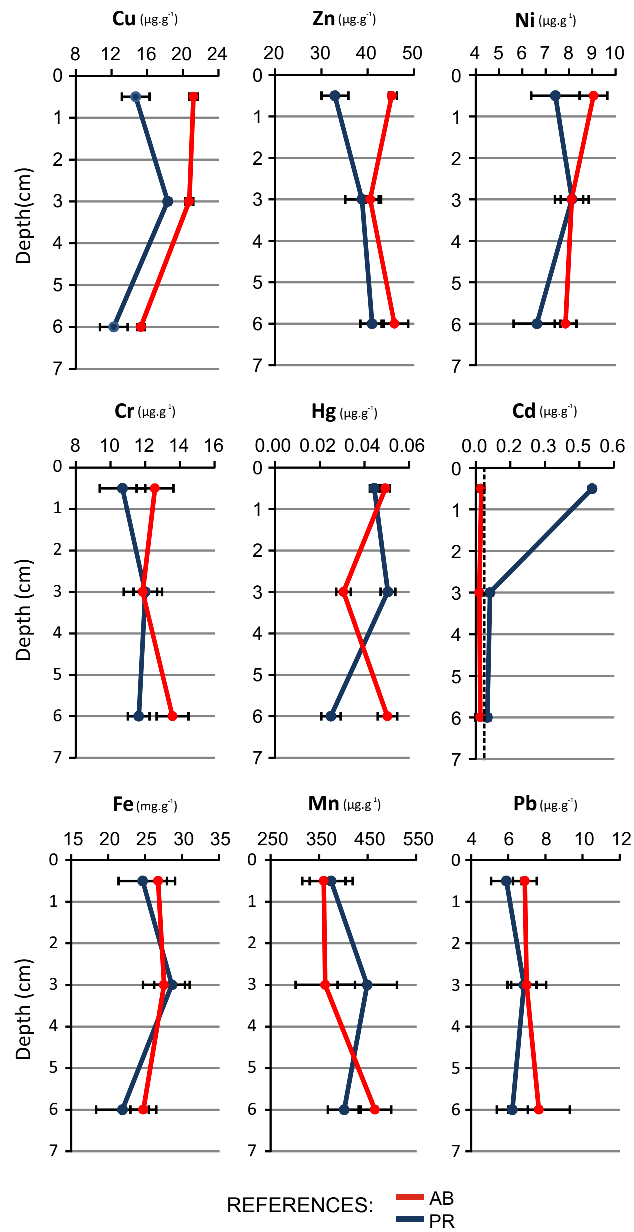


**Fig. 5** Average concentration of heavy metals in sediments of *PR* Puerto Rosales and *AB* Almirante Brown sites (mean ± 1 SE; $n = 3$). The *dashed black line* represents the method detection limit (MDL)

microphytobenthos of microbial mats of BBE, constituting up to 82% of the photoautotroph biovolume (Pan et al. 2013). In turn, the Mn concentration decreases toward topmost layers of the sediment and that could be explained by the less oxic conditions of sediments in deep (Caetano et al. 1995). As we mentioned before, the AB site is influenced by a small tributary (Maldonado stream) which could provide metals. The water in this stream contains urban sewages, as well as products from the neighboring land areas used for agricultural and livestock production (Botté et al. 2010), which then affect the seawater that covers the tidal flat during high tide. Besides, the old municipal dump (which was situated in higher levels of the tidal flat) could also act as a source of metals, introducing toxic elements that tend to leach from the land surface to lower strata reaching up the tidal flat by the groundwater gradient.

Given that Cd is one of the most toxic metals measured in this study, it is important to highlight the high content of Cd registered in the overlying microbial mat in the PR site (in AB, the level of Cd was where below MDL). Cadmium content on microbial mats of PR was 63 times higher than the concentration measured by Spetter et al. (2015) a year before the present study in the same place. Studies have shown that the amount of cadmium in sediments is related to the amount leached into the water (Neff 2002). La Colla et al. (2015) found higher levels of dissolve Cd in the PR site than in the AB site; however, that difference was no significant ($p = 0.40$). The main source of Cd would be from the untreated urban discharges from a nearby sewage channel, and also from anthropogenic activities that are carried out in the near harbor. It should be noted that Cd concentrations reported here did not represent a critical environmental threat; however, it would be adequate to keep monitoring Cd permanently, in case its concentration becomes hazardous.

The vertical distribution of the metals under consideration was relatively homogeneous within each site. However, the concentration ranges for each metal showed larger amplitude in AB than in PR (except for Pb and Cr). Many of the metals considered in this study showed concentration peaks in the underlying sediments compared with their concentration in the overlying microbial mats. Some authors (Des Marais 1995; Granger and Ward 2003) suggest that microbial mats may lead to the concentration of metals in the underlying sediments. Once mat microorganisms die, decomposition processes transfer the metals preferentially associated with organic matter into the sediment. Some studies show an important role of microorganism on the process of metal mineralization when microorganisms are in the presence of readily interchangeable free metal ions or metals absorbed electrostatically by the sediment (Widerlund 1996; Shine et al. 1998).

The metal values obtained in the present study were almost in the same order of magnitude than those obtained in previous reports from tidal flats in coastal areas of BBE (Botté 2005; Botté et al. 2010; Spetter et al. 2015; Table 2). However, some differences should be mentioned. The present study shows a content of Cu and Fe slightly higher, and concentrations of Pb and Ni lower than those reported by Botté et al. (2010) in a nearby area. Particularly, AB showed a threefold and twofold increases in Mn relative to Botté's results. There are previous studies of metals in sediments from intertidal zones (Martinez et al. 2012; Spetter et al. 2015) in the PR site as well. These previous reports showed lower values for overall metals relative to the concentrations reported here (except for Cd, in Martinez et al. 2012).

Background values considered for these systems are those from nonfunctional 3000-year-old tidal flats of not impacted by human activities (Grecco et al. 2006). Except for Fe, the present report shows higher concentrations of all metals relative to background levels (see Table 2).

The effect of urban sewage would have a similar impact on tidal flats than those produced by other sources like petrochemical industries, ports, and vessel (Grecco et al. 2006; Botté et al. 2010). However, other factors should be considered, such as the presence of old municipal landfills in which presence may be acting as a continuous input of toxic substances into the adjoining environment (near the AB area). The presence of microbial mats within the evaluated sites could thus influence the removal or sinking of some metals and also modify the depth distribution of metals in intertidal as well as supratidal environments. This is important given that the microbial mats may influence the geochemical transformation of some elements in the microenvironment surface of the tidal flat.

## Conclusions

The concentration of the metals assessed in supratidal sediment colonized by microbial mats showed spatial variation between two evaluated areas (AB and PR) in the Bahía Blanca Estuary. The presence of different human activities associated, for example, with industries, ports, and cities may contribute to the increase in metal contamination. Results from the present study demonstrate that the presence of microbial mats in the AB site influences the depth distribution of Cu (in the 5-cm firsts) and Mn (its concentration increases as sediment becomes less oxic). In addition, in the PR site, the concentration of Cd could be associated with the presence of mats. Similarly, a high interrelation between organic matter and fine sediments of microbial mats seemingly influences the distribution of metals in the studied environment.

Although both studied sites are located in areas nearby to the main ports within the estuary, the proximity of AB site to the industrial and city sewage discharges and the existence of the former Belisario Roldán open municipal dump contribute to the input and distribution of organic matter and metals in this coastal ecosystem. The present study allowed us to identify high values of some metals in the BBE, particularly, in the presence of microbial mats. Present findings represent a first diagnostic step to develop successful bioremediation strategies for human-affected coastal environments.

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