Dissolved Heavy Metal (Cd, Pb, Cr, Ni) Concentrations in Surface Water and Porewater from Bahía Blanca Estuary Tidal Flats

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Abstract The concentrations of dissolved cadmium, lead, chromium and níquel were determined in surface water column and pore water, collected from the extensive tidal plain at Bahía Blanca estuary, Argentina. Three different polluted areas were selected to study the spatial variation of these metals. The concentration ranges within the water column were slightly variable (Cd: 0.18–2.48 µg L^{-1}; Pb: 0.38–7.53µg L^{-1}; Cr: 0.89–5.83 µg L^{-1}; Ni: 0.81–3.49 µg L^{-1}), and displayed a clear gradient respect to the industrial area. Significant differences (contrast tests) between sites were detected for Cd, Pb and Ni. Very similar concentrations of Cd (0.18–3.41 µg L^{-1}), Pb (0.38–5.83 µg L^{-1}), Cr (0.89–9.37 µg L^{-1}), Ni (0.81–6.56 µg L^{-1}) were found in the porewater at all sites. The results suggested that both environmental compartments (water column and tidal flats porewater) may be affected by similar point and non-point heavy metal sources.

Keywords Dissolved heavy metals · Surface water · Tidal flats porewater · Argentina

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Estuaries worldwide frequently experience anthropogenic eutrophication, resulting in changes in the predominating biogeochemical conditions. Pollutants are not necessarily permanently immobilized in dredged sediments, and heavy metal remobilisation from sediment due to bioturbation and re-suspension constitutes a potential danger (Zoumis et al. 2001). Sediments may act both as sources as well as sinks for certain trace elements; most of the contaminants are adsorbed on suspended particulate matter (SPM) which can be transported into the sediment by flocculation and sedimentation (Blasco et al. 2000). In the sediment-water interface, articularly within the oxic zone, enhanced mineralization processes occur. Diagenetic reactions may partially redissolve the deposited materials into the porewater, from where diffusive fluxes, resulting from the concentration gradient at the sediment–water interface, may transport these dissolved contaminants from the sediments to the overlying water (Ciceri et al. 1992; de Mora et al. 2004). These kind of heavy metal fluxes in the sediment–water interface are particularly important in coastal areas with high productivity (Chase et al. 2005).

Even large information exists on the concentration and distribution of dissolved heavy metals in estuarine water

from different regions worldwide (i.e., Matthiessen and Law 2002; Mucha et al. 2004; Jayaprakash et al. 2005), it is very scarce on the corresponding relationship between metal contents within both estuarine and porewater in tidal flats from this kind of environment. The present study deals with the occurrence, concentrations and distribution of several heavy metals (Cd, Pb, Cr and Ni) dissolved in estuarine water and porewater within three wetlands on Bahía Blanca estuary, in Argentina.

Materials and Methods

Bahía Blanca is a mesotidal coastal plain estuary (Perillo et al. 2001) located between 38°45′ and 39°40′S, and 61°45′ and 62°30′W, in the southeastern area of Buenos Aires Province within Argentina (Fig. 1). It has an elongated form, northwestern–southeastern directed, about 80 km long within the Main Channel, and numerous streams, which separate islands and tidal flats (Perillo and Piccolo 1991). Water interchange within the bay is influenced by a semidiurnal tidal regime. The bay encompasses an area of 400 km^2, and at high tide the total area is close to 1,300 km^2 (Perillo et al. 2001). The hydrography of the estuary is strongly influenced by climatic conditions (Freije and Marcovecchio 2004). Several streams and channels flow into the bay, most of them affected by anthropogenic activities. The freshwater contribution is approximately 4,000 m^{3}day^{-1}. Tidal oscillations of 3 m and predominant northwesterly winds create strong tidal currents which facilitate water mixing, leading to an uniform vertical

Fig. 1 Locations of the sampling sites at Bahía Blanca estuary. (*PC* Puerto Cuatreros, *PG* Puerto Galván, *M* Maldonado)

distribution of the main oceanographic parameters (Piccolo and Perillo 1990).

Various ports, towns (with a population exceeding 300,000 inhabitants) and industries are located at the northern boundaries of the estuary. Oil refineries and terminals, petrochemical industries, meat factories, leather plants, fish factories, textile plants, wool washing plants, silos and cereal mills discharge their processing residues into the streams or directly into the estuary. Nearly 10 m^{3}day^{-1} of raw sewage are discharged into the study area (Andrade 2001; Ferrer 2001). This estuary is extensively used by fishing boats, oil tankers and cargo vessels and requires regular dredging. In this way, this coastal marine system receives contaminant inputs from municipal waste-waters, direct industrial discharges, harbour related operations and runoff water which carry materials from land development areas and aerial fallout from atmospheric pollutants. Three sample stations (*Puerto Cuatreros, Maldonado* and *Puerto Galvan*) have been established at the inner area of the estuary (Fig. 1), which represented different zones influenced by the above-mentioned potential sources of pollution.

Surface water samples were collected manually at <1 m depth with 1.5 L polyethylene-tereftalate (PET) bottles. Porewater samples were taken from inter-tidal area, from holes of 20 cm diameter and 30 cm deep. The samples were immediately transported to the laboratory and filtered through acid treated Millipore HA filters (0.45 μm mesh) for the determination of dissolved metals. The filtered samples were acidified at pH 2 using 1.5 ml of HCl analytical quality, in order to be stored. These samples were stored on darkness at 4°C up to the analytical treatment at the laboratory. Prior to use all the material employed for sampling, filtration and sample storage were carefully cleaned with diluted nitric acid (0.7%, HNO$_3$ suprapur, Merk) following internationally recommended protocols (APHA 1998).

The dissolved metals were simultaneously extracted from both, filtered water and porewater samples by chelation with ammonium pyrrolidine-dithiocarbamate (APDC) followed by methyl isobutyl ketone (MIBK) extraction, according to the method described by Koirtyohann and Wen (1973) and updated by El-Moselhy and Gabal (2004). All extracted water samples were combined to ensure homogeneity as well as to provide an adequate volume of matrix for the preparation of blanks and standards. Several aliquots of this matrix were treated along with the samples to obtain analytical blanks. The corresponding standards were prepared by adding increasing amounts of Cd, Pb, Cr and Ni to the matrix. Metal concentrations were determined with a Perkin-Elmer AA-2380 atomic absorption spectrophotometer with an air/acetylene flame. The MDL (in μg L^{-1}) for each metal are Cd: 0.18, Pb: 0.38, Cr: 0.89, and Ni: 0.81. Analytical grade reagents were used to make up the relevant

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

Metal analyzed	Estuarine water	Seawater
Cadmium	91.1%–95.3%	93.1%–95.7%
Lead	92.9%–96.5%	92.2%–97.5%
Chromium	91.6%–97.1%	91.0%–97.7%
Nickel	94.3%–98.6%	95.0%–98.8%

blanks and calibration curves, and the analytical quality (AQ) was tested against reference materials (Table 1) provided by The National Institute for Environmental Studies (NIES), from Tsukuba (Japan) as well as from the United Nations Environment Programme (UNEP).

A one-way statistical analysis of variance (ANOVA) was performed to assess different metal concentrations between the three sampling sites and among surface water (SW) column and pore water (PW). The SPSD (Statistical Package of Statistical Department, from Universidad Nacional del Sur) Scheffé contrast and least-significant-difference (LSD) contrast procedures were used to determine to which site correspond the observed differences.

Results and Discussion

Dissolved heavy metals (Cd, Pb, Cr and Ni) concentrations were determined in the estuarine water column within the studied sites (Puerto Cuatreros, Puerto Galvan and Maldonado) (n = 20). The mentioned water column showed to be homogeneous along the whole year and stratification has never been recorded (Freije and Marcovecchio 2004). For the three studied sites the water column has shown to be well oxygenated along the whole year, including long periods with significant oxygen super-saturation (greater than 100%) caused by photosynthesizing phytoplankton blooms (Freije and Marcovecchio 2004; Popovich et al., in press). But, such at Galván as at Cuatreros sites dissolved oxygen (3.6–3.5 mg L^{-1}) in waters were slightly lower than those above mentioned, corresponding to severe hipoxic values (<4 mg L^{-1}), at least in several periods of the year. Temperature was always homogeneous within the studied area, following the typical sinusoidal variation curve described for temperate estuaries (Ribbe 2006; Sylaios et al. 2006). Salinity has presented a wide range of variation, with well-defined minimum (10.2 psu at Puerto Cuatreros in spring) and maximum (37.6 psu at Puerto Galván in later summer) values, and they were similar to previous reports (Marcovecchio et al. 2003).

The range of dissolved cadmium values as determined has varied between 0.18 μg L^{-1} (at all sites) and 2.46 μg L^{-1} (at Puerto Galván). Nevertheless, corresponding
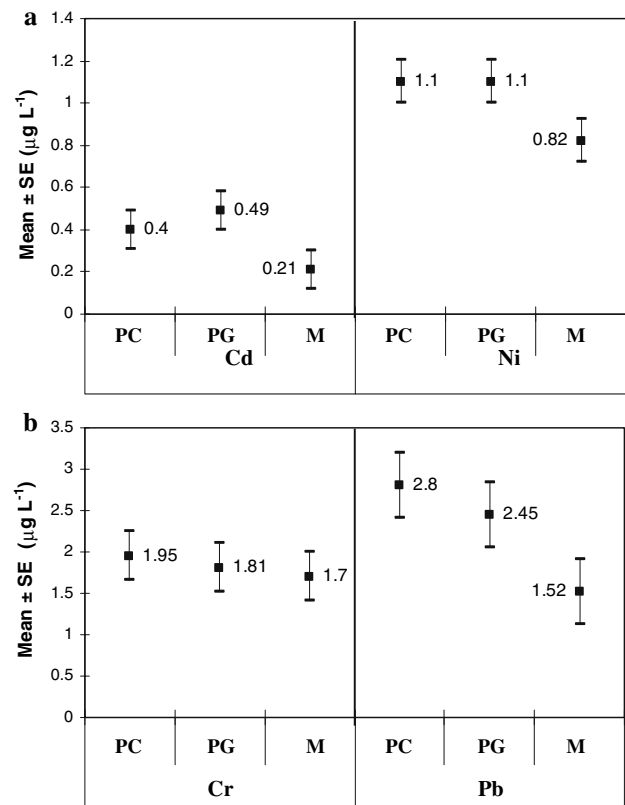

Fig. 2 Mean values (n = 20) ± Standard error (SE) of Cd–Ni (**a**) and Cr–Pb (**b**) at each sampling site in the surface water column (*PC* Puerto Cuatreros, *PG* Puerto Galván, *M* Maldonado)

average values as calculated for each sampling point (Puerto Cuatreros: 0.40 ± 0.36 μg L^{-1}, Puerto Galván: 0.49 ± 0.61 μg L^{-1}, and Maldonado: 0.21 ± 0.08 μg L^{-1}) has showed significant differences [$F(2,57) = 2.39$; ($p = 0.101$)] between them due to Maldonado site's values [Scheffé, $p = 0.125$ and LSD, $p < 0.05$ with SE (standard error) = 0.092] (Fig. 2). Recordable levels have been measured in most of the whole period of study, which indicates the occurrence of sources of cadmium within this area of the estuary. This has also agreed with previous reports, such as that from Andrade et al. (2000) finding <0.05–1.0 μg Cd L^{-1}, or by Ferrer et al. (2000) who reported mean Cd levels from 0.18 ± 0.11 μg L^{-1} in water from the Main Channel. The levels of dissolved cadmium in Bahía Blanca estuarine water as presented in this study were in the same magnitude to those reported by Mucha et al. (2004) at the lower Douro estuary, in Portugal, as well as those concerned with the Ennore Creek (Chennai, India) (Jayaprakash et al. 2005), both of them considered as anthropically stressed but not strongly polluted systems. Moreover, the values here presented were much lower than those reported for strongly polluted estuaries, such as the Rio Tinto-Ria Huelva on SW Spain (Achterberg et al. 2003), where values close to 45 μg L^{-1} (~400 nM) have

been reported. In addition, dissolved Cd mean values were significantly lower than that reported as the Cd chronic toxicity value for *Thalassiosira curviseriata* from Bahía Blanca estuary (~57 µg L^{-1}) (Andrade et al. 2000), which allowed to sustain that the present dissolved Cd concentrations did not represent a critical environmental status, even it would be adequate its permanently monitoring.

The levels of dissolved lead in samples of estuarine column water have varied from 0.38 µg L^{-1} (at all sites) and 7.53 µg L^{-1} (at Puerto Galván). The one-way ANOVA of the corresponding mean values as calculated for each sampling site (Puerto Cuatreros: 2.80 ± 1.63 µg L^{-1}, Puerto Galván: 2.45 ± 2.13 µg L^{-1}, Maldonado: 1.52 ± 1.36 µg L^{-1}) has showed significant differences between them [$F(2,57) = 2.90$; ($p = 0.063$)]. The Scheffé contrast and the LSD procedure indicated that Maldonado site was significantly different from the other two places ($p = 0.076$; $p < 0.10$ with SE = 0.388, respectively) (Fig. 2). The detectable values of dissolved lead, allowed to sustain that a continuous (or *quasi*-continuous) source of this metal occurs within the studied region. These results can be compared with those previously reported by Marcovecchio et al. (2003) for the inner area of the Main Navigation Channel, which have varied from non detectable values up to 4.51 µg L^{-1}. Dissolved Pb levels from Bahía Blanca estuary as presented in this study were also comparable with those reported by Vazquez et al. (1998) for Alvarado Lagoon water, in Mexico (9.39 ± 7.65 to 62.5 ± 38.1 µg kg^{-1}); by Kraepiel et al. (1997) for the Gironde estuary, in France (mean value = 0.26 µg L^{-1}); or, by Nayar et al. (2004) for the Ponggol estuary, in Singapore (mean value = 0.02 mg L^{-1}). Moreover, these dissolved Pb values as included in the present study were significantly lower than that reported as the Pb LC$_{50}$ (96 hs) for the first zoeae of *Chasmagnathus granulata* from Bahía Blanca estuary (1.0 mg L^{-1}) (Ferrer et al. 2000). This point has allowed to sustain that these dissolved Pb concentrations did not demonstrate to be at present extremely dangerous from an environmental viewpoint. Notwithstanding, it is strongly recommended to maintain the permanent monitoring programmer, considering that the occurrence of this metal indicated the occurrence of a source within the system, mainly in those sites (PG and PC) which area more closely related to the Main Navigation Channel.

The analysis of dissolved chromium in water of Bahía Blanca estuary has shown extreme values from undetectable levels (<0.86 µg L^{-1}; at all sites) to 5.83 µg L^{-1} (at Puerto Galván site), while the corresponding average values as calculated for each sampling point (Puerto Cuatreros: 1.95 ± 1.23 µg L^{-1}, Puerto Galván: 1.81 ± 1.48 µg L^{-1}, and Maldonado: 1.70 ± 1.25 µg L^{-1}) have presented non-significant differences [$F(2,57) = 0.18$; ($p > 0.84$)] between them and this can be confirmed by

both Scheffé contrast (ns) and the LSD procedure (ns, with SE = 0.297) (Fig. 2). These levels were compared with those previously reported by Marcovecchio et al. (2003) (0.1–2.0 µg L^{-1}), who have also informed that dissolved Cr presented detectable values in all their sampling stations and along the whole year. In addition, Andrade (2001) beforehand (1997–1999) have never detected dissolved chromium at Puerto Cuatreros site. This fact, in addition with the results here presented sustained the occurrence of a source of Cr within the studied area of Bahía Blanca estuary. Dissolved Cr levels were compared with those reported for different estuaries: Mirlean et al. (2001) at Patos Lagoon, in Brazil (0.02–2.84 µg L^{-1}); Mzimela et al. (2003) at Richards Bay and Mhlathuze estuary, in South Africa (14–226 µg L^{-1}); or, Jayaprakash et al. (2005) at Ennore Creek, in Chenai (India) (0.1–3.8 µg L^{-1}). Cr data could be compared with ecotoxicological framework, thus data on 96 h, Cr LC$_{50}$ (0.5–1.0 mg L^{-1}) for the grass shrimp (*Palaemonetes pugio*) reported as responsible of sublethal effects on this species (Doughtie and Ranga Rao 1984); or, those for grass shrimp, *P. pugio*, (3.60–14.50 mg L^{-1}) and for sheepshead minnows, *Cyprinodon variegatus*, (63–1,000 mg L^{-1}) reported as lethal effects by Conklin et al. (1983).

Finally, the levels of dissolved nickel in Bahía Blanca estuary water have varied from 0.81 µg L^{-1} (at all sites) to 3.49 µg L^{-1} (at Puerto Galván), while the corresponding mean values for each sampling site (1.10 ± 0.41 µg L^{-1} at Puerto Cuatreros, 1.10 ± 0.67 µg L^{-1} at Puerto Galván, and 1.03 ± 0.23 µg L^{-1} at Maldonado site) have shown significant differences [$F(2,57) = 2.54$; ($p = 0.088$)] between them. Then, the Scheffé contrast and the LSD procedure indicated that Maldonado site was significantly different from the other places ($p = 0.088$; $p < 0.10$ with SE = 0.101, respectively) (Fig. 2). The report by Andrade (2001) for samples of the inner area of the Main Navigation Channel from Bahía Blanca estuary, which has included dissolved nickel values ranging between 0.06 and 3.0 µg L^{-1}, is the unique antecedent data for this environment. These results allowed to sustain the occurrence of a source of Ni within of Bahía Blanca estuary. Ni values as determined in the present study could be compared with those reported by Whitworth et al. (1998) for the Tamar estuary, in South West Britain (3.5–48 nM); or by Beck et al. (2002) for San Francisco Bay, in USA (1.07 ± 0.03 to 2.03 ± 0.08 µg L^{-1}). Toxicological bioassays directed to asses the effect of Ni on *Thalassiosira curviseriata* from Bahía Blanca estuary have reported value of ~65 µg L^{-1} as Ni chronic toxicity value (Andrade 2001), which was significantly higher than those recorded within the present study. Furthermore, the papers by Santojanni et al. (2003) reporting Ni lethal toxicity of 100–150 µg L^{-1} for *Dapnia magna*; or, by Brix et al. (2004) who reported the acute
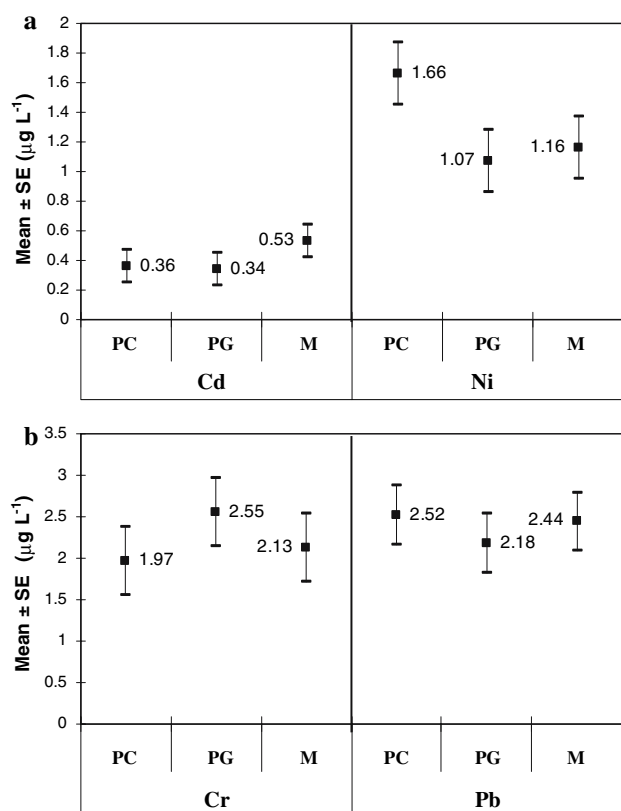
Fig. 3 Mean values (n = 20) ± Standard error (SE) of Cd–Ni (**a**) and Cr–Pb (**b**) at each sampling site in the pore water (*PC* Puerto Cuatreros, *PG* Puerto Galván, *M* Maldonado)
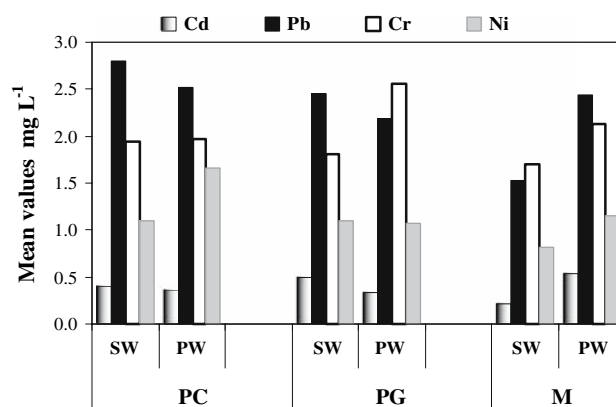

Fig. 4 Mean values of Cd, Pb, Cr and Ni between SURFACE WATER (*SW*) and PORE WATER (*PW*) at each sampling site (*PC* Puerto Cuatreros, *PG* Puerto Galván, *M* Maldonado)

median lethal Ni concentration (20.8 mg L^{-1}) and the 24-h gill median lethal accumulation (666 nmol g^{-1}, wet weight) for the rainbow trout, *Oncorhynchus mykiss*.

For the first time dissolved metal concentrations have been determined within tidal flats porewater at Bahía Blanca estuary. Cd values have ranged between 0.18 and 3.41 µg L^{-1}, with average values of 0.36 ± 0.34 µg L^{-1} at Puerto Cuatreros, 0.34 ± 0.32 µg L^{-1} at Puerto Galván, and 0.53 ± 0.73 µg L^{-1} at Maldonado site. One-way analysis of variance have shown that there was not significant differences between the studied samples sites [$F_{(2,57)} = 0.80$; ($p = 0.43$)] and both the Scheffé contrast and LSD procedure results allow to confirm that (ns with SE = 0.112) (Fig. 3). These values can be compared with those reported by Goody et al. (2002) within porewater from the Chalk system, at Salisbury (Wiltshire, UK) (0.10–2.76 µg L^{-1}); or by Man et al. (2004) for the Mai Po and Inner Deep Bay, on Western Hong Kong, in China (0.5–4 µM).

Pb values as recorded within porewater have varied between 0.38 and 5.83 µg L^{-1}. The corresponding average values for each studied site (2.52 ± 1.37 µg L^{-1} at Puerto Cuatreros; 2.18 ± 1.74 µg L^{-1} at Puerto Galván; 2.44 ± 1.46 µg L^{-1} at Maldonado site) have shown non-significant

differences [$F_{(2,54)} = 0.25$; ($p > 0.75$)] between them, and both the Scheffé contrast and LSD procedure results allow to confirm that (ns with SE = 0.351) (Fig. 3). The mentioned values can be compared with reports from other authors for different environments, such as Goody et al. (2002) in UK (0.22–3.80 µg L^{-1}); or by Man et al. (2004) in China (0.2–185 µM).

The analysis of dissolved chromium within porewater has presented results varying between 0.89 and 9.37 µg L^{-1}. Moreover, the corresponding mean values for each studied site (1.97 ± 1.45 µg L^{-1} at Puerto Cuatreros; 2.55 ± 2.43 µg L^{-1} at Puerto Galván; 2.13 ± 1.45 µg L^{-1} at Maldonado site) have shown non significant differences [$F_{(2,57)} = 0.53$; ($p = 0.587$)] among them and both the Scheffé contrast and LSD procedure results allow to confirm that (ns with SE = 0.410) (Fig. 3). Dissolved Cr data can be compared with previous reports by Goody et al. (2002) at the UK (0.32–2.85 µg L^{-1}); by Otero and Macías (2002) in salt-marshes from NW Spain (0.1–1.2 µM); or, by Man et al. (2004) in China (1.5–165 µM).

Finally, the levels of dissolved nickel within porewater of the studied sites have varied between 0.81 and 6.56 µg L^{-1}. The analysis of variance between the mean values of dissolved Ni (1.66 ± 1.38 µg L^{-1} at Puerto Cuatreros; 1.07 ± 0.57 µg L^{-1} at Puerto Galván; 1.16 ± 0.70 µg L^{-1} at Maldonado site) have shown significant differences among sampling sites [$F_{(2,57)} = 2.31$; ($p = 0.109$)]. So, the Scheffé contrast ($p = 0.117$) and the LSD procedure ($p < 0.10$, with SE = 0.211) indicated that Puerto Cuatreros site was significantly different from the other places (Fig. 3). These values of dissolved Ni were comparable to those previously reported by Goody et al. (2002) in UK (11–664 µg L^{-1}); or, by Otero and Macías (2002) in Spain (2.5–20 µM).

Dissolved heavy metal values between the estuarine water and the tidal flats porewater (Fig. 4) have shown the following:

Cd = non-significant differences at Puerto Cuatreros ($p > 0.76$) and at Puerto Galván ($p = 0.3538$), and significantly different at Maldonado site [$F(1,38) = 3.74$; $p < 0.061$].

Pb = non-significant differences at Puerto Cuatreros ($p = 0.5685$) and at Puerto Galván ($p = 0.6645$), but it has demonstrated to be significantly different at Maldonado [$F(1,38) = 4.18$; $p < 0.05$].

Cr = In all cases the values presented non-significant differences (Puerto Cuatreros, $p > 0.95$; Puerto Galván, $p > 0.25$ and Maldonado, $p > 0.33$).

Ni = non-significant differences only at Puerto Galván ($p = 0.8814$). Those from Puerto Cuatreros and Maldonado sites, were significantly different [$F(1,38) = 3.11$; $p < 0.10$ and $F(1,38) = 4.77$; $p < 0.05$, respectively].

Our preliminary results (Botté et al., submitted) indicated the occurrence of transference of metals from mud tidal plain sediments to the more bioavailable sediment porewater, which are in agreement with previous reports by other authors for similar environments (Man et al. 2004). The average dissolved concentration of trace metals in the sediment porewater showed only significant differences for Ni among studied sampling stations. The presence of metal chelates in the sediment porewater e.g. dissolved organic matters (DOM), increases the tendency of trace metals to partition into the aqueous porewater phase. As dissolved metal species in porewater are considered more bioavailable (Schubauer-Berigan and Ankley 1991; Green et al. 1993; Man et al. 2004), porewater data in the present study indicate that zones of potential metal ecotoxicity on the Bahía Blanca estuary occur in the vicinity of its salt-marshes and mud tidal plains.

The levels of trace metals in the mud tidal plain sediment porewater have shown to be similar (non significant differences) to those of the estuarine water column. This implies that both environmental compartments may be affected by similar point and non-point heavy metal pollution sources, particularly at Puerto Cuatreros and Puerto Galvan sites. The Maldonado site has shown significant differences in the distribution of three metals among both kind of water as well as between areas. It could be related with the lesser relationship between this site and the Main Navigation Channel, where most of the pollutant anthropic activities are developed. Present results will be quite useful in the framework of an Environmental Management Programme for Bahía Blanca estuary, which is at present being considered, and will provide the adequate scenario as to develop toxicological bioassays on the estuary's key species, to show a hollistic image of this environment.

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