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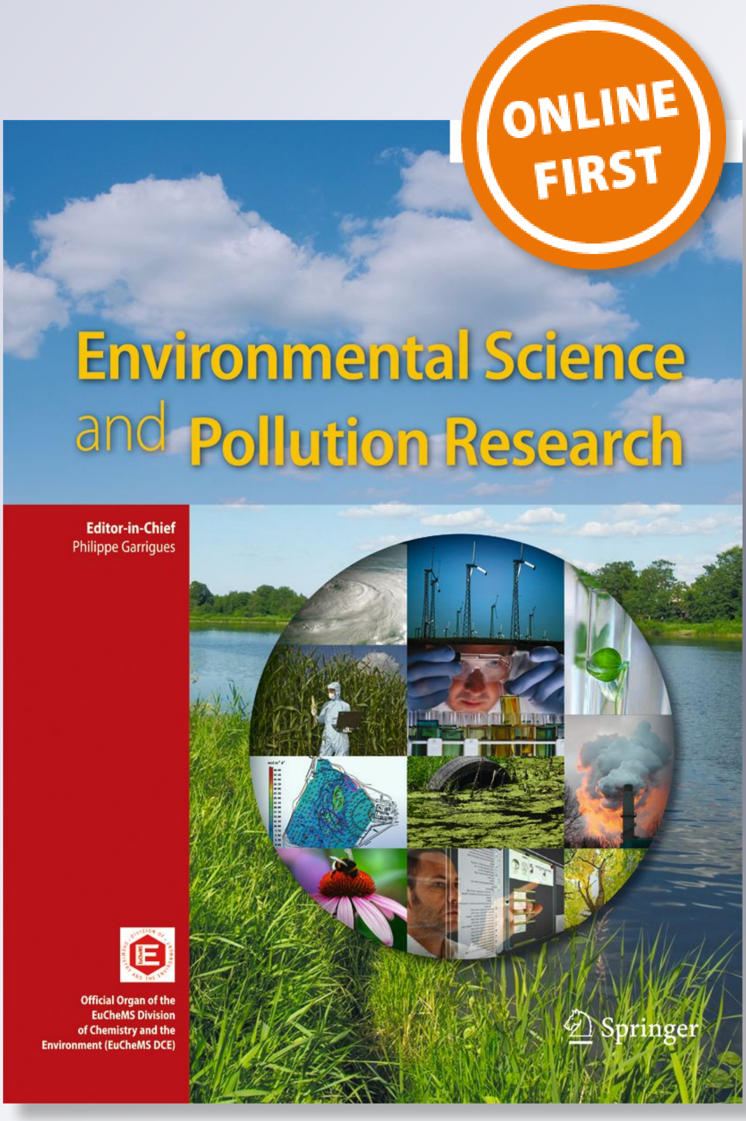

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RESEARCH ARTICLE

Assessment of trace metal accumulation in native mussels (*Brachidontes rodriguezii*) from a South American temperate estuary

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Abstract The present work provides the first results in heavy metal bioaccumulation in the autochthonous mussel *Brachidontes rodriguezii* from the Bahía Blanca Estuary (Argentina), one of the most important coastal environments of South America, subjected to different anthropogenic pressure. The study is based on the detection of Cd, Cu, Pb, Mn, and Fe in mussels' soft tissue and sediments' fine fraction by means of inductively coupled plasma atomic emission spectroscopy (ICP-OES), in order to analyze the potential relationship between both components of the aquatic system. Additionally, different indices are calculated with the purpose of obtaining detailed data. The heavy metal burden in mussels varied seasonally, showing a clearer pattern for the stations located in the internal area of the estuary. Metals exhibited maximum values in summer and to a lesser extent in winter, followed by a decrease during spring. Multiple international guideline assessment allowed classifying the area as moderately polluted, including a low range for Cd and medium for Cu and Pb. Moreover, the average detected levels were within the measured ranges in other coastal areas. Regarding human health, trace metal content in mussels met the national and international standards for safe consumption.

Keywords Coastal zone · Mussels · Sediments · Heavy metals · Pollution monitoring · Health hazard

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Introduction

Levels of contaminants in the marine environment have been increasing over the last decades as a consequence of anthropogenic activities. Pollutants can accumulate in organisms and in sediments, and subsequently be transferred to humans through the food chain. This is particularly enhanced for transitional and coastal environments, which are among the most productive marine ecosystems in the world under continuous human pressure. Specifically, estuaries have been recognized as dynamic, complex, and unique systems which act as sinks and/or transitional ways for several chemical contaminants between freshwater, land, and the marine environment (Chapman and Wang 2001).

Due to their long residence time in the trophic web and the potential risk to human health, heavy metals are considered some of the most toxic pollutants in the world (Van Vuuren et al. 1999) which highlights the need to monitor their levels and distribution in marine environments (Ferreira et al. 2005). In regards to marine biota, bivalve mollusks are particularly exposed to heavy metal pollution; they can take up contaminants from sediments, suspended particulate matter, water column, and also food supplies (Carvalho and Fowler 1993; Livingstone 1993; Laffon et al. 2006). Added to this, their sedentary nature, easily sampling, and wide geographical distribution in marine, estuarine, and freshwater environments have set them as target for chemical monitoring (identification and quantification of contaminants) and biomonitoring (effect assessment of the contaminants on organisms) in aquatic ecosystems (Zuykov et al. 2013; Anacleto et al. 2015). As result, mussels have been successfully used as sentinel organisms in international biomonitoring programs (e.g., International Mussel Watch: Farrington and Tripp 1995; European BIOMAR: Narbonne et al. 2005); nevertheless, for South America and, in particular, the Argentine coast, there is a scarcity of studies involving the analysis of both biological and chemical aspects of native mussel communities.

Tackling this knowledge gap, the present work focused at the Bahía Blanca Estuary (BBE)—located in the SW area of Argentina—which has been under a rapid increase in anthropogenic pressure due to the great industrial and urban development in the region during the last decades. In this context, the first aim of this work was to analyze the seasonal and spatial effects of Cd, Cu, Pb, Mn, and Fe levels in indigenous mussels from different sites of the estuary under distinct anthropogenic pressure. Additionally, in order to evaluate the possible relationship between heavy metal concentration in mussels and sediments, the same metals were studied in the fine fraction of sediments (<63 μm).

Materials and methods

Study site

The BBE is located in the SW area of Buenos Aires province, Argentina (38° 45′–39° 25′ S and 61° 45′–62° 30′ W) (Fig. 1). This estuary extends over about 2300 km^2 and comprises of several tidal channels, extensive tidal flats (1150 km^2) with patches of low salt marshes, islands (410 km^2) (Piccolo et al. 2008), and a State Natural Maritime Reservation which counts globally vulnerable species. The Multiple Use Reserve Bahía Blanca, Bahía Falsa, and Bahía Verde (National Law 12101/98) was established in 1998 as a state coastal marine reserve including the water around the emerging land. The estuary is a mesotidal system (Hayes 1979) with semi-diurnal tide prevalence; the mean tidal amplitude is 2.5–3.4 m during neap and spring tides, respectively. Two main freshwater tributaries enter the estuary from the northern shore: the Sauce Chico Stream (drainage area of 1600 km^2) and Napostá Grande Creek (drainage area of 1240 km^2). Various harbors (two commercial harbors), big cities (Bahía Blanca and Punta Alta), and industries (oil, chemical, and plastic factories) are established at the northern boundaries of the estuary, and their prefiltered effluents are directly introduced into the estuarine waters. In addition, the innermost area of the estuary presents low urbanized/rural lands, a tourist area, and an artisanal fishing/recreational port.

Sampling

Four sites were selected in the BBE: namely oxidized dock (OD), inflammable post (IP), Cuatreros Harbor (CH), and Villarino Viejo (VV) (Fig. 1). The sampled stations are located over the Main Navigation Channel of the estuary. OD and IP are located at Galvan National Harbor entrance, a commercial harbor with high shipping activity. Important industries have also been established in this area: oil, plastic polymers, by-product derivative refineries, and a small commercial fishing fleet. The OD is an old iron dock, near the collector channel of the industrial effluent. The IP dock is located on the west area of Galvan Harbor and is destined to the receipt and/or shipment of liquid and gaseous fuel products, as well as chemicals. CH and VV are both located in the internal area of the estuary; CH is at offshore waters of a recreational/fishing port, and VV station is in the vicinity of low urbanized/rural lands. Organism samples were collected at each site from October 2011 to October 2012, including two springs (Oct. 2011, 2012), a summer (Feb. 2012), and a winter (Aug. 2012). In addition, sediment samples were collected in winter from CH and VV and in spring 2012 from all the sites. The OD and IP samples corresponding to winter 2012 were discarded after not meeting the laboratory's quality protocol due to methodological problems. Finally, surface water temperature, pH, and salinity were recorded in situ using an HORIBA U-10 device.

Trace metals in organisms

The mytilid *Brachidontes rodriguezii* (d'Orbigny, 1846) is one of the dominant organisms on intertidal rocky substrata in the warm temperate shores of Argentina. It is a filter-feeder organism; water-suspended particles like diatoms and organic debris are some of its food items (Adami et al. 2004; Torroglosa 2015). In this study, 90 indigenous mussels from each site were collected by hand from dock columns and rocks in surface water (0–1 m). Immediately after collection, organisms were transferred inside cool ice boxes to the laboratory for storage at −20 °C until analysis. Three pools of 30 individuals from each sampling were cleaned and dissected to extract the whole soft tissues. Previously, the length (mm) of the shells, the wet and dry weight (g) (freeze dried) of the mussel soft tissue, and the dry weight (g) of shell valves were recorded. In the present work, although the intestines of mussels may contain

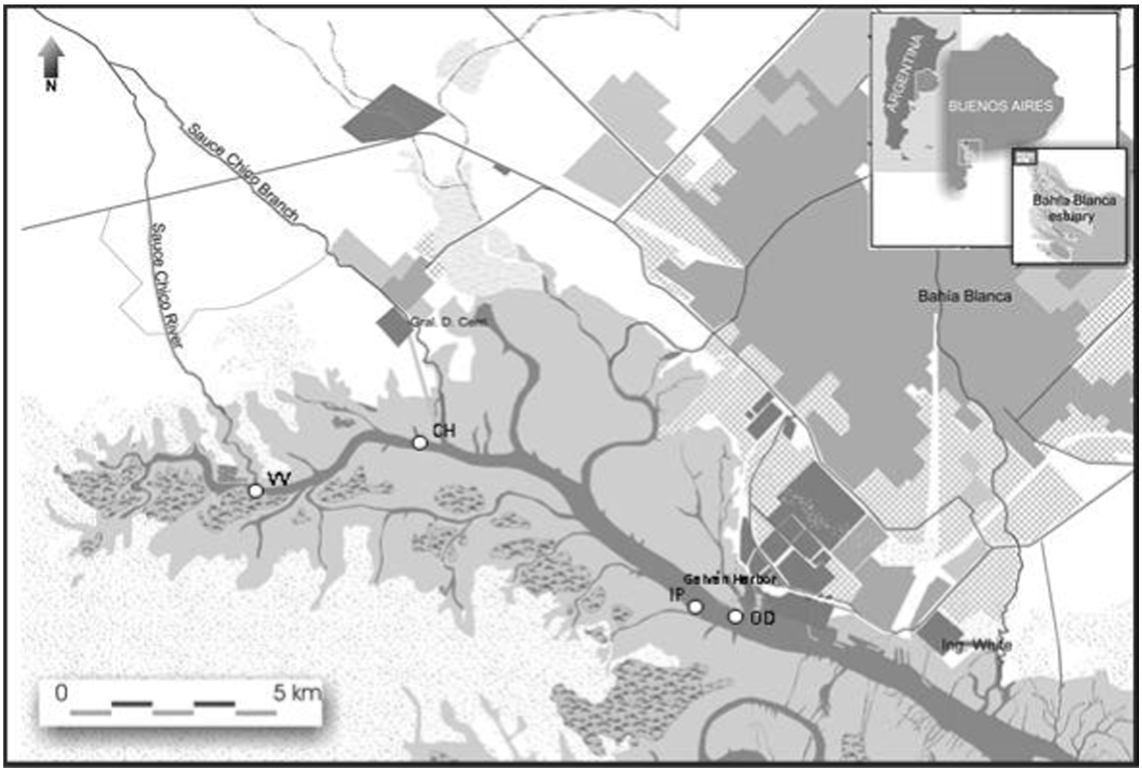

Fig. 1 Location of sampling sites in the Bahía Blanca Estuary, Argentina. *OD* oxidized dock, *IP* inflammable post, *CH* Cuatreros Harbor, *VV* Villarino Viejo

sediment and phytoplankton particles that may contain metals (Lobel et al. 1991), the intestinal contents of mussels were maintained for metal analysis. This is because wild mussels collected for human consumption are not depurated before preparation, and to monitor food safety, gut content should be included for the analyses. Finally, two aliquots of about 0.5 g were taken from each well-homogenized dry sample to determine the concentration of heavy metals (Cd, Cu, Pb, Mn, and Fe) following the methods described by Marcovecchio and Ferrer (2005). It includes a digestion with a mixture $HNO_3/HClO_4$ (5:1) at 110 ± 10 °C. Then, the extract (1 ml) is filled with 0.7% HNO_3 to a volume of 10 ml. Metal concentrations were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES Optima 2100 DV, PerkinElmer).

For the analytical quality control, reagent blanks, certified reference materials [CRMs (mussel tissue flour, Certified Reference Material No. 6, NIES, Tsukuba, Japan)], and analytical grade reagents (Merck or Baker) were used. The recovery percentages for all trace metals in CRM were higher than 90%, and the analytical precision expressed as coefficients of variance was <10% for all the metals based on replicate analysis. The detection limit of the method (MDL) was calculated as the standard deviation of 10 blank replicates (Federal Register 1984). Percentage of recovery, relative standard deviation, and detection limits of the method are shown in Table 1. For samples which values were lower than the applied analytical MDL, a value of one half the detection limits was assigned (Jones and Clarke 2005).

Prior to use, all the materials employed for sampling and sample storage were carefully cleaned and immersed in diluted nitric acid (5%, HNO_3 suprapur, Merck) following internationally recommended protocols (APHA-AWWA-WEF 1998).

The individual condition index (CI) of mussels was calculated according to Lucas and Beninger (1985) as

$$CI = \frac{\text{dry soft tissue weight}}{\text{dry shell weight}} \times 100$$

Table 1 Detection limit of the method and percentages of recovery in the analysis of reference material to assess analytical quality (mussel tissue flour, Certified Reference Material No. 6, NIES, Tsukuba, Japan)

Metal	Recovery (%)	RSD (%)	MDL (mg/l)
Cd	92.4–98.7	1.8	0.0030
Cu	93.1–97.9	3.0	0.0623
Pb	95.3–99.8	5.3	0.0937
Mn	91.2–97.9	4.5	0.0450
Fe	95.6–101.7	3.9	0.6139

RSD relative (%) standard deviation, *MDL* Detection limit of the method

Trace metals in sediments

Duplicate sediment samples were taken at each site using a plastic spoon and were stored in a plastic bag. They were stored at 4 °C until analysis. Samples were oven dried at 60 ± 5 °C until a constant weight. Before grounding, debris and biota fragments were removed from the dried sediments to be finally sieved in order to obtain the smallest fraction (<63 μm). Two subsamples (about 0.5 g) of fine sediments were taken to determine total metal concentrations (Cd, Cu, Pb, Mn, and Fe) following the method described by Marcovecchio and Ferrer (2005).

The following equation was used to estimate the enrichment factor (EF) of metals from each sample using Fe as a normalizer:

$$\mathrm{EF} = \frac{(\mathrm{Me/Fe})_{\mathrm{sample}}}{(\mathrm{Me/Fe})_{\mathrm{crust}}}$$

where $(\mathrm{Me/Fe})_{\mathrm{sample}}$ is the ratio of metal concentration (μg/g dw) to Fe concentration (% dw) in the sediment sample and $(\mathrm{Me/Fe})_{\mathrm{crust}}$ is the corresponding ratio in Earth crust. The EF is widely used to estimate the metal source (anthropogenic or natural) and the degree of contamination (Selvaraj et al. 2004). In this study, the Earth crustal metal concentrations were used as the background metal values. These values are taken from Martin and Maybeck (1979) and represent the average composition of the surface rocks exposed to weathering. These values are Fe 4.1%, Cd 0.2, Cu 32, Pb 16, and Mn 720 μg/g. Elements which are naturally derived have an EF value of nearly a unit, while elements of anthropogenic origin have EF values of several orders of magnitude. According to Sutherland (2000), EF values ≤1 indicate background concentration, 1–2 absence to minimal enrichment, 2–5 moderate enrichment, 5–20 significant enrichment, and 20–40 and >40 extremely high enrichment.

Biosediment accumulation factor (BSAF) was calculated according to Szefer et al. (1999) and Lafabrie et al. (2007) as

$$\mathrm{BSAF} = \frac{\text{metal concentration in the organism}}{\text{metal concentration in the sediment}}$$

Statistical analysis

A two-way analysis of variance (ANOVA) was performed to analyze interactions between sampling site and season, and Tukey's test was used for multiple comparisons. Normality and homogeneity of variances were tested by Shapiro-Wilk *W* and Bartlett tests, respectively. When necessary, data was log-transformed to meet the parametric assumptions. Statistical analysis followed Zar (1996). Nonparametric analyses (Kruskal-Wallis and Spearman's rank correlation tests) were conducted on condition index ratio data. The acceptable level of statistical significance was less than 5%. Data presented in the figures were not transformed. Error values, either in figures, in tables, or in the text, represent standard errors (SEs).

Results

Physical characteristic in water samples

Results of the environmental parameters measured in the sampling site waters are summarized in Table 2. The measured variables, except pH, presented clear seasonal but no spatial differences. Mean values were calculated as average including all sites. The mean winter temperature was 9.1 ± 0.2 °C while in summer was 23 ± 0.1 °C. Salinity showed higher values in summer (38.63 ± 0.08) than in spring (33.29 ± 0.70) and winter (32.51 ± 0.60). pH was slightly alkaline (8.61 ± 0.40) and with higher values in winter.

Trace metal bioaccumulation in organisms

The concentrations of Cd, Cu, Pb, Mn, and Fe in soft tissues of *B. rodriguezii* are shown in Table 3. Pb was below detection limit in all cases except in mussels collected in VV during summer 2012 (3.65 ± 0.02 μg/g dw). For this reason, statistical analysis of this metal was not performed.

Table 2 Physical characteristics of seawater

Season	Site	Temp (°C)	pH	Salinity (psu)
Spring 2011	OD	15.6	8.11	31.50
	IP	15.2	8.13	35.35
	CH	15.6	8.27	32.09
	VV	15.8	8.17	30.37
Summer 2012	OD	22.8	8.23	38.41
	IP	23.0	8.24	38.60
	CH	23.3	8.25	38.73
	VV	22.9	8.27	38.79
Winter 2012	OD	8.9	9.48	33.62
	IP	8.8	9.51	33.37
	CH	9.7	9.49	31.20
	VV	9.1	9.49	31.84
Spring 2012	OD	18.3	7.82	35.35
	IP	18.3	7.99	35.28
	CH	18.6	8.02	33.62
	VV	20.2	8.09	32.73

OD oxidized dock, *IP* inflammable post, *CH* Cuatreros Harbor, *VV* Villarino Viejo

Table 3 Heavy metal concentrations (µg/g dw) (mean ± SE) in *Bracchidontes rodriguezii* soft tissue, according to site and season

Metal	Site	Season			
		Spring 2011	Summer 2012	Winter 2012	Spring 2012
Cd	OD	0.94 ± 0.02a A	1.86 ± 0.05b A	1.81 ± 0.24b A	1.13 ± 0.10a A
	IP	1.14 ± 0.02a AB	2.89 ± 0.13b B	2.81 ± 0.18b B	1.20 ± 0.16a A
	CH	1.50 ± 0.04a B	3.32 ± 0.30b B	3.24 ± 0.06b B	1.35 ± 0.03a A
	VV	1.27 ± 0.10a AB	5.95 ± 0.59b C	3.46 ± 0.19c B	1.65 ± 0.11a B
Cu	OD	11.80 ± 0.43a A	13.37 ± 0.27a A	13.93 ± 3.66a A	11.97 ± 1.40a A
	IP	12.23 ± 0.67a A	29.76 ± 0.88b B	26.01 ± 2.78b B	12.57 ± 1.72a A
	CH	13.21 ± 1.13a A	25.32 ± 1.96b B	16.61 ± 2.14a A	11.84 ± 0.51a B
	VV	10.40 ± 0.19a A	66.86 ± 1.56b C	17.66 ± 0.47c A	17.437 ± 3.92c A
Mn	OD	17.31 ± 0.74a A	15.99 ± 0.24a A	15.66 ± 1.03a A	20.37 ± 1.15a A
	IP	14.99 ± 1.46a AB	19.79 ± 0.61ac A	27.00 ± 1.21b B	20.40 ± 1.35bc A
	CH	19.19 ± 1.82a A	30.33 ± 3.87b B	19.14 ± 1.28a AC	14.302 ± 0.46ab A
	VV	12.24 ± 1.35a B	52.02 ± 0.89b C	22.67 ± 0.18c BC	22.74 ± 2.78c A
Fe	OD	441.78 ± 11.88a AC	670.96 ± 107.06b A	297.40 ± 20.33c A	717.17 ± 10.17b A
	IP	573.16 ± 6.18a AB	929.24 ± 14.21b B	799.91 ± 97.21b B	738.88 ± 11.11ab A
	CH	658.40 ± 35.63a B	1033.51 ± 99.89b BC	425.19 ± 29.68c C	551.83 ± 20.64ac A
	VV	395.42 ± 36.99a C	1334.42 ± 178.68b C	940.46 ± 60.08c B	997.07 ± 132.96bc B

Tukey's test: Lowercases indicate significant seasonal differences in each site and uppercases significant spatial differences in each season

OD oxidized dock, *IP* inflammable post, *CH* Cuatreros Harbor, *VV* Villarino Viejo

The average concentrations of heavy metals in soft tissues of *B. rodriguezii* considering all sampling sites and seasons revealed the following order: Fe > Mn > Cu > Cd. In accordance with the sediment data, Fe was the most bioaccumulated metal in mussel soft tissue. The two-way ANOVA test showed that both factors (season and sampling site) as well as their interaction were highly significant for all the trace metals evaluated (Fig. 2). Due to the interaction between factors, the simple effects of each factor were analyzed by the multiple comparisons Tukey's test (Table 3). The heavy metals evaluated in mussels showed seasonal differences at each site. Their concentrations tended to be lower and similar during springs, higher during summer, and to a lesser extent during winter. These differences became more marked towards the inner area of the estuary and preeminent for Cd and Cu (Fig. 2; Table 3). Differences among sites in each season also were found. During summer, metal levels in mussel soft tissue tended to increase from the outermost zone to the innermost of the estuary, being lower in OD and higher in VV. This pattern was not observed during spring since the heavy metal concentration showed less variability among sites. The highest heavy metal concentrations in mussels were found at VV during summer 2012 (Cd 5.95 µg/g dw, Cu 66.86 µg/g dw, Mn 52.02 µg/g dw, and Fe 1334.42 µg/g dw), and the lowest were recorded during spring 2011 at OD for Cd (0.94 µg/g dw) and at VV for Cu (10.40 µg/g dw) and Mn (12.24 µg/g dw), respectively. In the case of Fe, the lowest values were found at OD during winter (297.40 µg/g dw) (Fig. 2; Table 3).

To assess the general health of the native mussels, the CI was measured at each time of collection at all sites (Fig. 3). Statistical analysis showed a strong negative correlation between the CI and Cd and the CI and Cu. Organisms with high concentrations of Cd and Cu showed worse body CIs than those with low concentrations of these metals (Spearman rank = −0.89 and −0.77, respectively). Values were significantly lower in organisms collected during summer and winter than those collected during spring, and further, the values found in spring 2011 were higher than in spring 2012. On the other hand, while a slight decrease was observed in the CI to the innermost zone of the estuary, no significant differences among sites were detected ($p = 0.178$).

Trace metals in sediments

The overall average concentrations of heavy metals in sediments revealed the following order: Fe > Mn > Cu > Pb > Cd (Table 4). Fe and Mn showed the highest levels with Fe averaging one order of magnitude higher than the other ones. During the sampling period, a decrease in Cd and Fe levels in the internal sites of the estuary (CH and VV) was observed. On the other hand, although Cd appeared to be higher in sediments from VV, no statistical differences were found ($p > 0.1$). During spring, Fe levels from Galvan area (OD

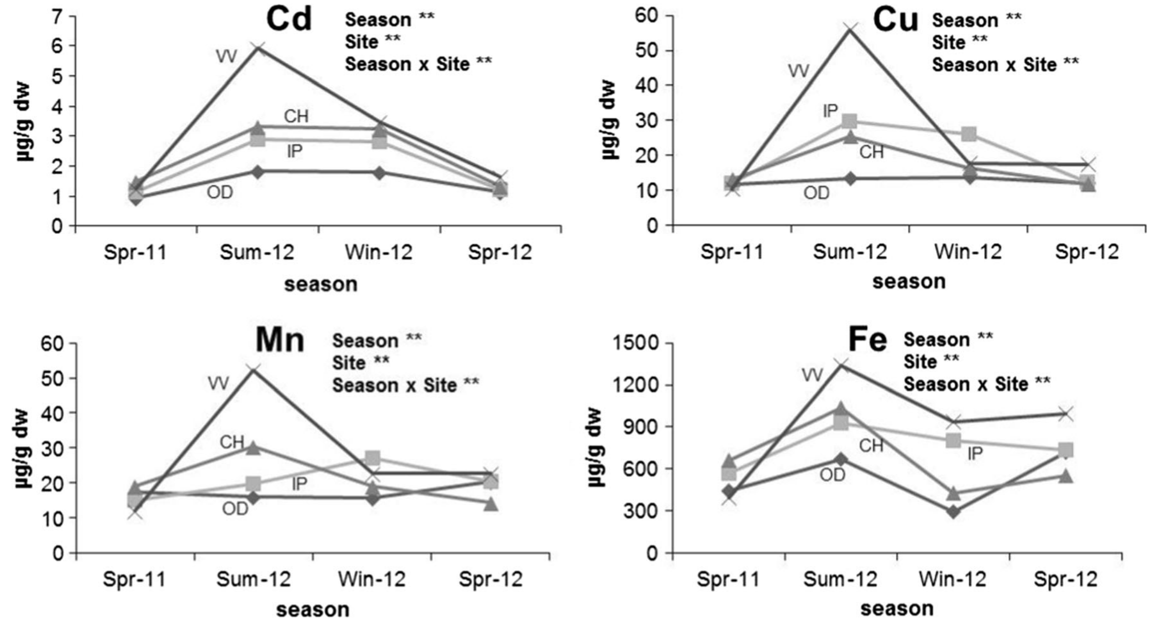

Fig. 2 Graphical effect of the interaction between "season and sampling site" on the average results (two-way ANOVA). Highly significant differences ($p < 0.01$) of heavy metal concentration (µg/g dw) in *Brachidontes rodriguezii* (*double asterisk*). *OD* oxidized dock, *IP* inflammable post, *CH* Cuatreros Harbor, *VV* Villarino Viejo

and IP) were higher than in CH. On the other hand, Pb and Mn tended to increase in CH and VV being more evident in CH. Finally, highly significant differences were found for Mn and Cu, with the highest levels in CH and OD, respectively.

The EF for each site in winter and spring 2012 is listed in Table 4; EF was calculated for Cd, Cu, Pb, and Mn in relation to Fe. The EF mean values were in the following order: Cu (0.58) > Mn (0.40) > Cd (0.30) ≥ Pb (0.29). According to Sutherland (2000) classification, EF values of the trace metals evaluated were <1, indicating no enrichment by these metals in the sediments of the BBE. Finally, BSAF values higher than a unit were found for Cd and Cu. Cd showed extremely high values in all the evaluated seasons and sites (27.55 ± 3.87), while Cu revealed values slightly higher than a unit only for VV in winter 2012 (1.022). In general, BSAF tended to be lower in spring, with the exception of Mn and Fe.

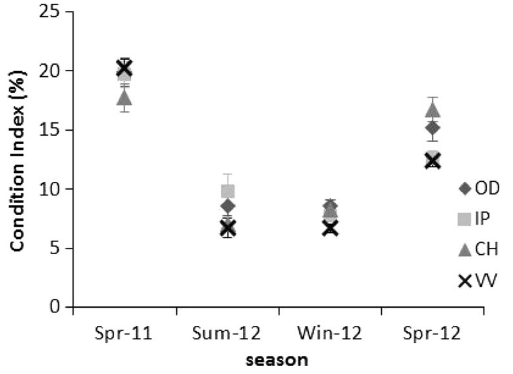

Fig. 3 Seasonal variation of condition index in *Brachidontes rodriguezii*, from four sites inside the Bahía Blanca Estuary (mean value ± SE). *OD* oxidized dock, *IP* inflammable post, *CH* Cuatreros Harbor, *VV* Villarino Viejo

Discussion

The physical-chemical parameters (pH, temperature, and salinity) of the environment were in accordance with previous results (Freije and Marcovecchio 2004; Arias et al. 2009), indicating a relative stability of the system.

In regards to sediments' fine fraction (<63 µm), Cu and Pb at the inner sites of the BBE tended to be higher at CH than at VV in both seasons; contrarily, Cd levels tended to be higher at VV. On one hand, this area is affected by a freshwater input—the permanent Sauce Chico River—whose watershed comprises intensive agriculture and cattle breeding lands and thus receives the influence of the agrochemical inputs. Then, it can be hypothesized that the higher Cd levels in sediments from the head of the estuary are related to the application and subsequent runoff of Cd-containing phosphate fertilizers (Ray and Macknight 1984). On the other hand, levels of Cu and Pb at the area can be attributed to both the widespread presence of small artisanal fishing boats and the discharges at CH of a small water stream which crosses General Cerri city. Further, the intermittent Saladillo de García stream which flows in the nearness contributes with organic matter and wastewater discharges of General Cerri city (Limbozzi and Leitão 2008). Beyond the distance, its influence is not excluded because of the strong currents driving the sediment distribution at the area. In comparison to previous results, Botté et al. (2010) reported higher

Table 4 Summary of trace metal concentration (μg/g dw; Fe in mg/g dw) and enrichment factor (EF) of heavy metals in sediments' fine fraction from different areas of the Bahía Blanca Estuary (mean ± SE)

Season	Site	Cd		Cu		Pb		Mn		Fe
		Mean ± SE	EF	Mean ± SE	EF	Mean ± SE	EF	Mean ± SE	EF	Mean ± SE
Winter	CH	0.077 ± 0.03	0.28	22.71 ± 1.70	0.52	4.11 ± 0.41	0.19	318.75 ± 19.65	0.32	56.32 ± 5.50
	VV	0.096 ± 0.02	0.39	17.29 ± 0.29	0.44	3.23 ± 0.34	0.16	340.40 ± 5.00	0.38	50.41 ± 1.32
Spring	OD	0.06	0.23	26.29 ± 0.47	0.63	5.21 ± 0.23	0.25	234.35 ± 14.77	0.25	53.77 ± 0.27
	IP	0.055 ± 0.01	0.23	17.35 ± 0.28	0.45	3.84 ± 0.03	0.20	282.35 ± 3.44	0.33	49.10 ± 1.09
	CH	0.068 ± 0.002	0.44	23.18 ± 0.43	0.94	8.50 ± 0.04	0.69	437.80 ± 6.10	0.79	31.74 ± 0.12
	VV	0.074 ± 0.01	0.33	17.11 ± 0.70	0.48	3.87 ± 0.07	0.22	283.23 ± 14.71	0.35	45.76 ± 5.12
	BBE	0.068 ± 0.006		20.95 ± 2.23		4.73 ± 0.64		301.70 ± 30.10		48.75 ± 2.00
	RV	0.11[a,b]		33.00[a]		19.00[c]		770.00[c]		41.00[a,c]

OD oxidized dock, *IP* inflammable post, *CH* Cuatreros Harbor, *VV* Villarino Viejo, *BBE* Bahía Blanca Estuary, *RV* recommended values of unpolluted sediments

[a] GESAMP (1982)

[b] IAEA (1989)

[c] Salomons and Förstner (1984)

Cd, Pb, and Mn concentrations but lower Cu and Fe levels in the fine sediments of CH. In regards to VV, the innermost site of the estuary, these are the first results obtained from the analysis of heavy metals in the sediments' fine fraction. Considering the Galvan Harbor area, Cd, Cu, and Pb showed higher values in OD than in IP. Despite the fact that both stations are within the Galvan Harbor area, OD is located at the core of the industrial area and is surrounded by wastewater discharge pipelines, industrial vents, docks, shipsides, shipbreaking, etc., which are all potential sources of these metals. In addition, the grain size of the sediments favored the accumulation of trace metals since the proportion of clay at OD and CH was higher than at IP and VV, being classified as silty clay and silty, respectively (Oliva 2015). Grecco et al. (2006) and Botté et al. (2010) studied Galvan Harbor area; they found higher Cd, Pb, and Mn but lower Fe than the values reported here for OD and IP. On the other hand, the Cu concentration found in IP was similar to the values reported by these authors, while Cu levels in OD were higher.

The high levels of Fe and Mn found in this study are mainly attributed to weathering of heavy minerals widespread in the region (magnetite, amphiboles, pyroxenes, and biotites) (Teruggi 1957; Grecco et al. 2006). Iron is frequently used as an indicator of natural changes in the heavy metal charge of the sediments (Rule 1986), and its level is related to the metal reactive component abundance not significantly affected by human activities (Luoma 1990). Manganese is an element of low toxicity having considerable biological significance and is one of the most active and biogeochemical transition metals in the aquatic environment (Evans et al. 1977).

The EFs for the tested trace metals were higher in CH, but in no case exceeded the unit. Although these results indicated no metal enrichment in the sediments, Hasan et al. (2013) mentioned that areas with EF < 1 should be viewed with caution since they imply the release of these elements, thus being more bioavailable.

According to the results provided by worldwide literature (Villaescusa-Celaya et al. 2000; Buggy and Tobin 2008; Yang et al. 2012), the present overall heavy metal levels were below the recognized thresholds of a characteristic polluted environment. Moreover, the trace metal levels found in this study did not overcome the recommended values of unpolluted sediments by GESAMP (1982), IAEA (1989), and Salomons and Förstner (1984) (Table 4). Despite this, considering the Sediment Quality Guidelines (SQGs), the concentration of Cu in sediments from OD and CH was above the marine threshold effect level (TEL) (Cu 18.70 μg/g dw) but below the probable effect level (PEL) (Cu 108.20 μg/g dw). Taking this into account, Cu concentration in sediments was occasionally associated with adverse biological effects (Macdonald et al. 1996) in the study area.

In regards to trace metal in mussels, the present results provide new evidence of metal bioaccumulation in the soft tissue of the native mussel *B. rodriguezii* at the area of study. Metal accumulation in these organisms revealed a different pattern from the observed in sediments; in fact, no significant correlation between both matrices was found. Similar results were obtained by Gundacker (1999), Giarratano et al. (2010), and Duarte et al. (2011). A possible explanation is that mussels are not in direct contact with sediment, as they are usually attached to rocks or dock columns. Instead, they are only exposed to fine sediments that are resuspended by wave action. In addition, the lack of correlation can be attributed to the differences in trace metal bioavailability. According to

Pempkowiak et al. (1999), metal speciation occurring in the sediments is expected to influence metal bioavailability and metal content in biota and, particularly, in the soft tissue of mussels. It is important to highlight that the extraction technique used in this study allows the removal of the total heavy metal burden of the sediments while mussels incorporate just the bioavailable fraction (Förstner 1989). In addition, it is well known that several environmental and biological factors such as salinity, seawater temperature, seasonality, organic matter, tidal height, reproductive status, and physiological condition of mussels influence the metal bioaccumulation (Szefer et al. 2004; Mubiana et al. 2006). Added to this, mussels usually feed on particulate matter and microorganisms of seston and microplankton (Kehrig et al. 2006) which can act as a heavy metal source. In recent years, an increase in microzooplankton (Barría de Cao et al. 2011) and phytoplankton blooms (Guinder et al. 2012, 2013) has been detected during summer seasons in the area of study, pointing to an additional trace element source through trophic transference. Probably, the high levels of heavy metals in mussel's tissues detected during summer and to a lesser extent during winter, especially in the innermost area of the BBE, are related to an increase in food particles and metals associated with them since they could act as regular carriers of both organic carbon and metals to the mussels (Davies et al. 1997; Luoma et al. 1998).

Although a significant statistical relationship between Cd levels in mussels and sediments was not found, the highest concentrations of this metal were found in VV in both cases. Despite Cd concentration in sediments was shown to be low, it was detected in all mussel samples. These results were in agreement with those reported by Vázquez et al. (2007) in *B. rodriguezii* from Patagonia and by Gil et al. (2006) and Apeti et al. (2009) in mussels from different areas. This pattern can be explained because under aerobic conditions, Cd is found mostly in dissolved form, increasing its availability to be incorporated by biota (Bewers et al. 1987). In this way, Cd in marine organisms could be many times greater than the metal level in the surrounding environment, as is evidenced by the BSAF (Ansari et al. 2004; Apeti et al. 2009). The opposite occurred with Pb, as this metal was detected in sediments from BBE but not in *B. rodriguezii* tissue. Giarratano and Amin (2010) showed that Pb was not accumulated by the mussel *Mytilus edulis*, due to its association with the residual fraction of the sediments. This might not be the case of BBE sediments, as previous studies have shown that Pb is represented in the bioavailable fractions (Botté et al. 2010; Grecco et al. 2011). Another possibility is a more pronounced physiological control of Pb storage in the organisms. Szefer et al. (2006) found that the byssus of mytilids is more selective and sensitive to variations in metal concentrations in their environment (with the exception of Cd) compared with the soft tissue. They suggest a significantly more effective transfer of soft tissue Pb to the byssus, in contrast to Cd which is strongly accumulated by the hepatopancreas (George 1980). Although in this study the byssus was discarded, we may assume that the absence of Pb in soft tissue is probably due to its effective transfer to the gland and/or to the low rate of Pb accumulation as reported Boisson et al. (1998) and Shulkin et al. (2003). Copper is an essential micronutrient element for all higher organisms; nevertheless, high concentrations of bioavailable Cu may be toxic. The presence of Cu in the aquatic environment is related to recreational boats, urban runoff, or industrial waste (Piola et al. 2009). In this study, high Cu concentrations were detected in mussels collected from the rocks of VV during summer 2012. As mentioned in the above paragraphs, VV is located at the innermost site of the estuary, which shows slow water circulation; the residence time for the estuary is calculated around 28 days (Perillo et al. 2001). Cu occurrence also depends on the amount of local water movement making its density higher in areas with less water circulation and tidal flushing as in VV (Pineda et al. 2012), an effect that is more marked during summer due to a higher evaporation rate.

The CI is a standardized indicator for the physiological state of a bivalve, which has been used to reduce strong variance in data due to size or differences in trophic conditions. It has been observed that under stressful environmental conditions and/or exposure to pollutants, the physiological condition of the mussels could be reduced (Widdows et al. 1997; Blanck 2002; Mauri and Baraldi 2003). Furthermore, the variability of the CI depends on the complex interaction between extrinsic and intrinsic factors, such as reproductive stage, temperature, salinity, availability of food, and quality of the diet (Oliva et al. 2017). Preliminary studies indicate that the reproduction of *B. rodriguezii* in the BBE is maintained throughout the year to decline in the coldest months (Eder Dos Santos personal communication). Probably, the seasonal variation of the CI observed in this study is related to the reproductive cycle of the mussel, as has been described in other studies (Orban et al. 2002; Cardellicchio et al. 2008; Oliva et al. 2017). Nevertheless, the results of this work suggest that pollution by heavy metals is one of the most important factors influencing the health status of *B. rodriguezii*, since mussels with high concentrations of Cd and Cu showed worse body CIs than those with low concentrations of these metals. The observed seasonal pattern in metal bioaccumulation in mussels from BBE was similar to other studies: higher metal concentrations when mussel CI is low and vice versa (Ivankovic et al. 2005; Gorbi et al. 2008; Strogyloudi et al. 2012).

Some countries established quality criteria to both evaluate the environmental situation of their coastal water and serve as risk assessment criteria for several well-known hazardous metals. Although the control levels derived from these criteria have been developed for the assessment of the environmental situation in some particular countries, they may be useful for comparing the results of the present study. According to the Norwegian Pollution Control Authority (Molvaer et al. 1997;

Table 5 Values of heavy metal concentrations (μg/g dw) in bivalves from worldwide locations and this study

Mussel	Location	Range heavy metals (μg/g dw)					Reference
		Cd	Cu	Pb	Mn	Fe	
Africa							
Perna perna	Gulf of Annaba, Algeria	n.d–0.56	5.71–27.86	n.d–1.75	5.17–22.95	369.44–938.02	Belabed et al. (2013)
Mytilus galloprovincialis	*El Jadida, Morocco*	7.20	26.80	9.60	20.80	w.d	Maanan (2008)
Asia							
Mytilus edulis	Eastern coast, China	n.d–4.96	n.d–22.58	0.06–2.43	w.d	0.29–882.50	Fung et al. (2004)
Crenomytilus grayanus	Amurskiy and Ussuriyskiy Bay, Japan	1.40–26.00	3.9–119	1–287	w.d	w.d	Shulkin et al. (2003)
Perna viridis	Hong Kong coastal waters	0.24–0.86	9.20–43.80	4.40–13.00	37.40–57.60	330–934	Liu and Kueh (2005)
P. viridis	The Straits of Malacca	0.40–3.15	6.19–103.0	1.98–61.00	w.d	257–1224	Yap et al. (2016)
Europe							
Mytilus galloprovincialis	Spanish Atlantic–Galician and Northern areas	0.61–0.84	4.92–8.01	1.63–6.11	w.d	w.d	Besada et al. (2011)
M. galloprovincialis	Spanish Mediterranean coast	0.28–1.67	5.98–11.31	1.82–57.83	w.d	w.d	Fernández et al. (2010)
M. galloprovincialis	Apulian coast, Italy	0.38–1.84	4.66–19.22	0.37–3.25	w.d	w.d	Spada et al. (2013)
M. galloprovincialis	Goro Bay, Italy	3.70–4.30	9.40–21.20	15.80–29.00	w.d	w.d	Locatelli (2003)
M. galloprovincialis	Saronikos Gulf, Greece	0.54–1.34	6.60–20.00	w.d	11.50–24.50	431–599	Strogyloudi et al. (2012)
M. galloprovincialis	Thermaikos Gulf, Greece	0.77–1.2	4.46–6.11	0.97–2.16	9.68–23.58	w.d	Catsiki et al. (2001)
South America							
P. perna	Macaé coast, Brazil	0.29–0.65	4.11–6.24	0.49–0.91	8.69–18.50	257–743	Santiago et al. (2016)
M. edulis	Patagonian coast, Argentina	1.12–3.89	4.37–9.00	1.82–8.07	w.d	w.d	Gil et al. (2006)
Mytilus edulis chilensis	Ushuaia Peninsula, Argentina	0.98–1.36	4.43–5.95	2.15–3.80	w.d	190–210	Duarte et al. (2012)
Brachidontes rodriguezii	Bahía Blanca Estuary, Argentina	1.43–3.11	12.77–27.48	n.d–3.65[a]	17.33–27.76	531.83–928.70	This study

n.d no detectable, *w.d* without data

[a] Data for a site in a season

Green et al. 2008), mussels from BBE got included in class II (moderate concentration) among five classes (class I "insignificantly polluted" to class V "extremely polluted"), while considering the National Status and Trends "Mussel Watch" Program, NOAA (Kimbrough et al. 2008) mussels are classified in the low (for Cd) and medium (for Cu and Pb) categories. Finally, comparing with other coastal areas of the world, the average trace metal levels found in mussels from the BBE are comparable to the eastern coast of China, the Gulf of Annaba (Algeria), and the Saronikos Gulf (Greece) (Table 5).

As a final point, the heavy metal concentration in mussels from BBE was compared with international standards for human consumption of metals in mollusks/shellfish. Most of these limits were presented in standard units of fresh weight. Wet weight concentrations can approximately be transformed into dry weight by multiplying them with a factor of 5 (USEPA, Environmental Protection Agency 2002) to facilitate a comparison between standards and measured concentrations. Levels of Cd and Pb in soft tissues of *B. rodriguezii* were below the limits allowed by the Argentine National Safety and Quality Food Service for mollusk bivalves (Cd 5.00 μg/g dw, Pb 7.5 μg/g dw) (SENASA, Servicio Nacional de Sanidad y Calidad Agroalimentaria 2008). In the case of Cu, there are no Argentine regulations for mollusks; however for general foods, the maximum permissible metal level is 50 μg/g dw. The mean concentration of Cu in mussels from BBE was below the mentioned limit, although levels detected during summer in VV barely exceeded it. Finally, the trace metal mean values obtained in this study were lower than the permissible limits set by several international regulations for Cd (5.0 μg/g dw—EU 2006; CEE, Comunidad Económica Europea 2001), Pb (7.5 μg/g dw—EU 2006; CEE, Comunidad Económica Europea 2002), and Cu (150.0 μg/g dw—Nauen 1983) in fishery products.

Conclusions

Overall results indicated a significant influence of seasonal and spatial variability on trace metal bioaccumulation in mussel *B. rodriguezii* from the BBE, being higher in summer and to a lesser extent in winter. At the same time, during these seasons, trace metal levels tend to increase from the outermost zone to the innermost of the estuary. This is probably due to the increase in food particles carrying associated metals and to the slow water circulation in the area. The measured concentrations were similar to those reported for mussels from other coastal areas of the world and according to international criteria; BBE can be classified as moderately polluted or between the low and medium categories of pollution. Anyway, from the public health point of view, mussels met the national and international standards set for trace metals for human consumption.

Heavy metal levels in mussel's tissue were not correlated with sediment concentrations probably due to different bioavailability patterns or differences in physiological control of trace metal bioaccumulation.

The metal pollution observed in the fine sediments from Galvan Harbor area confirms that the major sources of heavy metals are harbor activities—industrial and urban wastewater discharges. While heavy metal contamination in the inner area of the BBE can be attributed to the agricultural and rural activities carried out at the wide lands surrounding the Sauce Chico River together with urban wastewater discharges. On the other hand, other factors such as residence time and water circulation may be influencing the metal concentration at BBE. In addition, the measured concentrations in sediments were lower than those reported for other heavily industrialized estuaries and do not represent a risk to aquatic life according to the Sediment Quality Guidelines except for Cu. Finally, considering the constant increase in human activities within the study area, it is important to carry out periodical monitoring of metals in order to control early environmental changes and related biological effects.

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