

The role of the smooth cordgrass *Spartina alterniflora* and associated sediments in the heavy metal biogeochemical cycle within Bahía Blanca estuary salt marshes

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Abstract

Background, aim, and scope Bahía Blanca estuary is characterized by the occurrence of large intertidal areas, including both naked tidal flats and salt marshes densely vegetated with *Spartina alterniflora*. The estuary is strongly affected by human activities, including industrial and municipal discharges, harbor maintenance, cargo vessels

and boat navigation, oil storage and processing, etc. Even numerous studies have reported the occurrence and distribution of heavy metals in sediments and biota from this estuary, although the function of the halophyte vegetation on metals distribution was at present not studied. The main objective of the present study was to understand the potential role of the salt marshes as a sink or source of metals to the estuary, considering both the obtained data on metal levels within sediments and plants from the studied areas at naked tidal as well as vegetated flats.

Materials and methods The selected study area, named Villa del Mar, was located in the middle estuary coast. The sampling was carried out under low tide conditions, and the sampling area was divided into two parts: A (close to Villa del Mar) and B (north-westerly of Villa del Mar). In each part, two integrated samples of *S. alterniflora* (the first in the medium-salt marsh and the second in the higher one) were collected. Also sediments associated with the roots of *S. alterniflora* were taken at the same locations, in addition to another sediment sample from the naked zones of the tidal flats (without any vegetation). After corresponding treatment at the laboratory, plant and sediment samples were mineralized according to Marcovecchio and Ferrer, *J Coast Res* 21:826–834, 2005, in order to measure their metal concentrations by atomic absorption spectroscopy (AAS). Analytical quality (AQ) was checked against certified reference materials from NIES, Tsukuba (Japan). **Results** Most of the *Spartina* samples have shown highest Cd and Mn concentrations in the aerated parts of the plants, indicating an allocation process from the roots up to the leaves. Most of the samples have presented non-detectable Pb and Cr values. Cu, Fe, Ni, and Zn have presented highest concentrations in the underground parts of the plant, suggesting an accumulation process in the roots and rhizomes. In the case of sediments, samples from those sites

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located far away from Villa del Mar have presented greater concentrations on the sediments associated with underground parts of *Spartina* than those from the naked tidal flat, for almost all of the metals studied. Unlike this, the samples from the site close to Villa del Mar have shown the higher concentrations in sediments from the naked tidal flat.

Discussion Marsh plants are known to absorb and accumulate metals from contaminated sediment, and this is one reason that allows wetlands to be used for wastewater treatment. It was observed that those sets of samples from the same salt marsh levels (e.g., A.1 and B.1, or A.3 and B.3) have shown similar heavy metal distribution trends, although even their corresponding concentrations could be different. Thus, the concentrations of Cu, Zn, Ni, and Fe in the medium-salt marshes were higher in the underground tissues (roots plus rhizomes), with the exception of Mn, which was seen to be higher in the aboveground parts. The same tendency occurs at high-salt marshes for these heavy metals, with the exception of Ni. This fact was sustained regarding the fact that the levels mentioned (medium-salt marsh and high-salt marshes) must have the same exposition to heavy metal sources, similar physical-chemical conditions regulating metal distribution within the compartments on the salt marshes or, simultaneously, both mentioned processes. Moreover, metals in this macrophyte can remain after the leaves have died and turned into detritus. The metals present in the detritus can be passed on to consumers (Quan et al., *Mar Environ Res* 64:21–37, 2007)). Keeping in mind that Bahía Blanca estuary's salt marshes are inundated twice each day by tidal water for 3–4 h, macrophytes may act as a conduit for the movement of metals from the sediment to the estuarine body and near-coastal system.

Conclusions and recommendations Considering the comments on the previous paragraphs, salt marshes from Bahía Blanca estuary are sources or sinks for metals? It can be sustained that both are the case, even if it is often stated that wetlands serve as sinks for pollutants, reducing contamination of surrounding ecosystems (Weis and Weis, *Environ Int* 30:685–700, 2004)). In the present study case, the sediments (which tend to be anoxic and reduced) act as sinks, while the salt marshes can become a source of metal contaminants. This is very important for this system because the macrophytes have been shown to retain the majority of metals in the underground tissues, and particularly in their associated sediments. This fact agreed well with previous reports, such as that from Leendertse et al., *Environ Pollut* 94:19–29, 1996) who found that about 50% of the absorbed metals were retained in salt marshes and 50% was exported. Thus, keeping in mind the large spreading of *S. alterniflora* salt marshes within Bahía Blanca estuary, it must be carefully considered as a redistributor of metals within the system.

Keywords Environmental quality · Heavy metal distribution · Role of macrophytes · Salt marshes · Sediments · Smooth cordgrass · *Spartina alterniflora*

1 Background, aim, and scope

Heavy metals are ubiquitous materials within the environment, which can originate from both natural as well as anthropogenic sources (Markert and Friese 2003). These pollutants require special attention in coastal areas due to their toxicity and persistence in the environment (Skeaff et al. 2002). This concept is particularly important in those coastal environments, which include large industrial nuclei (such as Bahía Blanca estuary); consequently, a permanent input of pollutants occurs, which can produce a significant damage for the ecosystem (Ferrer et al. 2000). In this way, it will be necessary to identify and quantify both the sources and sinks of heavy metals within the studied environment (Marcovecchio 2000).

As a matter of fact, several investigations about heavy metal content in water, sediments, and organisms from Bahía Blanca estuary were already reported (e.g., Marcovecchio and Ferrer 2005; Ferrer et al. 2006; De Marco et al. 2006).

On the other hand, macrophytes have been shown to play important roles in marsh biogeochemistry through their active and passive circulation of elements. Thus, wetlands are often considered to be sinks for contaminants, and there are many cases in which wetland plants were utilized for the removal of pollutants, including metals (Weis and Weis 2004). In addition, Weis and Weis (2002) have reported that *Spartina alterniflora* can accumulate metals from sediments via the roots, and translocate some portion to aboveground tissues. Therefore, these plants are a conduit for the movement of metals from sediments into the food webs of marshes and near-shore waters. Furthermore, *S. alterniflora*, as well as other macrophytes, can be used to immobilize metals and store them below ground in roots and/or soil (“hytostabilization”) (Weis and Weis 2004).

Root–sediment interactions are extremely complex and the amount of metal that is taken up by plants is dependent on their availability in the sediment, which is governed by a wide range of sediment and plant factors including pH, cation exchange capacity, plant species, and seasonal factors (Cacador et al. 2000). In addition, Almeida et al. (2004) have pointed out that plants can alter the chemical composition of the sediment surrounding its roots (for instance, causing changes in pH and redox potential), and thus creating a different microenvironment, commonly called rhizosphere. Moreover, plant roots are known to exude organic compounds capable of complexing metals (Jones 1998), which can also modify metal availability in the rhizosediment.

The present study deals with the determination of several heavy metals (Cd, Cu, Cr, Fe, Mn, Ni, Pb, Zn) in sediments of wetlands located at the middle zone of the estuary, as well as in the halophyte *S. alterniflora* (smooth cordgrass) from the same areas. A primary objective of this work is the comprehension of this halophyte metal accumulation ability, which would help to understand its role on the corresponding biogeochemical cycle of metals within this environment. The results would allow one to give recommendations on the use of the land within these systems, also considering future possibilities to enlarge human structures (e.g., industrial locations, port facilities, fishery fleet, oil transport, processing and storage, etc). A second specific goal is to compare metal dynamics in sediments with and without vegetation, and the relation between those and underground parts of the plants (roots and rhizomes).

2 Materials and methods

2.1 Study area

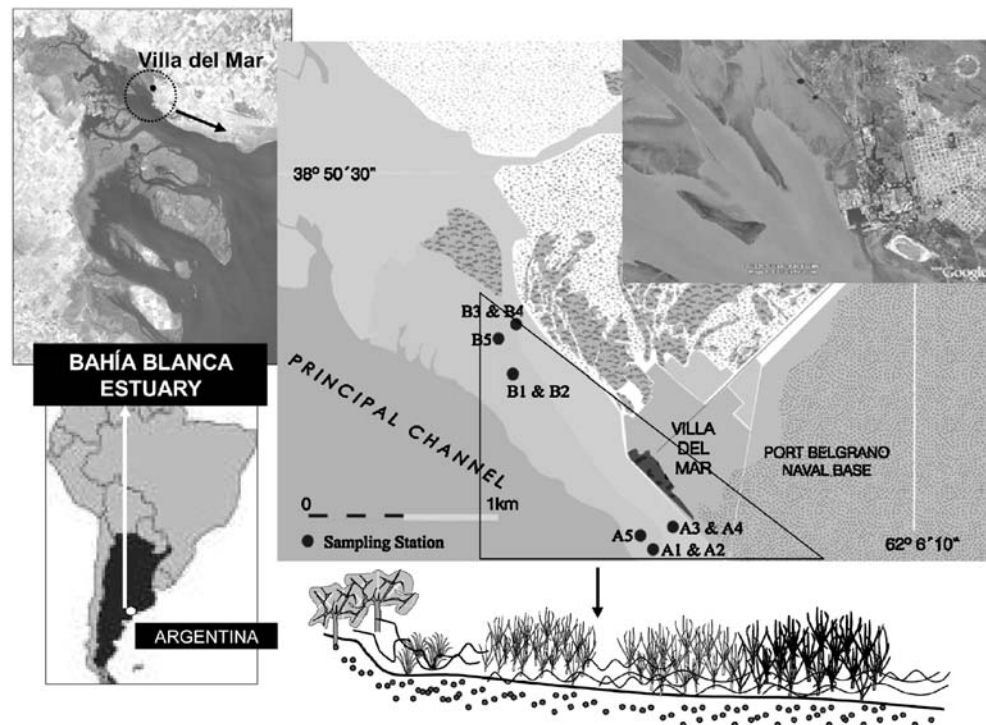
The Bahía Blanca estuary is located between 38°45′–39°40′ S, and 61°45′–62°30′W in the southeast of Buenos Aires Province, Argentina (Fig. 1). It is a mesotidal coastal plain estuary, which is formed by tidal channels, several islands, and tidal flats, and covers an area close to 2,300 km² (Perillo et al. 2001). The estuary's wetlands are dominated by halophyte vegetation, such as *S. alterniflora* or *Sarcocornia perennis*, as well as populations of the digging crab

Chasmagnathus granulatus. The main channel (canal principal) extends about a length of 80 km in a north-west–southeast direction with depths between 3 and 20 m and a width varying from 200 m to 3–4 km (Piccolo and Perillo 1990; Perillo et al. 2001).

Most of the freshwater inflow is contributed by the Sauce Chico River and the Naposta Grande Creek. Both the occurrence of north-westerly winds parallel to the axis of the main channel, as well as the oscillation of the semidiurnal tidal wave (approximately 3 m) lead to the vertical mixing and homogeneous distribution of the main oceanographic parameters (Piccolo and Perillo 1990), except in the inner zone during rainfall periods during which it could eventually function as a partially stratified system.

The estuary is strongly influenced by several towns, industries and ports located at its northern boundary. Processing water from different anthropogenic activities (e.g., oil refineries, petrochemical industries, textile plants, or fish factories) is directly or indirectly discharged into the estuary. Raw sewage and runoff from the extensively used agricultural areas also provides an impact on the water quality (Perillo et al. 2001). One of the most important harbor complexes of Argentina is located at the inner area of Bahía Blanca, and the estuary is therefore intensively used by fishing boats, cargo vessels, and oil tankers. This also leads to the necessity of regular dredging (Marcovecchio and Ferrer 2005). Due to these mentioned facts, the Bahía Blanca estuary appears to be an ideal system to investigate the behavior of pollutants, e.g., heavy metals.

Fig. 1 Location of sampling station at Bahía Blanca estuary



2.2 Sampling

In Villa del Mar, a small village located near Punta Alta city (approximately 20 km southeast of the port Ingeniero White, within Bahía Blanca estuary), the present study was developed (see Fig. 1). The sampling was carried out under low tide condition (when the tidal plains were uncovered). The sampling area was divided into two parts: A (close to Villa del Mar) and B (north-westerly of Villa del Mar). In each part, two integrated samples of *Spartina alterniflora* (the first in the medium-salt marsh and the second in the higher one) were collected. These samples were stored in plastic boxes and transported to the laboratory. Sediments associated with the roots of *Spartina alterniflora* were taken at the same locations, in addition to another sediment sample taken from the naked zones of the tidal flats (without any vegetation). All samples were taken by hand, using a spade covered with plastics, and working at ~20 cm depth.

The sampling was carried out as it is representative. The sample taken, for example, has the same chemical composition as the origin system. Furthermore, the probability for the sample to be removed is the same for every point within the system. Plastic gloves were worn during the sampling and the sampler (spade) was wrapped with a cover made of plastic to avoid contamination. After this, the samples were stored in double polyethylene bags, transported to the laboratory and kept in the refrigerator at 4°C until further treatment to avoid volatilization and chemical reactions.

Details of the samples obtained are included in Table 1.

2.3 Sample preparation

All samples were immediately treated in the days after the sampling. In a first step, plant samples were washed with tap water to remove the attached sediment, algae and mussels. After this the plants were divided into aerial and underground parts and cut with stainless steel blades into smaller pieces. Each part was washed several times again with tap water until the washing water was clear. The final wash was carried out three times in distilled water (Botté 2005). Due to the object of this investigation, the washing is very important and has to be very accurately carried out, because the risk of contaminating the plant sample with soil particles is very high (Markert 1995). To obtain a constant reference value, two aliquots were removed from each sample and oven-dried at 50±5°C for 5 days up to a constant weight. The homogenization of the plant samples was carried out in a mill previously cleaned with nitric acid (HNO₃; 0.7%).

A representative portion from the sediment samples was taken, and all organisms and the rest of the plants were carefully removed with tweezers, which were wrapped with

Table 1 Different samples taken at Villa del Mar saltmarsh

Sample No.	Kind of sample	Subsample	Description
A1	<i>Spartina alterniflora</i> in medium salt marsh	A1.1	Aerial parts
		A1.2	Underground parts
A2	Sediment associated with A1.2		
A3	<i>Spartina alterniflora</i> in high salt marsh	A3.1	Aerial parts
		A3.2	Underground parts
A4	Sediment associated with A3.2		
A5	Sediment from tidal flats (without plants)		
B1	<i>Spartina alterniflora</i> in medium salt marsh	B1.1	Aerial parts
		B1.2	Underground parts
B2	Sediment associated with B1.2		
B3	<i>Spartina alterniflora</i> in high salt marsh	B3.1	Aerial parts
		B3.2	Underground parts
B4	Sediment associated with B3.2		
B5	Sediment from tidal flats (without plants)		

Teflon® tape to avoid contamination. The samples were oven-dried at low temperature (50±5°C) up to a constant weight. After 5 days of drying, the samples were treated in a mortar and the remaining biological material was removed.

Samples were stored in double polyethylene bags in an exsiccator until their digestion. The method used for the digestion of plant and sediment samples was described by Marcovecchio and Ferrer (2005), modified from that previously described by Marcovecchio et al. (1988). Subsamples of approximately 0.5 g were separated into two test tubes. Afterward, each sample was spiked with 3 ml of concentrated nitric acid (65%) and 1 ml of concentrated perchloric acid (HClO₄; 70–72%) and taken to a heated glycerine bath at a temperature of 120±5°C. When the digestion was finished, the residue was transferred into centrifugal tubes and completed with diluted nitric acid (0.7%) up to 10 ml.

Metal concentrations of these solutions were measured by Atomic Absorption Spectroscopy (AAS) with air-acetylene flame. In all cases, a Perkin-Elmer AA-2380 spectrophotometer was used to perform the corresponding

Table 2 Percentages of recovery in the analysis of NIES certified reference materials (*Pepperbush*, R.M. No. 1 and *Pond Sediments*, R. M. No. 2) for AQ assessment

Metal analyzed	Percentage of recovery (% range)	
	R.M. No. 1	R.M. No. 2
Cadmium	95.1–99.4	93.7–99.3
Copper	96.5–99.1	92.9–99.6
Chromium	93.3–99.7	95.2–99.1
Iron	94.1–99.3	91.9–99.0
Manganese	92.5–98.8	93.3–98.9
Nickel	95.3–99.2	94.4–99.4
Lead	94.7–98.9	93.6–99.3
Zinc	95.3–99.6	93.8–99.8

analyses. Analytical grade reagents (Merck or Baker) were used to build up the corresponding blanks and calibration curves. Analytical quality (AQ) was checked against certified reference materials (*Pepperbush*, R.M. No. 1 and *Pond Sediments*, R.M. No. 2) (Table 2) provided by The National Institute for Environmental Studies (NIES), from Tsukuba, Japan, with significantly good recovery values (Marcovecchio and Ferrer 2005).

Statistical comparisons were developed using analysis of variance (ANOVA) and mean values assessment (Tukey’s test) (Sokal and Rohlf 1979).

3 Results

3.1 Plant samples

The determined metal concentrations (mean values) in plant samples from Villa del Mar are shown in Table 3.

Most of the *S. alterniflora* samples analyzed presented non-detectable values of lead and chromium.

The concentrations of cadmium have ranged between non-detectable values and 0.83 µg g⁻¹ d.w., and were very scattered among the different samples, while the concentration for manganese involved values between 7.77 and 63.32 µg g⁻¹ d.w. In both cases, the highest values were

measured in the aerated part of *S. alterniflora* in the medium-salt marsh of site B (B.1.1).

This Cd concentration as well as those from the higher-salt marsh of site A (A.3 (A.3.1 and A.3.2)) showed higher values than the other obtained samples. With the exception of the higher-salt marsh of site A (A3), cadmium concentrations were higher in the aerated parts of the plants. Thus, the distribution of Cd would indicate an allocation process from the roots up to the leaves.

In the case of Mn, site A concentrations were up to two times higher than in the equivalent sample of site B. It should also be mentioned that the plants of the higher-salt marsh showed higher concentrations than the plants of the medium-salt marsh.

In the cases of copper, nickel, zinc and iron, it can be noted that the higher concentrations of both metals were found in the underground parts (see Table 3). Indeed it suggested an accumulation process of both metals primarily in the roots and rhizomes. In both subsamples of A.1 (medium-salt marsh), the values of copper were much higher (approximately three to four times) than in the other. Comparing the observed trend from site A, this mentioned difference between medium and high-salt marshes for both parts of the plants was not recorded in site B.

The content of zinc in the aerated parts was nearly similar in site B for all samples. In addition, the highest zinc concentrations measured in the underground parts of *S. alterniflora* have occurred within the high-salt marsh, with the highest value being at site B. In these cases, the concentrations reached from 3.82 µg g⁻¹ d.w. to 37.38 µg g⁻¹ d.w. for copper, and from 18.15 µg g⁻¹ d.w. to 103.47 µg g⁻¹ d.w. for zinc.

Nickel values have varied between 1.92–5.21 µg g⁻¹ d.w. The plant of the higher-salt marsh demonstrated in contrast to all other samples showed lower values in the underground parts. This fact allowed one to maintain that a translocation from roots or aboveground tissues to the leaves has not occurred. The maximum value of nickel has been detected in the A.1.2 sample.

The results of iron have shown the distribution trend of a normal element uptake from the roots to the leaves in all

Table 3 Metal concentrations (mean values ± standard deviation, n=12) in *Spartina alterniflora* samples (in µg.g⁻¹ d.w.)

Sample	Cd	Pb	Cu	Zn	Cr	Ni	Mn	Fe
A 1.1	0.10±0.04	<0.12	13±2	27±3	<0.02	5.0±0.6	57±8	365±20
A 1.2	<0.01	<0.12	37±4	46±5	<0.02	5.0±0.4	14.3±1.6	510±23
A 3.1	0.5±0.1	2.1±0.2	4±0.2	19±2	<0.02	3.0±0.2	63±5	185±11
A 3.2	0.6±0.1	<0.12	8.7±0.3	75±8	<0.02	2.0±0.2	18±2	197±23
B 1.1	0.8±0.1	<0.12	5.0±0.4	19±3	<0.02	3.0±0.3	25±2	199±22
B 1.2	0.10±0.06	2.0±0.2	12.0±1.5	63±5	<0.02	3.6±0.2	7.8±0.9	239±25
B 3.1	0.3±0.1	2.0±0.3	5.2±0.4	18±3	<0.02	2.7±0.3	35.8±4.3	182±15
B 3.2	0.20±0.04	<0.12	14±2	103±15	<0.02	3.3±0.4	15.0±2.4	284.15±35.39

analyzed samples, e.g., the concentrations of the aerated parts were lower than those from the underground ones. Moreover, the concentration of iron has varied between 182 and 510 $\mu\text{g g}^{-1}$ d.w.

3.2 Total sediment

The mean value of the determined heavy metal concentrations from the sediments of the wetlands at Villa del Mar is presented in Table 4.

For all analyzed metals, with the exception of manganese and iron, the concentrations on the sediment without any vegetation at site A were higher than within the sediments associated to the roots of *S. alterniflora*. In contrast, for the same elements at site B, the contents on the sediments without plants were lower than those associated with the underground tissues. Finally, comparing both tidal flat sediments, the concentrations of these metals at site A were more than twice as high as at site B. Only in the case of iron, the concentrations were very similar.

Also a significant difference between the medium and the high-salt marshes has been recognized for iron at both sites, with higher values in the medium-salt marsh than in the higher-salt one. The concentrations in the high-salt marsh were similar to those from the sediments without vegetation. In addition, the highest contents of iron (27.06 to 29.49 mg g^{-1} d.w.) were recorded within those sediments associated with *S. alterniflora* underground parts from the medium-salt marshes. The whole Fe concentration range was from 14.15 to 29.49 mg g^{-1} d.w.

Cadmium (nd–1.10 $\mu\text{g g}^{-1}$ d.w.), chromium (3.61–6.99 $\mu\text{g g}^{-1}$ d.w.), copper (9.92–20.04 $\mu\text{g g}^{-1}$ d.w.) and nickel (7.77 $\mu\text{g g}^{-1}$ d.w. and 17.26 $\mu\text{g g}^{-1}$ d.w.) concentrations in the samples associated with the underground parts of the plant have presented no significant differences between high and medium-salt marshes at site A, but medium-salt marshes had higher concentrations than higher-salt marshes at site B.

Lead has shown different distribution trends between the medium and high-salt marsh within the different sites. In contrast to the higher concentrations in A.4 (high-salt marsh), the higher values in site B were detected in the medium-salt marsh. Lead concentrations between 9.01 and 27.64 $\mu\text{g g}^{-1}$ d.w. were measured. Also the same

distribution tendency has occurred in the analysis of zinc between both salt marshes. This metal was recorded in a concentration range between 33.12 and 64.74 $\mu\text{g g}^{-1}$ d.w.

In the case of manganese, the higher concentrations were found in the high-salt marsh, whereby even the difference in site A was not significant. The corresponding values have ranged between 125.44 and 243.04 $\mu\text{g g}^{-1}$ d.w. It should also be mentioned, for both sites, that the sediments without any vegetation have presented lower concentrations than the sediments associated with the underground parts of *S. alterniflora*. In comparison, B.4 Mn concentration has shown to be much higher than the other samples of the studied area.

4 Discussion

The concentration and distribution of several heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) have been studied in both aerial and underground parts of *S. alterniflora* from salt marshes within Bahía Blanca estuary. Marsh plants are known to absorb and accumulate metals from contaminated sediment (Giblin et al. 1980; Sanders and Osman 1985; Burke et al. 2000). This absorption of contaminants is one reason that wetlands are being used for wastewater treatment. However, metals incorporated into plant tissue have been observed to make their way into primary consumers such as crabs, which feed on plant detritus, and consequently into the whole trophic web (Nabawi et al. 1987; França et al. 2005).

Our results have shown several particular trends, which deserve to be considered. None of the medium and high-salt marsh plants studied have showed detectable values of Cr, while Pb was only detectable on samples A.3.1, B.1.2, and B.3.1, presumably due to an uptake via stomata of metals at this position (Xiao et al. 1998; Patra et al. 2004; Wang 2004). Moreover, and keeping in mind that both leaf-concentrations could be found in the high-salt marsh near to the land, it is possible to presume that a deposition from the air through dust is occurring. *S. alterniflora*'s Cu, Fe, Ni, and Zn concentrations were higher in the underground tissues than in the aerial parts of the medium-salt marsh; in addition, the distribution trend mentioned was also similar in both sites: close to and far away from Villa del Mar village.

Table 4 Metal concentrations (mean values \pm standard deviation, $n=12$) in total sediment ($\mu\text{g/g}$ d.w.–Fe in mg/g d.w.)

Sample	Cd	Pb	Cu	Zn	Cr	Ni	Mn	Fe
A.2	0.9 \pm 0.2	14.4 \pm 3.2	15.1 \pm 2.8	55 \pm 9	6.0 \pm 0.3	14 \pm 3	182 \pm 34	27 \pm 3
A.4	0.8 \pm 0.2	19.3 \pm 4.2	15 \pm 4	60 \pm 13	6.0 \pm 0.5	14 \pm 3	188 \pm 37	17 \pm 1
A.5	1.1 \pm 0.3	27.7 \pm 6.4	18.7 \pm 4.5	65 \pm 18	7 \pm 1	17 \pm 5	174 \pm 27	17 \pm 1
B.2	0.8 \pm 0.2	20.5 \pm 4.5	20.0 \pm 3.8	64 \pm 15	6.0 \pm 0.8	16.5 \pm 4.0	152 \pm 21	29 \pm 3
B.4	0.2 \pm 0.1	16.7 \pm 3.8	12.4 \pm 3.0	41 \pm 14	3.7 \pm 0.3	10.4 \pm 2.3	243 \pm 40	17 \pm 3
B.5	0.4 \pm 0.1	9.0 \pm 2.3	10.0 \pm 1.8	33 \pm 7	3.6 \pm 0.5	7.8 \pm 1.9	125 \pm 20	14 \pm 3

In addition, measured values of Ni within both B.1 and B.3 sites were closely similar (see Table 3). It is possible to observe that those sets of samples from the same salt marsh levels (e.g., A.1 and B.1, or A.3 and B.3) have shown similar heavy metal distribution trends even their corresponding concentrations could be different. So, in the medium-salt marshes the concentrations of Cu, Zn, Ni, and Fe were higher in the underground tissues (roots plus rhizomes), with the exception of Mn, which was seen to be higher in the aboveground parts. The same tendency occurs in high-salt marshes for these heavy metals, with the exception of Ni. The role of manganese as an enzyme activator in photosynthesis and as an electron donor in photosystem II (Schulte and Kelling 1999) could be a reason for its high levels within the aerial parts of *S. alterniflora*. In addition, Cd concentrations as recorded in this study deserve to be highlighted so that, with the exception of the high-salt marsh at site A, Cd—similar to Mn—was always in higher concentrations in the aerial parts than in the underground parts of *S. alterniflora*.

This is an important fact considering that Cd is an extremely toxic metal, and—as it was commented in previous sections—can be transferred to the top levels of the trophic webs, with the corresponding potential risk to human health. In this sense, several mechanisms have been hypothesized to explain the entry of Cd into the plant via roots; for instance, Almeida et al. (2004) proposed that Cd could enter root cells by competitive relationships between this metal and nutrients, due to Cd's similarity with Ca and Zn. Moreover, the efficiency of this process could be improved—for instance by increasing the occurrence of chelator agents (Duarte et al. 2007) or enlarging the cell's capacity to store metals or to immobilize them (Sousa et al. 2008).

Even though the rest of heavy metals principally remain in the roots and rhizomes, meaning they do not represent a critical problem as far as release to the environment is concerned, heavy-metal concentrations, as measured in aerial parts of the plants, were as high as several estuaries recognized as anthropically impacted (Burke et al. 2000; Quan et al. 2007). This fact allowed one to maintain that the mentioned levels (medium-salt marsh and high-salt marsh) must have the same exposition to heavy metal sources, similar physical–chemical conditions regulating metal distribution within the compartments on the salt marshes, or both mentioned processes simultaneously. In addition, and considering that *S. alterniflora* can release large amounts of metals through the excretion of metal-containing salts produced by leaf salt glands (Burke et al. 2000; Weis and Weis 2002, 2004), the densely vegetated salt marshes from Bahía Blanca estuary may influence the metal flux between the tidal flat and the water body. Moreover, metals in this macrophyte can remain after the leaves have died and turned into detritus. The metals

present in the detritus can be passed on to consumers (Quan et al. 2007).

Two different distribution trends of the studied metals have been observed in the sediment samples taken from the plant soil blocks within the selected area. The samples from those sites located far away Villa del Mar (e.g., B ones) have presented greater concentrations on the sediments associated to underground parts of *S. alterniflora* (B.2 and B.4) than those from the naked tidal flat (B.5) for almost all of the metals studied, with only an inverse trend for Mn between tidal flat sediment and sediments associated with high-salt marsh plants. This type of distribution pattern fully agreed with those reported by other authors on different salt marshes, such as Burke et al. (2000) on Hackensack Meadowlands (close to New York City and New Jersey, USA).

Unlike this, the samples from the site close to Villa del Mar (e.g., A ones) have shown a significantly different trend, with the higher concentrations in sediments from the naked tidal flat (A.5) than in those linked to the plants (A.3 and A.4) for most of the metals studied (Cd, Pb, Cu, Zn, Cr, Ni), with an opposite trend for Mn and Fe. In this sense, it must be considered that the dynamics of metals is affected by a wide range of environmental characteristics of the sediments, most notably the pH and redox potential (Cacador et al. 2000; Sundareshwar et al. 2003). Our data have shown that vegetated sediments from the A site presented predominantly reduced conditions while those from the B site were oxidized (Negrin et al. 2008). It is well-known that tidal wetland sediments tend to be reduced, and that, in a reduced condition, most of the metals often tend to be immobilized in the form of insoluble sulfides, being unavailable to plant uptake (Williams 2002; Weis and Weis 2004).

However, the metals do not remain inert (Lacerda et al. 1997) and the wetland plants themselves modify the redox potential of the soils in their immediate vicinity by transporting oxygen down to the roots via parenchymal tissue and releasing oxygen from the roots (Giblin et al. 1986; Quan et al. 2007). By thus generating an oxidizing soil environment in the rhizosphere, the marsh plants alter the sediment chemistry and make the metals more bioavailable (Weis and Weis 2004). When marsh sediment has accumulated high concentrations of metals, macrophyte roots can absorb and translocate them to aboveground biomass, which may lead to the increase of metal bioavailability within the salt marsh (Windham et al. 2003). The roots of salt-marsh plants can accumulate high concentrations of metals, but only a low proportion of the metal is allocated to aerial tissues, which indicates a restriction of transport upwards (Weis and Weis 2004; Windham et al. 2003). Metals in leaves can remain after the leaves have died and turned into detritus, and they can be passed on to consumers furthermore (Weis and Weis 2002).

Consumption of metal-laden detritus can cause deleterious effects in consumers (Dorgelo et al. 1995). In the present case, and as was explained in previous paragraphs, even though most of the metals were stored on roots, the translocated amount of metals is sufficiently large to be environmentally considered. As metals on the leaf surface (from excretion or direct deposition of leachate) may be dissolved in water at flood tides or through rainfall, more metal becomes available in the food web. Thus, *S. alterniflora* is capable of exporting heavy metals to the surrounding ecosystem via both detritus and excretion. Keeping in mind that Bahía Blanca estuary's salt marshes are inundated by tidal water for 3–4 h twice every day, macrophytes may act as a conduit for the movement of metals from the sediment to the estuarine body and near coastal systems.

5 Conclusions and recommendations

Considering the comments in the previous paragraphs, are salt marshes from Bahía Blanca estuary sources or sinks for metals? It can be sustained that both are the case, even if it is often stated that wetlands serve as sinks for pollutants, reducing contamination of surrounding ecosystems (Weis and Weis 2004). In the present study case, the sediments (which tend to be anoxic and reduced) act as sinks, while the salt marshes can become a source of metal contaminants. This is very important for this system because the macrophytes have been seen to retain the majority of metals in the underground tissues, and particularly in their associated sediments. This fact well agreed with previous reports, such as Leendertse et al. (1996), who found that about 50% of the absorbed metals were retained in salt marshes and 50% was exported. Thus, and keeping in mind the large spreading of *S. alterniflora* salt marshes within Bahía Blanca estuary, it must be carefully considered as a redistributor of metals within the system.

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