

Distribution and behavior of zinc in estuarine environments: an overview on Bahía Blanca estuary (Argentina)

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Abstract Zinc concentrations and distribution have been fully studied within Bahía Blanca estuary, an area which is strongly influenced by urban and industrial stress. Not only metal dissolved in estuarine water were measured but also measured were sediments and suspended particulate matter (SPM), as well as associated with estuarine organisms. In all cases, internationally standardized protocols were applied to metal measurements, including analytical quality check test through analysis of certified reference materials. Total metal contents from surface sediments and SPM were compared with those from a historical database of the area, as well as with values representing the natural geochemical baseline within the system. Results showed that heavy metal pollution is mainly localized in the areas close to both industrial effluents discharge system and urban sewage outfall discharge. Data from sequential extractions indicate that metals from anthropogenic sources

are potentially more mobile than those inherited from geological parent material. The influences of other potential sources of metals (i.e., streams, runoff) were also considered. SPM was clearly identified as the main carrier of the studied heavy metals within the system, and its significance to metals input into sediments and/or biota was verified. Zinc has been accumulated within the different biological species from Bahía Blanca estuary, and their kinetics of accumulation have also been considered. Finally, the combination of the obtained results allowed suggesting the maintenance of a surveillance program to assess the environmental quality of this environment.

Keywords Estuaries · Pollutants transport · Coastal biogeochemistry · Intermediate processes · Sources and sinks · Biological effects

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Introduction

Estuaries have been recognized as dynamic, complex and unique systems, which are included among the most productive marine ecosystems in the world (Chapman and Wang 2001; Gallegos and Neale 2015; Tweedley et al. 2015). The pollution problem within estuaries can be characterized through extremely complicated interactions between their dynamic physical, chemical, biological and geological conditions, hindering the efforts to assess the impact of anthropogenic activities on estuarine quality (Dauvin 2008; da Costa Souza et al. 2014). In addition, estuarine characteristics also determine the corresponding pollutants behavior; thus, depending on the nature of the contaminant and the estuarine condition, two different features are possible during the mixing: (1) either the contaminant is removed from the water to settle in the

sediments (sediments as a sink) or (2) contaminants are added to the water as they rise from the sediments (sediments as a source; Erftemeijer and Lewis 2006). Thus, it is critical that sediment contamination in estuaries and its biological and ecological significance can be properly and fully assessed (Chapman and Wang 2001).

Another point that deserves to be carefully considered is the potential transference route of materials into the sea, considering estuarine systems, has been recognized as major transport paths for metals of natural and anthropogenic origins from the continent to the coastal waters (Masson et al. 2006; Dumas et al. 2015). In this sense, the suspended particulate matter (SPM) has been identified as the main carrier of heavy metals within estuarine systems (Bibby and Webster-Brown 2006) and in many cases has demonstrated a significant role in the transference processes of metals to the organisms (Fang et al. 2006; Fernández Severini et al. 2013).

In aquatic ecosystems, plankton and SPM have an affinity for most of the trace metals (Balls 1989; Sanders and Riedle 1998; Elskens et al. 2014). Thus, these fractions play important roles in the biogeochemical cycle of the metals (Fowler and Knauer 1986; Libes 2009). Suspended particulates are instrumental in controlling the reactivity, transport and biological impacts of substances in aquatic environments and provide a crucial link for chemical constituents between the water column, bed sediments and food chain (Turner and Millward 2002). Particulate metals eventually settle to the bottom and may be available to benthic organisms or may be released to the water column through resuspension, adsorption/desorption, reduction/oxidation reactions or degradation of organisms. Throughout this process, the role of interstitial water is also very important (mainly to superficial level of the bottom sediment) by acting as a reaction center which changes the chemical properties of metals and acts as a means of transport between the sediment and the water column. In plankton, metals may be adsorbed onto the cell surface or by crossing the cell walls. The adsorption of metals by plankton is very variable, and in general, this fraction presents high surface/volume ratio. Consequently, plankton has high concentration factors, especially for non-reactive particles. Once incorporated into plankton fraction, metals may be transferred along the food chain and transformed by the organisms, enhancing or alleviating their toxicity (Fisher and Reinfelder 1995; Monterroso et al. 2003).

Trace metals have shown to be significantly hazardous pollutants in aquatic environments, even at very low concentrations (Salomons and Förstner 1984; Alloway 2013). Unlike organic pollutants, which can be degraded to less harmful components by biological or chemical processes, metals are considered as non-degradable pollutants. In this sense, the study of the occurrence, fate and distribution of

trace metals in coastal marine and estuarine environments has received major attention, mainly because of the persistent toxic effects of heavy metals (Sfakianakis et al. 2015) and their ability to be accumulated within compartments of these environments (McComb et al. 2014; Phillips et al. 2015). The effects of metal pollution on local environments and organisms can be substantial and long lasting in spite of years of restoration efforts (Pan and Wang 2012). Thus, a large amount of environmental monitoring programs has been carried out in order to assess metal distribution within coastal ecosystems (i.e., Lacerda et al. 1999; Vaz de Melo et al. 2015). Within this framework, one of the most studied trace elements is zinc. The presence of this metal in the aquatic environment comes from both natural and anthropogenic sources, since it has many industrial applications such as surface coating, corrosion protection components, tanning and rubber manufacturing agents, oil additives and paint pigments. It is relevant to point out that toxic metals can be taken up by marine organisms, entering the food chain and be potentially transferred to the upper trophic levels, which can eventually lead to adverse effects on humans due to the consumption of contaminated seafood (Wang 2002; Alves et al. 2014).

Zinc is an important essential heavy metal because it is an integral part of a wide variety of metalloenzymes. It is also a cofactor for regulating the activity of specific zinc-dependent enzymes, including carbonic anhydrase, which is involved in crustacean ecdysis (Henry and Kormanik 1985). Besides its biological properties, zinc can also act as a stress factor for aquatic animals, as regards with most of what is known about its toxic effects and according to acute studies with freshwater fish and *Daphnia*. Zinc toxicity has been linked to the inhibition of Ca^{++} ion regulation (Hogstrand et al. 1996) as well as to the disturbance of acid–base regulation (Spry and Wood 1984).

Within this theoretical framework, the main goal of the present study was to analyze relationships between different estuarine compartments concerning zinc occurrence, concentrations and transference processes. Keeping in mind that a long lasting environmental monitoring program is being developed in Bahía Blanca estuary since several decades ago, and zinc levels in water, sediments, SPM and organisms are regularly studied (Marcovecchio et al. 2013), this system has been considered as a study case. Taking this fact in account, the main aim of this study was to review the existing information on zinc levels, distribution and accumulation in the different environmental compartments within Bahía Blanca estuary (i.e., sediments, SPM, estuarine water, organisms), as well as to assess the role of different processes (i.e., physical–chemical, oceanographic or biological ones) which can govern the observed trends.

Materials and methods

Description of the study area

Bahía Blanca estuary (Fig. 1) is formed by a series of NW–SE tidal channels separated by extensive intertidal flats, low marshes and islands (Piccolo et al. 2008). The principal channel, which includes our study area, covers a total length of 80 km and a width varying from about 3–4 km at the mouth (22 m depth) to 200 m at the head (3 m depth). The principal energy input to Bahía Blanca estuary comes from a standing semidiurnal tidal wave (Piccolo et al. 2008). Strong NW and N winds dominate the typical weather pattern of the region, with a mean velocity of 24 km h⁻¹ and gusts surpassing 100 km h⁻¹ (C.de Steffens and C.de Ferreras 2004). Freshwater input is low on the northern coast from the Sauce Chico River (drainage area close to 1600 km²) in the inner area and from the Napostá Grande Stream (drainage area of 1237 km²) in the mid-zone of the estuary (Fig. 1), both with an annual mean runoff of 1.72 m³ s⁻¹ (with a maximum flow rate of

18.32 m³ s⁻¹) and 1.05 m³ s⁻¹ (with a peak of 167.1 m³ s⁻¹), respectively (Melo and Limbozzi 2008). The water column is vertically homogeneous all throughout the estuary, although it may be partially mixed in the inner zone depending on freshwater runoff conditions (Marcovecchio et al. 2009). In addition, the inner zone is highly turbid as a result of the combined effect of winds and tide currents, containing large amounts of suspended matter (Piccolo et al. 2008).

Dissolved oxygen values are usually close to the saturation level ones as a result of the high dynamics of the system, which stimulates both oxidation and re-mineralization of organic matter within the estuary (Freije et al. 2008). It is common to register supersaturating oxygen levels of up to 130 % during the typical winter/early spring phytoplankton bloom within the estuary (Popovich and Marcovecchio 2008). Nutrient concentrations are also high except during the bloom period when they undergo a notorious decrease as a result of phytoplankton consumption (Freije et al. 2008; Popovich et al. 2008; Spetter et al. 2015).

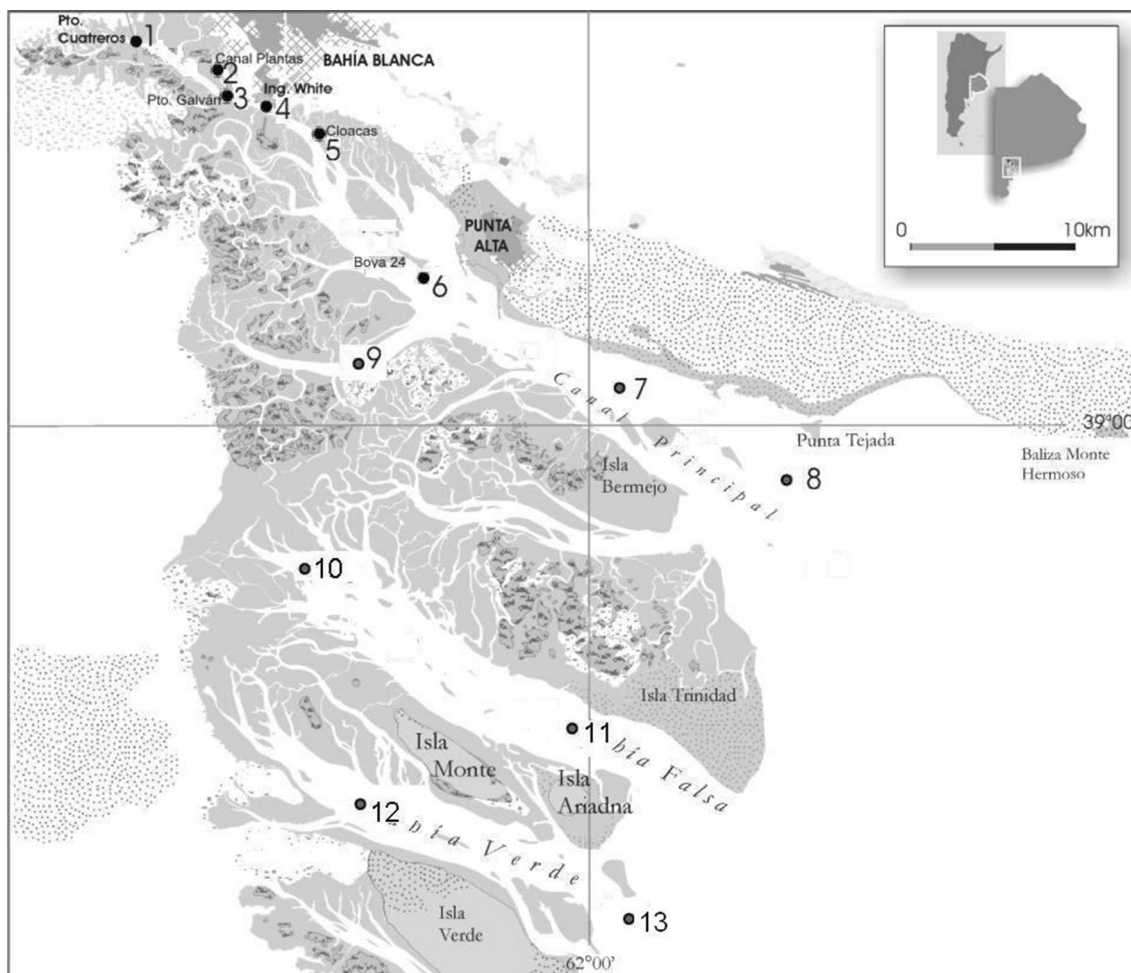


Fig. 1 Location of sampling stations within Bahía Blanca estuary (Argentina)

Various ports, towns (with over 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. Significant volumes of raw sewage are discharged daily into the study area (Marcovecchio et al. 2008). This estuary is extensively used by fishing boats, oil tankers and cargo vessels and requires regular dredging. In this sense, this coastal marine system receives contaminant inputs from municipal wastewaters, direct industrial discharges, harbor-related operations and runoff waters that carry materials from land development areas as well as aerial fallout from atmospheric pollutants.

The corresponding sampling stations have been established along the estuary (Fig. 1), and they include different areas influenced by the above-mentioned potential sources of pollution.

Sampling and analytical methods

Samples of surface sediments, SPM, estuarine water and estuarine organisms (i.e., zooplankton, fish) and halophyte vegetation from the study area were analyzed to determine their zinc contents. Surface sediment samples (the upper 10 cm) were obtained at the indicated sampling stations (Fig. 1) using a stainless steel sediment sampler; they were kept in plastic bags and stored in portable ice chests on board until treated in the laboratory. First, sediment samples were oven-dried at low temperature (50 ± 5 °C) up to constant weight. Afterward, two subsamples were separated: (1) one of them was sieved through a stainless steel mesh in order to separate sediment with grain size <63 μm , representing the silt–clay fraction of the sediment; this fraction was stored in acid-cleaned glass bottles in desiccators, prior to analytical treatment. (2) The other subsample was homogenized in a porcelain mortar and also stored in acid-cleaned glass bottles in desiccators, prior to analytical treatment; moreover, sediment samples for both organic matter determination and geological characterization were removed from this second subsample.

Surface water samples were collected at ~ 1 m depth in 1.5 L polyethylene terephthalate (PET) bottles; they were immediately transported to the laboratory and filtered through acid-treated Millipore HA filters (0.45 μm mesh) to determine dissolved metals and to obtain the corresponding SPM samples. In all cases, water samples have been obtained between tide extremes (from high tide to low tide). The filtered samples were acidified at pH 2, using 1.5 mL of HCl analytical quality, in order to be stored in darkness at 4 °C up to the analytical treatment phase at the laboratory. On the other hand, filters with the SPM samples

were oven-dried at low temperature (50 ± 5 °C) up to constant weight until analytical treatment. Prior to their use and following internationally recommended protocols (APHA-AWWA-WPCF 1999), every piece of material employed for the sampling, filtration and sample storage process was carefully cleaned with diluted nitric acid (0.7 %, HNO_3 suprapur, Merck). In all cases, acids free of metals were used for analytical procedures.

Zn concentrations in sediments (in both total sediment and <63 - μm grain-size fraction) as well as in SPM samples were determined according to the method described by Marcovecchio and Ferrer (2005), including acid mineralization under controlled temperature measurement through both atomic absorption spectroscopy (AAS) with air–acetylene flame and induced coupled plasma with optical emission spectrometry (ICP-OES). In addition, geochemical fractionation of the <63 - μm sediment fraction by a sequential extraction method was applied, according to the description of Marcovecchio and Ferrer (2005), based on the methods reported by Megalatti et al. (1983) and modified by Lacerda et al. (1988). This methodology has provided information on the metal content of five geochemical fractions: (1) **F1** exchangeable-adsorbed metals; (2) **F2** oxidisable metal complexes; (3) **F3** metals in carbonates; (4) **F4** metals in reducible compounds; and, (5) **F5** residual metals. It must be considered that **F5** is the fraction which characterizes the crystalline matrix of the sediment; the other fractions represent chemical forms which allow metals to circulate within the aquatic environment, and the physical–chemical condition of the system governs the predominance of each other.

Zooplankton samples (1 m deep from the water surface) were taken aboard the “R/V Buen día Señor” at each sampling station. These samples for the metal determination were prefiltered using 1.5-mm and 500- μm mesh-size nets in order to analyze only the mesozooplankton. Then, the samples were vacuum-filtered following the same procedure as the SPM. In both cases, the filters with the retained material (SPM or zooplankton) were dried at 50 ± 5 °C to constant weight, weighed in analytical balance and stored in a desiccator until their analytical treatment. Subsequently, the filters were subjected to acid digestion, following the methodology of Marcovecchio and Ferrer (2005).

Fish samples (narrownose smooth-hound shark *Mustelus schmitti*) were obtained with commercial nets. In all cases, and after morphometric measurements, samples of dorsal muscle and liver were removed, stored in plastic bags and frozen at -20 °C until analytical treatment.

Samples of burrowing crab (*Neohelice granulata*) and the halophytes woody glasswort (*Sarcocornia perennis*) and smooth cordgrass (*Spartina alterniflora*) were collected by hand at the estuary’s tidal plains. Soft tissues

were removed in the laboratory and were dried and stored as previously described for zooplankton. Halophyte tissues were cleaned, dried (50 ± 5 °C to constant weight), ground in porcelain mortar and stored in desiccators until analytical treatment.

In all cases, biological samples were subjected to acid digestion, following the methodology of Marcovecchio and Ferrer (2005) in order to determine their Zn contents.

Moreover, dissolved Zn concentrations were determined following Botté et al. (2007) guidelines, including chelation with ammonium pyrrolidine-dithiocarbamate (APDC), extraction with methyl isobutyl ketone (MIBK) and measurement through AAS with air-acetylene flame.

In all cases, a PerkinElmer 2380 AAS and a PerkinElmer Optima 2100-DV ICP-OES have been used for the corresponding measurements.

Analytical grade reagents were utilized not only for sediment mineralization but also for blanks and calibration curve standards built up. In all cases, bi-distilled water was used to prepare the corresponding solutions.

The limit of detection of the applied analytical techniques was: $0.05 \mu\text{g g}^{-1}$ for Zn in solid samples; $0.01 \mu\text{g L}^{-1}$ for dissolved Zn (Botté et al. 2007, 2010).

Analytical quality was checked against international certified reference materials [pond sediment flour (R.M.N°82) and estuarine water (R.M.N°39)] provided by The National Institute for Environmental Studies (NIES) from Tsukuba University (Japan) and seawater (RM 425/A) from the United Nations Environment Programme (UNEP). For all the analyzed metals, recovery percentages concurred with official NIES and UNEP calibration exercises (Table 1).

Statistical comparisons were developed using analysis of variance (ANOVA), mean values assessment (Turkey’s test), correlation analysis and single linear regression analysis (Sokal and Rohlf 1979). Moreover, factorial analysis was performed to reduce the number of variables recorded and to detect structure in the relationships between physicochemical parameters and account for the variation present in the data set matrix. Factors were calculated from the correlation matrix and treated by varimax rotation in order to maximize the load of each variable on one factor. Factors were extracted by principal components. All statistical tests were performed using the

Statistica software package (version 7.1). Significance was set at $P < 0.05$.

Results

Zinc concentrations—both dissolved in estuarine water and particulated in surface sediments—were determined in the Bahía Blanca estuary (Table 2). The spatial distribution of dissolved Zn values along the estuary (Fig. 2) allows to identify two different data groups that present significant differences ($P < 0.01$) among them. The first one, including dissolved metal values recorded at the sampling stations located in the first 20 km from the estuary’s head, reached up to $71 \mu\text{g Zn L}^{-1}$ (Figs. 1, 2, respectively). The second one including values recorded at the sampling stations between 25 km and the estuary’s mouth denoted dissolved Zn up to $11 \mu\text{g Zn L}^{-1}$ (Figs. 1, 2). This spatial division is limited to “inner” and “outer” samples, considering that Bahía Blanca estuary is not associated with a significant fluvial system.

Simultaneously, the distribution of zinc concentrations within surface sediments from Bahía Blanca estuary was also considered (Figs. 1, 2). The resulting distribution trend fully agreed with the one identified for dissolved metals levels, even though the corresponding concentrations were significantly different ($P < 0.01$) (Fig. 2). As previously stated, two groups of metals were identified in the sediment data set: (1) those corresponding to the first 20 km of the inner estuary showed high values, reaching up to $90 \mu\text{g Zn g}^{-1}$ d.w. (r.v.: 36 ± 5 – $90 \pm 5 \mu\text{g Zn g}^{-1}$ d.w.). (2) Those recorded from ~25 km from the estuary’s head to its mouth proved to be significantly lower than the ones of the first group ($P < 0.01$; Fig. 2), with values varying between 16 ± 3 and $45 \pm 5 \mu\text{g Zn g}^{-1}$ d.w. Such identified spatial distribution, which fully agrees with the previously described for the dissolved phase, has also linked metal concentrations within sediments with the recognized potential sources, describing the highest values close to the industrial discharge area, the main ports within the estuary, as well as the area of discharge of Bahía Blanca city sewage system (Figs. 1, 2).

Furthermore, significantly high Zn concentrations were determined within the corresponding finest grain-size sediments ($<63 \mu\text{m}$), values varying from 19 ± 6 to $384 \pm 60 \mu\text{g Zn g}^{-1}$ d.w. (Table 2). Also, the observed spatial distribution has fully agreed with the previously mentioned one, highest Zn values at the inner zone of the estuary (~75P90 % is silt-clay sediment) and decreasing toward its mouth (mainly sandy sediment).

In addition, and also studying the same grain-size fraction of the sediment ($<63 \mu\text{m}$), the geochemical fractioning of zinc was also considered within the inner stations of the

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

Analyzed metals	Percentage of recovery		
	Pond sediment	Estuarine water	Seawater
Zinc	95.3–99.1	91.6–96.3	93.2–97.5

Table 2 Zinc concentrations in surface sediment (total and <63- μm grain-size fraction) and water from Bahía Blanca estuary

Sampling stations	Zinc concentrations			
	Total sediment ($\mu\text{g g}^{-1}$, d.w.)	< 63- μm grain size		Dissolved ($\mu\text{g L}^{-1}$)
		% <63 μm	[Zn] ($\mu\text{g g}^{-1}$, d.w.)	
Station #1	62.96 \pm 5.67	59.82	274.14 \pm 73.33	23.72 \pm 5.31
Station #2	72.34 \pm 5.82	60.15	300.64 \pm 51.23	41.04 \pm 5.32
Station #3	90.21 \pm 4.86	61.34	372.78 \pm 78.32	71.44 \pm 8.16
Station #4	78.06 \pm 5.27	57.66	251.11 \pm 50.24	45.15 \pm 5.53
Station #5	71.02 \pm 5.43	52.03	384.24 \pm 60.18	31.14 \pm 9.16
Station #6	35.73 \pm 4.92	40.14	91.16 \pm 23.38	25.15 \pm 4.35
Station #7	23.24 \pm 5.06	23.12	49.46 \pm 11.34	10.12 \pm 4.48
Station #8	21.66 \pm 6.14	16.14	39.32 \pm 10.36	10.66 \pm 3.82
Station #9	44.46 \pm 5.06	38.35	68.54 \pm 18.76	8.83 \pm 3.30
Station #10	23.63 \pm 4.68	21.26	41.93 \pm 20.26	9.14 \pm 3.39
Station #11	29.93 \pm 4.76	19.15	30.27 \pm 9.41	11.63 \pm 4.42
Station #12	16.36 \pm 4.38	23.64	27.29 \pm 7.72	9.65 \pm 3.71
Station #13	15.66 \pm 2.86	15.52	19.12 \pm 6.60	6.64 \pm 2.54

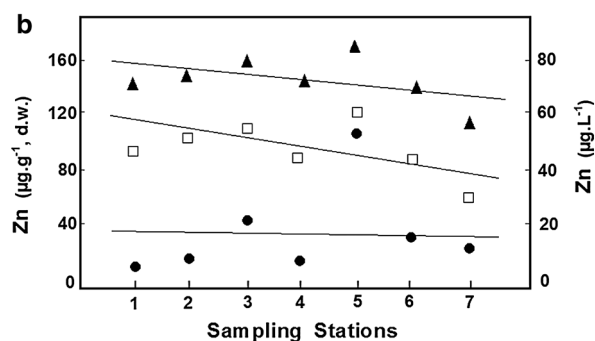
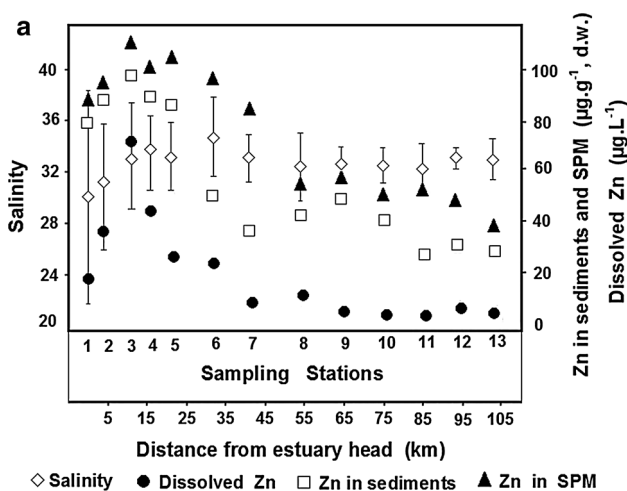


Fig. 2 Zinc distribution in water, surface sediment and suspended particulate matter from Bahía Blanca estuary

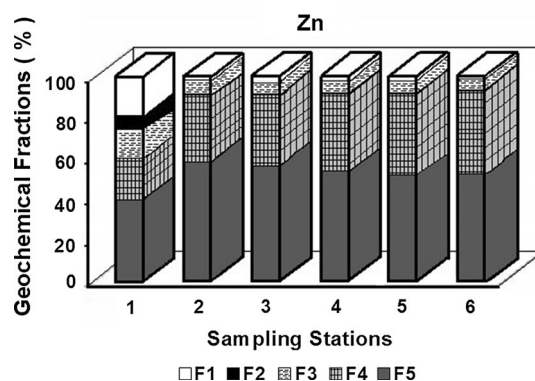


Fig. 3 Geochemical partitioning of zinc in the <63- μm grain-size fraction of sediment within Bahía Blanca estuary

estuary; it allowed to identify the main geochemical association of this metal in the sediments (Fig. 3), also including the magnitude of its potentially bioavailable fraction (PBF) (Marcovecchio et al. 1998). Zinc geochemical partitioning followed the trend: 40 \pm 0.5–67 \pm 3 % in the F5 (residual); 19 \pm 2–31 \pm 1.5 % in the F4 (reducible); 4 \pm 1.7–16 \pm 1.5 % in the F3 (carbonates); 1.5 \pm 0.3–7 \pm 0.5 % in the F2 (oxidisable), while 1 \pm 0.2–19 \pm 0.5 % was in the F1 (exchangeable) (Fig. 3). The analysis of spatial distribution of Zn geochemical partitioning has shown that for Zn-F1, Zn-F2 and Zn-F3, Station #1 (at the inner area of the estuary) showed quite high percentages (19 \pm 0.5, 6.5 \pm 0.5 and

16 ± 1.5 %, respectively), other values were significantly lower (no more than 3 ± 0.2, 4.5 ± 0.6, and 6 ± 0.4 %, respectively) in all the outer areas. In the case of Zn-F4, the lowest value (19 ± 1.7 %) was recorded at Station #1 (inner area), while the highest value (31 ± 1.5 %) was measured at Station #5 (close to the main sewage outfall discharge). Furthermore, Zn-F5 has shown the minimum value (40 ± 0.5 %) at Station #1 and the corresponding maximum (67 ± 3 %) was recorded at Station #2 (close to industrial effluents discharge). In the case of zinc, the PBF varied between 3 and 25 %, which indicated the potential level of this element to be assimilated by organisms.

The factorial analysis of the physicochemical parameters revealed that 77.15 % of the total variance could be explained by three factors (Table 3). The first factor accounts for 34.62 % of the variance including Zn in sediments (both total sediment and <63 µm fraction) and pH, and consequently associated with deposition processes. This factor explains more than a quarter of the total variation, meaning that it is a dominant factor. Factor 2 is correlated with dissolved Zn and that in the SPM, as well as pH, thus explaining 27.68 % of the variance and representing transference processes among both compartments. The third factor (14.85 % of total variance) showed a positive correlation with Zn in SPM and salinity, which could be related to metals transport within the estuarine mixing zone (Table 3).

The contents of zinc in SPM, microplankton (20–200 µm) and mesozooplankton (200 µm–2 mm) of the inner area of the estuary have also been studied, and concentration ranges vary between 30–631, 56–612 and 147–1269 µg Zn g⁻¹ d.w., respectively (Fig. 4). This accounts for relevant information since it is pointing out the occurrence of zinc transference from the abiotic

compartments to the biological ones within the ecosystem. In addition, organisms caught at several points of the studied region have presented higher Zn levels than those from other areas (i.e., microplankton showed the highest concentrations of Zn at the station of the sewage discharges).

Moreover, analysis of Zn in tissues of burrowing crab *Neohelice granulata* presented values between 12 and 350 µg Zn g⁻¹ d.w. in gills and between 56 and 259 µg Zn g⁻¹ d.w. in hepatopancreas (Fig. 5); Zn levels in muscle of the narrownose smooth-hound shark *Mustelus schmitti* have ranged between non-detectable and 5 µg Zn g⁻¹ d.w., while in liver varied from 5 to 23 µg Zn.g⁻¹ d.w. (Fig. 5). Finally, when the tissues of the main halophyte vegetation (i.e., woody glasswort *Sarcocornia perennis*, smooth cordgrass *Spartina alterniflora*) were analyzed, corresponding range levels of 39–127 µg Zn.g⁻¹ d.w. and 16–227 µg Zn.g⁻¹ d.w., respectively, were obtained (Fig. 5).

Discussion

Zn is a very conspicuous element, which cycles on all ecosystems of the world, shares both types of sources natural and anthropic ones and circulates through many processes, could be trapped, transformed or reintroduced via numerous facies or mechanisms (Fig. 6). In the particular case of estuaries, several of the steps are exclusive within other environments, while others are also observed in most ecosystems.

Along the whole study period, dissolved zinc values as recorded within the estuary water were mostly clear to detect, and the corresponding values proved to be quite higher than the analytical method detection limit (Table 2). This fact indicates that a permanent input of this dissolved metal occurs within the estuary. Bearing in mind that this chemical form of metals can remain only for a short time after being transferred into SPM, sediments or biota (Beck et al. 2012; Oursel et al. 2013), it can then be assumed that a continuous (or quasi-continuous) source of zinc exists within this estuarine environment.

These spatial distributions identified for the dissolved Zn fraction within Bahía Blanca estuary were strongly linked with several of the potential sources closely located to this system. Thus, the area that included the highest concentrations of this dissolved metal (i.e., Sampling Stations #2, #3, #4 and #5) fully agreed with the location of the former solid-waste dumping site of the city (S.S. #2), the industrial discharges (S.S. #3), the main ports (S.S. #4) or the discharge of Bahía Blanca city sewage system (S.S. #5) (Figs. 1, 2). It should be pointed out that dissolved Zn values from each of the 6 inner sampling stations (i.e.,

Table 3 Rotated varimax factors loaded for environmental variables, eigenvalues and explained variance for each factor extracted

Variables	Factor 1	Factor 2	Factor 2
Dissolved Zn	0.111524	0.638046	0.009253
Zn in total sediment	0.938306	0.010448	-0.09027
Zn in <63-µm grain size	0.921004	0.087453	0.02534
Zn in SPM	0.11641	0.71306	0.48482
pH	0.51963	0.49303	0.04771
Salinity	-0.091206	0.19305	0.92027
Dissolved oxygen (%sat)	-0.057338	0.02004	0.09924
Eigenvalue	4.520253	3.613722	1.938923
%Total variance	34.622854	27.679285	14.851171
Cumulative variance	34.622854	62.203129	77.153309

Bold values represent highly significant

Extraction: principal components

Marked loadings are >0.45

Fig. 4 Zinc distribution in SPM, microplankton and mesozooplankton from the inner area of Bahía Blanca estuary

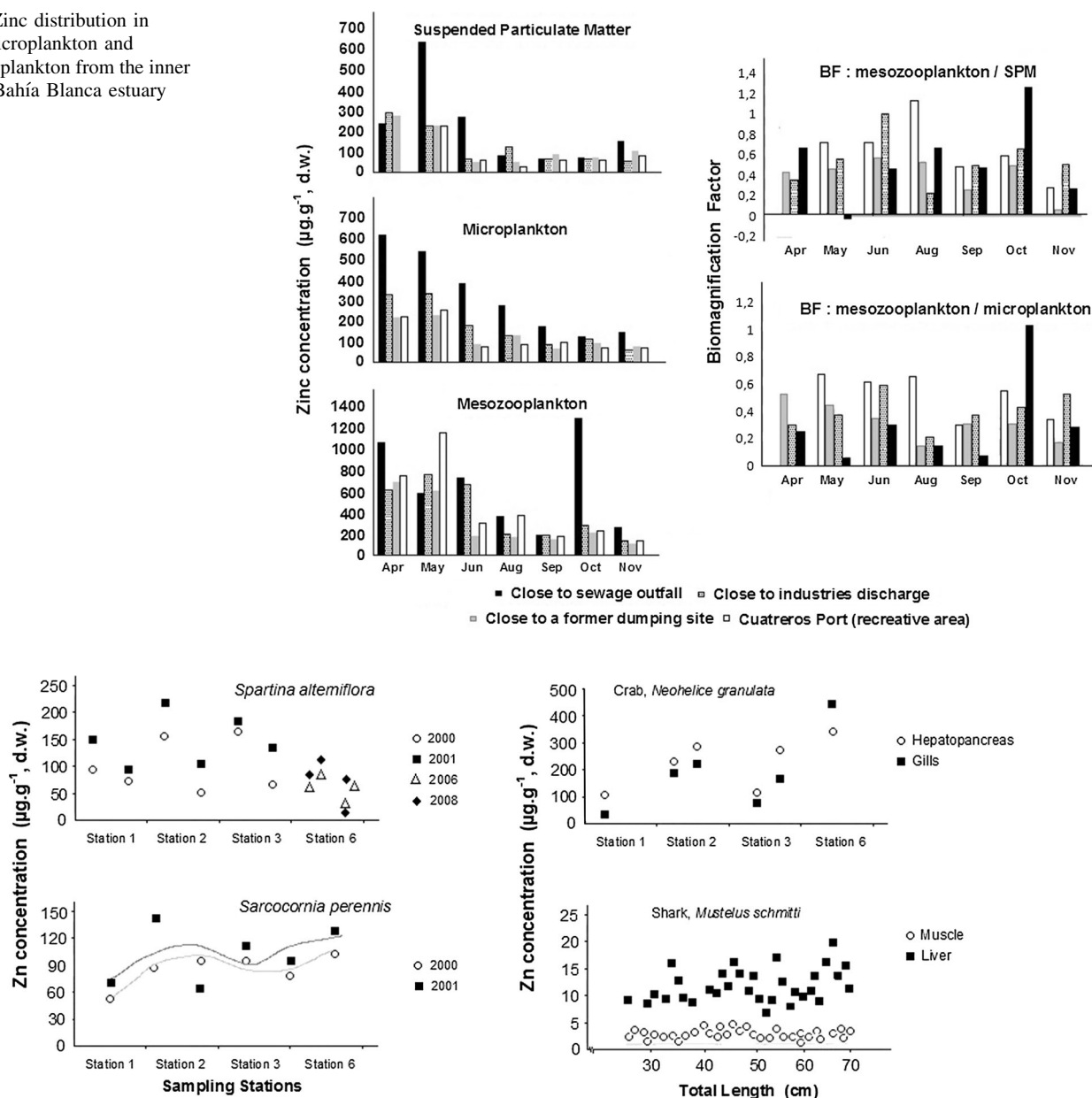


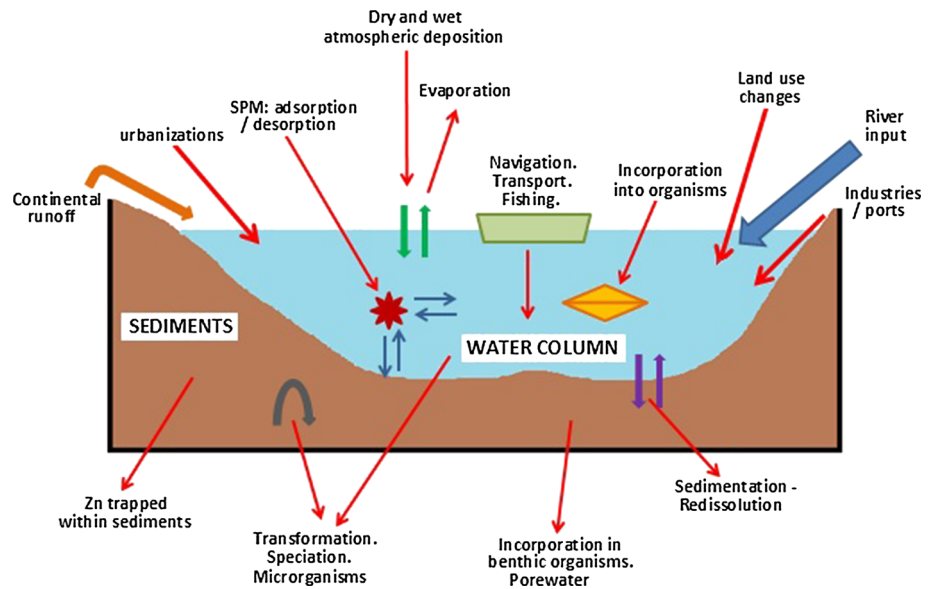
Fig. 5 Zinc distribution in different organisms (*Spartina alterniflora*, *Sarcocornia perennis*, *Neohelice granulata* and *Mustelus schmitti*) from Bahía Blanca estuary

S.S.#1 to S.S.#6, Fig. 1) were significantly higher ($P < 0.01$) than values of the outer ones, which varied between $\sim 24 \pm 5$ and $71 \pm 8 \mu\text{g Zn L}^{-1}$, against 7 ± 2 and $12 \pm 4 \mu\text{g Zn L}^{-1}$, respectively (Table 2). This kind of spatial distribution of dissolved metals closely restricted to the main sources or input points within the studied environment was in accordance with other former descriptions for different estuaries or coastal systems, like the Seine river estuary, France (Dauvin 2008); the Tagus estuary, Portugal (Duarte et al. 2014); or, the Sidney estuary, Australia (Beck and Birch 2014), among others. Several previous studies have pointed out that metals may

be complexed with organic ligands in surface waters, and theoretical models for chemical speciation indicated that in aqueous solutions would also be complexed first with Cl^- , which is a dominant ion among salinity contributors (Wang and Liu 2003).

Such identified spatial distribution, which is in fully accordance with that previously described for the dissolved phase, has also linked metal concentrations within sediments with the recognized potential sources, describing the highest values close to the industrial discharge area, the main ports within the estuary and the area of discharge of Bahía Blanca city sewage system (Figs. 1, 2). This

Fig. 6 Zinc cycle in an estuarine environment: the case of Bahía Blanca estuary



coincidence between both distribution trends allowed assuming the occurrence of the same metals' sources for both phases within the system, as well as the regulation mechanisms that may control metals' transference between water and solid compartments (sediment and SPM). However, though close agreement between both distribution trends can be observed in Fig. 2 (Zn dissolved and in sediments), differences between them can be also recognized. So, in several areas of this graphic, significant increases of metal contents in sediments coincided with decreases in corresponding dissolved levels and vice versa; such changes were also connected with changes in salinity values: increased in the first case and decreased in the other one (Fig. 2). In previous reports on this environment, it has been demonstrated that metal levels did not vary during the tidal cycle, neither dissolved (Botté et al. 2007) nor particulate ones (Marcovecchio et al. 2008).

The variation of salinity was highlighted as one of the regulator mechanisms of transference between both phases (Chapman and Wang 2001). It is one controlling factor for the distribution of contaminants in estuaries through (1) desorption, due to increasing complexation with seawater anions and/or increasing competition for particle adsorption sites with seawater cations, and (2) coagulation, flocculation and precipitation processes (Dauvin 2008). This fact strongly supports the occurrence of the highest Zn concentrations within the inner area of the estuary, not only due to the location of the main identified metals sources but also because the maximum variation of salinity has been recorded there (Fig. 2). Consequently, it would be inferred that dissolved Zn was strongly associated with small particles and colloids, and the salt-induced coagulation of these particles was an important mechanism for the removal of dissolved metal fraction during water mixing

within the estuary (Wang and Liu 2003). Results denoted that although Zn is a soluble element at middle and high salinities and shows desorption behavior, removal singularly occurred in the low-salinity zone and may be induced by flocculation and/or adsorption reactions. It is important to emphasize that the studied metal easily remained in the dissolved phase when the system presented a more oxidative condition, which is in accordance with the comment made by Adamo et al. (2005) for Naples coastal system.

In the present study, the concentration of dissolved oxygen (DO) within estuarine water was also considered, keeping in mind that this is a shallow estuary, and the water movement (through tide, waves and freshwater discharges) usually removes the surface sediment from the extensive tidal flats and bottom of channels (resuspension), generating a high amount of suspended particles (Perillo et al. 2001, 2008). In this sense, significant changes in DO concentration determine changes in the redox condition within surface sediments. Likewise, the resuspension of sediments and/or deflocculating of particles may also affect the behavior of dissolved metals and even disturb the coagulation process, especially at shallow and tidal-dominated estuaries, as well as in those ones that have high concentration of suspended matter, both conditions which characterize Bahía Blanca estuary (Perillo et al. 2001). In addition, the present results show that dissolved zinc clearly displayed a non-conservative behavior, which is common in many other estuaries (i.e., Chapman and Wang 2001).

Furthermore, zinc proved to be also strongly accumulated within the SPM (Fernández Severini et al. 2011), where recorded concentrations were much higher than both dissolved and sediment ones (Fig. 2). As an example, SPM Zn concentrations have reached up to $\sim 180 \mu\text{g g}^{-1}$, which were almost twice higher than maximum values measured

in sediments of this system (Table 2). This fact fully coincided with previous reports by other authors, like Beck et al. (2014) on the Jade Bay in NW Germany; or Deycard et al. (2014) in the Gironde Estuary, France; as well as Botté (2005) who reported maximum values between 217 and 300 $\mu\text{g g}^{-1}$ within this estuary. SPM includes the finest grain sediment, usually clay and slime; consequently, these kind of particles—with a large surface: volume relationship—present great ability to trap substances or elements through sorption processes (Pasternack and Brown 2006; He et al. 2012). In agreement with other authors, our results confirm the widespread concept that the SPM acts as the main carrier of metals in estuarine environments (i.e., Shynu et al. 2012; Fu et al. 2013), representing the main transference step between water and sediments or organisms (Chapman and Wang 2001; Alquezar et al. 2007). Metals bonded to suspended particles can either remain there or be removed according to physical–chemical conditions at the corresponding environment (Jiann and Ho 2014).

During this study, a strong relationship between Zn adsorbed to SPM and the pH was observed, thus describing a significant metal removal at a decreasing pH and the opposite when pH increased (Fig. 7), facts that agreed with those reported by Duinker and Nolting (1978), as well as with studies by Hatje et al. (2001) in Port Jackson (Australia) and Mietta et al. (2009) in the lower Western Scheld (Belgium). In this case, the recorded variations of pH can be related to natural biological processes, with significant decreases during the main annual phytoplankton bloom (later autumn–early winter) and increases during summer (Popovich et al. 2008). Even though other studies (i.e., Shi et al. 1998; Lu and Allen 2001) have shown a decrease in metal adsorption to SPM with increasing SPM concentration in the water column, commonly attributed to the “particle concentration effect” (Benoit and Rozan 1999; Fischer et al. 2012), this kind of process was not observed during the present study.

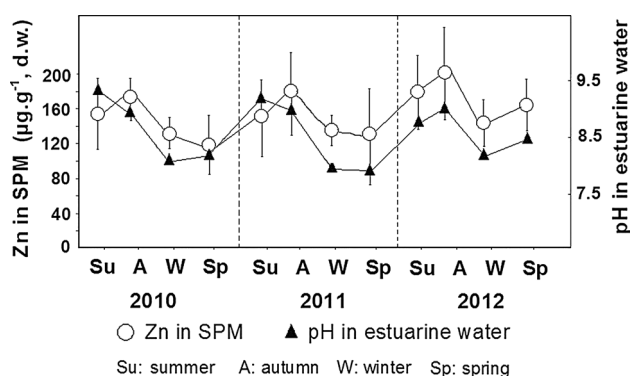


Fig. 7 Zn in SPM versus water pH along three annual cycles within Bahía Blanca estuary

The significant association between trace metals and the finest grain-size sediment as observed within Bahía Blanca estuarine system has opportunely been reported by different authors (i.e., Bartoli et al. 2012; Muñoz-Barbosa and Huerta-Diaz 2013), together with the corresponding dilution effect that can be defined by relating metal levels in total sediments and that in the $<63\ \mu\text{m}$ was explained considering the percentage of finest grain-size particles (63–92.6 %) within Bahía Blanca estuary sediments (Gelós et al. 2004). Nevertheless, Fig. 8 shows particular biases between both distributions (Zn in total sediment and Zn in $<63\text{-}\mu\text{m}$ grain size), which can be attributed either to spatial changes in the percentage of fine grain-size fraction (with the consequent modification of the dilution effect) or changes in the physical–chemical conditions (i.e., pH, redox condition); thus, it modifies the corresponding adsorption–desorption processes, leading to alternative increases or decreases in metal sediment contents or transferences to SPM or even to the dissolved phase (Chapman and Wang 2001; Dauvin 2008).

Analysis of the spatial distribution of the Zn geochemical fractions within the finest grain-size sediments simultaneously denoted several differences as well several similarities between levels at all sampling stations ($P < 0.01$) (Fig. 3). On the one hand, Zn geochemical fractions F1, F3, F4 and F5 have presented recordable values in all sampling stations along the whole study period, even though quite different levels have been measured for each of them (Fig. 3). On the other hand, the Zn-F2 geochemical fraction has only been recorded within sampling Station #1, while corresponding values were very close to the method analytical detection limit for the other sampling stations (Figs. 1, 3). Moreover, it is important to highlight that zinc potential bioavailable fraction ($\text{PBF} = \text{Zn-F1} + \text{Zn-F2}$, according to Marcovecchio et al.

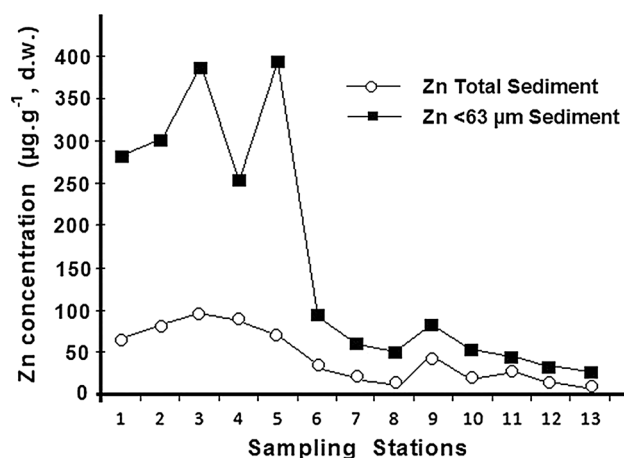


Fig. 8 Zinc distribution in total sediment and in $<63\text{-}\mu\text{m}$ grain-size fraction of sediment within Bahía Blanca estuary

1998) has varied between ~ 2.5 up to ~ 25 % along the study period, which indicates low to medium probabilities that this element can be assimilated by organisms within the estuary. This is a reasonable result, considering that zinc is an essential trace element with important biological functions, depending on the structural and/or catalytic role played by zinc ions in a large variety of enzymes. Zinc plays a critical role in cellular integrity, protein synthesis, nucleic acid metabolism, contributing to cell growth, proliferation, differentiation and death (Faa et al. 2008), so it is not unusual that organisms incorporate this element from their environment. An interesting point to be considered is the extent to which organisms can incorporate Zn without the occurrence of toxicity effects; however, other kind of studies would be developed to properly answer that question. Nevertheless, this metal has demonstrated to be potentially toxic even at very low concentrations (i.e., Song et al. 2010; Nordberg et al. 2014), and consequently the present results deserve to be carefully considered within this estuary. The occurrence of those extremely mobile fractions (i.e., F1 and F2) clearly indicated Zn enrichment on the studied sediments, as it was opportunely reported by other authors (i.e., Resongles et al. 2014; Hamdoun et al. 2015).

Unlike these facts, the lowest percentage of Zn-F3 (3.7 ± 1.7 %) was recorded at Station #6 and the corresponding highest one (15.8 ± 1.5 %) at Station #1; the lowest Zn-F4 (18.8 ± 1.7 %) has been recorded at Station #1 and the highest one (31.1 ± 1.5 %) at the Station #5; while the lowest Zn-F5 (40.0 ± 0.5 %) was found at Station #1 and the highest one (67 ± 3 %) at Station #2 (Figs. 1, 3). These percentages deserve to be carefully considered bearing in mind that they include immobile fractions (i.e., F5) or with much reduced mobility (i.e., F3 or F4) and consequently represent metal mass with very low probability of being incorporated by biota.

Along the study period and in agreement with the described abiotic scenario, zinc was also recorded within organisms from different trophic levels (i.e., halophyte vegetation, crabs, zooplankton, fish) and corresponding values were always detectable, even though quite different concentrations have been determined for each of these groups (Figs. 4, 5).

The study of the bioavailable fraction of trace metals in marine systems is extremely important to determine the quality of this environment because their toxicity depends on the concentration of exposure to this fraction. It can only be detected as from the content of metals incorporated by organisms, which is absolutely relevant to biomonitoring studies (Kahle and Zauke 2003; Zauke and Schmalenbach 2006). To access this fraction, it is necessary determining the amount of metals in organisms, because it depends on the metal species incorporated, the

detoxification mechanisms and metabolic requirements rather than the concentration in the soluble phase. According to Connell and Sanders (1999), microplankton accumulates dissolved trace metals to levels greatly in excess as that of *background* concentrations, resulting in a major potential source of particulate metal to higher trophic levels. Thus, microplankton of the Bahía Blanca estuary would incorporate or sorb metals through the dissolved phase and then increase the concentrations of metals in the SPM. The enrichment of metals in phytoplankton organisms, as an important part of microplankton in the estuary, depends primarily on metal content in the water, and a slight increase in the concentration of dissolved metals could lead to a significant increase in phytoplankton (Förstner and Wittmann 1983). This is related to the large surface of plankton organisms in relation to their mass unit and their active metabolism, leading to rapid adsorption of various pollutants (Ravera 2001). Additionally, changes in metal concentrations during a phytoplankton bloom may be attributed to biological activity. For example, Luoma et al. (1998) showed that Cd, Ni and Zn were bioavailable because they were depleted from the water during the bloom. Also, Luengen et al. (2007) found that concentrations of several metals (i.e., Mn, Co, Zn, Ni and Pb) increased as the bloom degrades, demonstrating that decay of the bloom also affected metal cycling. Wang et al. (2012) have determined that in microplankton, essential metals like Cu, Fe, Ni, Zn, Mn show greater penetration into the cytoplasm of the algal cells, while non-essentials like Cd, Pb remain adsorbed to the cell surfaces (Michaels and Flegal 1990). The roles of Mn and Zn in controlling phytoplankton productivity are less studied. Both metals are required micronutrients, and it is well known that Zn may induce toxic responses in phytoplankton at high concentrations (Chakraborty et al. 2010; Lafabrie et al. 2012). In the present study, Zn showed the highest concentrations at the station located close to the Bahía Blanca city sewage discharge, located at Canal Vieja, Sampling Station #5 (Fig. 5).

When considering mesozooplankton from the studied estuary, Zn levels were high in the station located at Canal Vieja (SS #5) (Bahía Blanca city sewage outfall) as well as at the innermost station (Puerto Cuatros, SS #1), located quite far from the industrial area (Fig. 2). It is well known that when marine invertebrates, such as copepods, are exposed to pollutants from both dissolved and particulate phases, metals dissolved in water may be accumulated by direct adsorption to body surfaces and particulate metals can be accumulated by animals following food ingestion and digestion (Wang and Fisher 1999). In this sense, for suspension feeders such as mussels and copepods, uptake from the dissolved phase and food ingestion can be as important as metal accumulation (Wang and Fisher 1999).

According to Rainbow et al. (2012), Zn is highly assimilated by zooplankton and, once incorporated into the fecal pellets, they are rapidly released into the dissolved phase (Cardwell et al. 2013).

In addition, zinc biomagnification, meaning the process in which this metal is transferred from food to an organism resulting in higher concentrations (Gray 2002), was assessed in the present study. Biomagnification factors (BMFs) were calculated from the ratio of the concentration of metals in mesozooplankton and SPM. Positive values indicate some degree of biomagnification of the metal, while negative ones indicate a higher concentration of the metal in the SPM. Zn biomagnified all over the period studied. In addition, another BMF was calculated considering the ratio of metals in the zooplankton and metals in the microplankton (Fig. 4). In accordance with the previous calculated BMF, Zn also biomagnified when considering zooplankton and microplankton. As previously mentioned, the incorporation of metal through the food is considered one of the most important routes for the accumulation of these elements in marine organisms (Wang 2002). Therefore, these results indicate that mesozooplankton from the BBE incorporated a great proportion of Zn from SPM and microplankton but it was not eliminated at all and thus possibly transmitted to higher trophic levels.

Moreover, the analysis of zinc in tissues of both the burrowing crab (*Neohelice granulata*) and the narrow nose smooth-hound shark (*Mustelus schmitti*) from Bahía Blanca estuary has demonstrated that they accumulate this metal not only in different tissues but also at different accumulation kinetic rate (Fig. 5). Several authors have demonstrated the occurrence of a differential distribution of metals (zinc among them) within tissues of crustacean species. Beltrame et al. (2010) identified *Neohelice granulata* hepatopancreas as the most important accumulator organ within Mar Chiquita coastal lagoon, Argentina. The same trend has been reported by Reichmuth et al. (2010) for the blue crab *Callinectes sapidus* from both the Hackensack Meadowlands district and Tuckerton-Little Egg Harbor in New Jersey (USA). On the other hand, De Boeck et al. (2010) acquainted a similar Zn tissue distribution as that of the present study for the spotted dogfish *Scyliorhinus canicula* from the Mediterranean waters, as well as Yilmaz et al. (2010) did with different demersal fish species (i.e., *Triglia lucerna*, *Lophius budegassa*, *Solea lascaris*) from the Iskenderun Bay, Turkey.

The results obtained in the halophyte vegetation have shown that both studied species (woody glasswort *Sarcocornia perennis* and smooth cordgrass *Spartina alterniflora*) have a significant capacity to store zinc within their tissues (Fig. 5). Macrophytes have shown to play important roles in marsh biogeochemistry through their active and passive circulation of elements, which could be extremely

important, considering that wetland sediments are generally recognized as a sink for metals and—in the anoxic zone—may contain very high concentrations of metals in a reduced state (Weis and Weis 2004). Several authors have reported that salt marsh plants can tolerate and accumulate high contents of toxic elements (Zn among them) disregarding the fact that elevated concentrations of this metal in soils can lead to toxicity symptoms in most plants, including nutrient imbalances and inhibition of photosynthesis, thus resulting in impairment of plant growth (Cambrollé et al. 2013). Both studied species within Bahía Blanca estuary looked healthy did not present injuries potentially linked to toxic effects, and their biological productivity proved to be high (González Trilla et al. 2009; Negrin et al. 2011). Salt marsh species greatly influence the inputs and outputs of metals and nutrients in the marsh due to their different ability of uptake these elements (Duarte et al. 2010). It has been reported that plant litter decomposition includes three stages: (1) a rapid leaching process; (2) a slower microbial decomposition; and (3) a refractory phase where the decomposition rate is almost null (Zawislanski et al. 2001). After decomposition metals can remain trapped in the sediments or be released to the water column, according to physical–chemical conditions of the system (i.e., pH, ORP, etc.) (Duarte et al. 2010). The occurrence of one of these alternative ways would determine the magnitude of the metal cycling as well as the potential fraction which could be incorporated by organisms.

Concluding comments

The study of zinc within Bahía Blanca estuary along the last two decades allowed an understanding of its behavior in this environment as well as to suggest several strategies for future surveillance programs. The main facts as observed are:

1. Extreme removal of dissolved Zn occurred at lowest salinity ranges, with concentrations dropping from 29.6 to $\sim 20 \mu\text{g Zn L}^{-1}$ at the most.
2. SPM showed the highest ability to trap zinc at this estuary, as well as to be the main metal carrier within the system. Besides, the corresponding transference processes (i.e., adsorption from dissolved phase or flocculation into sediment) seemed to be strongly related to the corresponding water pH.
3. $<63\text{-}\mu\text{m}$ sediment fraction was identified as the main reservoir of zinc within Bahía Blanca estuary.
4. The partitioning of heavy metals through sequential-extractive techniques was also used in this study in order to acquire information on the heavy metal origin

and form of occurrence and to identify the proportion of metals, which are chemically mobile and bioavailable.

5. Results obtained showed that Zn was clearly enriched within sediments and anthropic activities appeared to be a significant source.
6. Most of the transference processes of zinc have been geochemically regulated, and the main identified regulators were salinity, pH, redox potential (or even dissolved oxygen) and grain size of the sediment particles.
7. Organisms at the BBE have accumulated zinc even at different kinetic rates, and no toxic effects deriving from this metal have been reported up to now.
8. The obtained results highlight the importance of maintaining a surveillance program to assess the evolution of the environmental quality within this valuable estuarine environment.

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