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RESEARCH ARTICLE

Hazardous metal pollution in a protected coastal area from Northern Patagonia (Argentina)

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Abstract The San Antonio Bay is a protected natural coastal area of Argentina that has been exposed to mining wastes over the last three decades. Iron and trace metals of potential concern to biota and human health (Cd, Pb, Cu, and Zn) were investigated in the sediments from the bay and in the soils of the Pile (mining wastes). Concentrations of Cd (45 mg kg^{-1}), Pb (42,853 mg kg^{-1}), Cu (24,505 mg kg^{-1}), and Zn (28,686 mg kg^{-1}) in the soils Pile exceeded guidelines for agricultural, residential, and industrial land uses. Risk assessment due to exposure to contaminated soils (Pile) was performed. Hazard quotients were superior to non-risk (HQ >1) for all trace metals, while accumulative hazard quotient index indicated a high risk for children (HI = 93) and moderate for adults (HI = 9). In the bay, sediments closest to the Pile (mudflat and salt marsh) exceeded sediment quality guidelines for protection of biota. Results of different acid extraction methods suggest that most of the pseudototal content was potentially mobile. Principal component analysis indicated that the sites near the Pile (Encerrado channel) were more polluted than the distal ones. Tissues of *Spartina* spp. located within Encerrado channel showed the highest metal levels among all studied sites. These results show that the problem still persists and the mining wastes are the sources of the pollution. Furthermore, the Encerrado channel is a highly impacted area, as it is shown by their metal enriched sediments.

Keywords Heavy metals · Mining wastes · *Spartina densiflora* · *Spartina alterniflora* · Salt marsh

Introduction

Pollution of the environment with "heavy metals" is a serious problem all over the world. Mining activities extract metals of commercial interest and simultaneously generate wastes with high pollutant loading. These residues usually remain in open air and can become an important source of toxic elements including As, Cd, Pb, Hg, Cu, and Zn in the surface (Clevenger 1990; Lee et al. 2001). Once released, uptake by organisms depends on bioavailability, which depends on environmental variables. Metals with non-essential role to biological functioning (e.g., Cd, Hg, and Pb) can be toxic at relatively low concentrations, while others essential to plants and/or animals (e.g., Co, Cr, Cu, Fe, Mn, Mo, Ni, and Zn) can exert negative effects by being either too high or too low in concentration (Smith 2007).

The San Antonio Bay (SAB), located in the northwest extreme of San Matías Gulf (Patagonia, Argentina) (Fig. 1), constitutes a case of study which, despite its ecological importance, suffers from chronic metal pollution. The system is used as a resting, feeding, and nesting area for many migratory birds and it has been declared an International Site for Western Hemisphere Shorebird Reserve Network (WHSRN) and Natural Protected Area by the Province of Río Negro in 1993 (Law N° 2670 1993). A dense crab population

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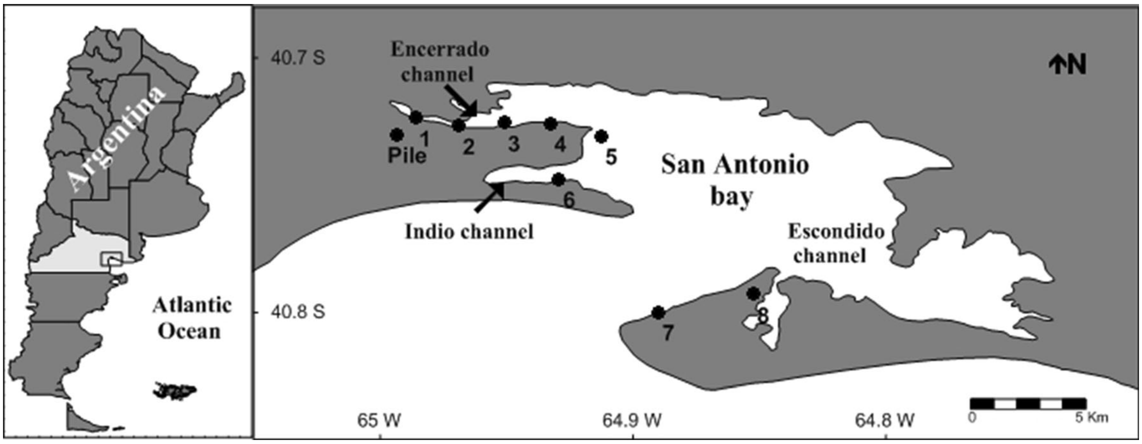


Fig. 1 Sites sampled in the San Antonio Bay. Measurements in mudflat were performed in sites 1 to 8, while in salt marsh, in sites 1, 3, and 5 for *S. densiflora* and in sites 5 and 8 for *S. alterniflora*

(*Neohelice granulata*) coexists with an extensive salt marsh of the *Spartina alterniflora* Loesel and *Spartina densiflora* Brong, favored by the very high tidal amplitude and the large sandy plain crossed by channels that is exposed at low tide. This gives the landscape a special physiognomy called "cangrejal" or "espartillar," depending on the crab or cordgrass dominance, respectively (Bortolus et al. 2004; Bas et al. 2005; Isacch et al. 2006; Luppi et al. 2013).

Surprisingly, during the last six decades, SAB has been coexisting with mining wastes that have been abandoned close to the coast and near the low dense populated town of San Antonio Oeste. By the mid nineties, it was detected for the first time the existence of hazardous metal contamination in the inner part of the bay (Encerrado channel) (Gil et al. 1999). Further studies identified mining wastes covering a total area of 95,000 m^2 and a total volume of 22,500 m^3as the principal source (Bonuccelli et al. 2004).

The responsible mining industry operated between the 1960s and 1980s, extracting principally minerals of Pb, Zn, Ag, and V. Subsequent research reported high levels of metals in invertebrates, such as the crab *N. granulata* (Gil et al. 2006) and the bivalve *Brachidontes rodriguezii* (Vázquez et al. 2007), suggesting not only metal remobilization from the pile due to chemical-related processes (acidity and/or oxidation-reduction) and/or physical-related processes (wind/rain/flood) but also its bioavailability within the bay. More recently, research on *S. densiflora* informed that below-ground structures reflect the soil metal concentration pattern but is not so evident in above-ground structures (Idaszkin et al. 2015).

It is widely known that metal behavior and mobility in coastal environments highly depend on complex biogeochemical reactions that are influenced by metal speciation, salinity, pH, redox potential (Eh), organic matter, and particle size of the sediment (Fitzgerald et al. 2003; Smith 2007; Zhang et al. 2014). Interactions of these factors influence the percentage of lability (and hence the potential bioavailability) of the total metal concentration in the sediments. The finest particles of the sediment play a significant role in these processes, because they are the principal carriers of functional groups capable of trapping metals (Jayaprakash et al. 2008) and because of their importance not only in resuspension and general transportation of sediments but also in the exchange of contaminants across the sediment-water interface (Zhang et al. 2014). Furthermore, in salt marsh environments like in SAB, plants may also have a dominant role in metal cycling given its high capacity to modify the surrounding sediment through different processes (Weis and Weis 2004). Some plants can transport oxygen down to the roots via aerenchyma tissue and release it to the sediment, thus generating an oxidizing environment in the rhizosphere capable of oxidizing the metal sulfides (Burke et al. 2000). Moreover, the roots can produce exudates of organic substances capable of complexing metals and changing their bioavailability (Mucha et al. 2005). Other plant species are able to form rhizoconcretions of Fe and Mn oxyhydroxides on the roots, with high capacity to adsorb metals (Vale et al. 1990; Sundby et al. 1998). Usually, only a small amount of non-essential metals are absorbed by the root tissue and transported to the aerial parts (Marchand et al. 2010). In this way, plants can modify their surrounding environment causing a redistribution of metals in the sediment.

There are several studies to date that have assessed the pollution extent in SAB (Gil et al. 1999; Bonuccelli et al. 2004; Gil et al. 2006; Vázquez et al. 2007; De Pietri et al. 2008; Idaszkin et al. 2015), but none of them made a risk assessment. In this research, we performed a screening-level ecological risk assessment by (a) examining the concentrations of metals in soils from the pile and in sediments from the mudflat and the salt marsh; (b) comparing them with background and/or guideline values and, in addition, making an approach to human risk health through the exposition to pile-soils; and (c) quantifying concentrations in plants to assess retention in the salt marsh.

Materials and methods

Study area

The San Antonio Bay (40° 46′ S, 064° 50′ W) is located in a semi-arid region (average rainfall 240 mm/year) without any river input. It has a semidiurnal macrotidal regime (up to 9 m amplitude) with extensive sand-cobble intertidal flats, leaving it exposed up to 85% of its total surface during low tide (Fucks et al. 2012). The shoreline contains large rocky flats, shells, and tidal channels. Among the later, the most important are the Encerrado channel (northbound from San Antonio Oeste city with 4-km length and a mean of 0.9-m depth), the Indio channel (southbound from San Antonio Oeste city with 2-km length and 0.8-m depth), and the Escondido channel (N-S direction with 7-km length and 1.2-m depth) (Carbone et al. 2014) (Fig. 1). The upper zones are characterized by the presence of salt marsh, dominated by *S. alterniflora*, *S. densiflora*, and *Sarcocornia perennis* (P. Mill) A. J. Scott (Isacch et al. 2006) and the mid and low intertidal are distinguished by the presence of the burrowing crab *N. granulata* (Bas et al. 2005).

The extensive salt marsh of BSA includes two genera: *Spartina* (*S. alterniflora* and *S. densiflora*) and *Sarcocornia* (*S. perennis*) (Bortolus 2006; Isacch et al. 2006; Montemayor et al. 2014). The former has been widely cited in the literature as a good heavy metal phytostabilizer (Reboreda and Caçador 2007; Cambrollé et al. 2008; Redondo Gómez 2013; Curado et al. 2014), and for that reason, it was selected in this study. Even though *S. densiflora* is the plant with less coverage in the bay, it was also included because it is the only species of *Spartina* that grows inside the Encerrado channel. Outside the channel, *S. alterniflora* shows a remarkable predominance over *S. densiflora* (Isacch et al. 2006).

Sampling and analysis of soils and sediments: environmental variables and trace elements

In November 2012 (spring), in the mining wastes (Pile) and mudflats sites (1 to 8) (Fig. 1), one composite sediment sample was collected in each site in order to minimize localized variability. It consists in five individual subsamples separated 1 m approximately from each other and 10 cm in depth. They were placed into a single plastic container and thoroughly mixed to form one homogeneous composite sample.

In salt marsh (sites 1, 3, 5, and 8) (Fig. 1), three sediment samples were collected (20 × 20 × 15 cm) in each site associated to the roots of *Spartin*a plants.

In each site, the Eh and pH were recorded in situ using a portable pH/mV meter, after a period of 10-min stabilization ($N = 3$). In the laboratory, samples were oven dried at 60 °C until constant weight and then sieved through a plastic sieve in order to discard particles larger than 2 mm. The retained sample (hereafter *bulk*) was used to determine percentages of sandy and silt-clay fraction (sieving through a 63-μm plastic mesh); organic matter content (OM) (calcination at 450 °C for 4 h, according to Byers et al. 1978) and metal burdens differentiate both pseudototal and labile contents with strong and weak acid extractions, respectively.

For the strong acid extraction, 1 g of the bulk sample was digested using 10 ml of aqua regia ($HCl:HNO_3$ proportion 3:1) at 85 °C (MacGrath and Cunliffe 1985; ISO 1995). This type of digestion extracts between 70 and 90% of the total content of metals (pseudototal content) (Hung and Chmura 2007) and it is suitable for samples containing less than about 20% (*m*/*m*) of organic carbon (ISO 1995) as expected for these samples. For the weak acid extraction, 1 g of the bulk sediment was used to make a cold extraction with 25 ml of 0.5 N HCl. This method is an approach to quantify labile or potentially bioavailable metals (Agemian and Chau 1976). Weak extraction was also performed on the finest fraction (silt-clay grains), not only because of its importance in metal cycling and transport but also to compensate for grain-size effects that occur in the bulk samples (Beck et al. 2013).

Human risk of non-carcinogenic toxic effects due to exposure to contaminated soils

To assess the potential non-carcinogenic toxic effect of metals from the Pile, a hazard quoting (HQ) was calculated as the ratio of the concentration of a metal in the environmental matrix to the recommended safety level: HQ = CDI/RfD, where CDI = (Cs*IR*ED*EF)/(BW*AT), CDI is the chronic daily intake, RfD is the reference dose (mg kg^{-1} day^{-1}), Cs is the metal concentration in soil (mg kg^{-1}), IR is the ingestion rate (mg day^{-1}), ED is the exposure duration (years), EF is the exposure frequency (days/year), BW is the body weight (kg), and AT is the average exposure time (days). The Risk Assessment Information System (RAIS 2008) was used to calculate reference values considering a recreational use and differentiating between children and adults.

To assess the overall potential effects posed by all metals, the HQ estimated for each metal was summed up (assuming an additive effect) and expressed as the hazard index (HI) (ACS, RFF 1998). A HQ <1 was considered a safe lifetime of exposure. If HI >1, then a chronic non-cancer effect is likely to occur (Lemly 1996; Zabin and Howladar 2015).

Sampling and analysis of trace elements in plants

Three plots of *Spartina* sp. (20 × 20 × 15 cm) were collected in each site depending on plant presence: *S. densiflora* in sites 1, 3, and 5 and *S. alterniflora* in sites 5 and 8. Plants were placed in bags and thereafter transported to the laboratory. In the laboratory, they were separated into shoot tissues (stems and green leaves) and root tissues (rhizomes and roots), which were then washed with deionized water and oven dried at 60 °C until constant weight. After grinding up with a Butt mill, aliquots of 1 g of powdered tissue were calcined in a furnace during 6 h at 400 °C and then placed on a hot plate at 85 °C with concentrated HNO_3 until dryness. The last two steps were repeated until white ashes were obtained (Yoong 1998).

The response of plants to the presence of metals in their surrounding sediments was evaluated in terms of bioconcentration and translocation factors (BCF and TF, respectively). BCF was calculated as the metal concentration in root tissue relative to labile concentration in the surrounding bulk sediment. TF was calculated as the metal concentration in shoot tissue in relation to the concentration in root tissue (Yoon et al. 2006; Gupta et al. 2008).

Quality control of metal analysis

All samples for metal analysis (soils, sediments, and plant tissues) were processed by duplicate including blanks. Analytical grade reagents (Merck® or Baker®) were used. Measurements of metals Cd, Cu, Pb, Fe, and Zn were carried out using an Atomic Absorption Spectrophotometer IL 754 (Instrumentation Laboratory, USA) with air-acetylene flame. Results are reported on a dry weight basis. The accuracy of the methods was checked by the analysis of reference material of marine sediment (PACS-2) and aquatic plants (BCR-060 *Lagarosiphon major*). Percentages of recoveries and detection limits of the methods are shown in Table 1. The variation coefficients tested for five replicates were always below 10%.

Statistical analysis

Principal component analysis (PCA) with varimax rotation was used in order to integrate all information obtained in the sediments. To compensate for strongly skewed distribution and/or to avoid the dominance of high concentrations in the mathematical model, all data were log-transformed. Statistical tests were performed to compare (a) mean metal concentrations between inside (impacted area by mining wastes) and outside (unimpacted area) the Encerrado channel (for mudflat as well as for salt marsh sediments) (Student's t test), (b) mean metal concentrations in tissues and sites for *S. densiflora* (two-way ANOVA), and (c) mean metal concentrations between tissues and species two-way ANOVA). The Shapiro-Wilk and Levene tests were used to assess normality and homogeneity of variance, respectively. Metal concentrations of sediments and plants were transformed using log function when necessary. Tukey's multiple comparisons were used after significant ANOVA tests. All statistical analyses were carried out using Infostat (version 2015).

Results and discussion

Actual concentrations of metals in soils from the pile and their risks to human health

The soils from the Pile were mainly composed of fine sand particles (88.7%) with 11.3% of grain-size below 63 μm. Concentrations of the studied elements in this substrate are shown in Table 2, where Argentinean and Canadian soil quality guidelines were included for comparison purposes. The order of metal concentrations was Fe > Pb > Zn > Cu > Cd for pseudototal concentrations (pc) and Fe > Zn > Cu > Pb > Cd for labile concentrations (lc). The percentages of labile with respect to pseudototal concentrations presented the following orden: Cd 82%, Zn 57%, Cu 32%, Fe 7% and Pb 5%. It is interesting to highlight that even labile concentrations exceeded the reference values for agricultural, residential, and industrial land uses (Law N° 24.051 1992; CCME 2001). According to this, the pile can still be considered a metal hotspot and a health risk for biota and humans, as it was previously reported (Gil et al. 1999;

Table 1 Percentages of metal recovery (%R) from two reference materials: PACS-2 (marine sediment) and BCR-060 (aquatic plant *Lagarosiphon major*). Concentrations are expressed in milligrams per kilogram dry weight, except for Fe which is in % (N = 5)

Element	PACS-2				BCR-060			
	OC	CC	%R	DL	OC	CC	%R	DL
Cd	1.8 ± 0.1	2.1	84	0.25	2.1 ± 0.1	2.2	97	0.10
Pb	164.7 ± 2.2	183	90	5.00	56.3 ± 1.0	64	88	1.00
Cu	262.3 ± 6.5	310	85	0.63	46.2 ± 1.2	51	90	0.25
Zn	369.0 ± 20.9	364	101	0.25	316.2 ± 12.2	313	101	0.10
Fe	3.2 ± 0.1	4.1	78	1.25	2342.7 ± 255.6	2378*	99	0.50

OC obtained concentration, *CC* certified concentration, *DL* detection limit

*Calculated from Fe_2O_3

Table 2 Pseudototal and labile metal concentrations in soil of the Pile (composite sample, mg kg^{-1}) and Soil Quality Guidelines for different land uses

	Pile		Agricultural		Residential		Industrial	
Element	Pseudototal	Labile	AHWL	CEQG	AHWL	CEQG	AHWL	CEQG
Cd	45	37	3	1.4	5	10	20	22
Pb	42,853	2301	375	70	500	140	1000	600
Cu	24,505	7955	150	63	100	63	500	91
Zn	28,686	16,235	600	200	500	200	1500	360
Fe	340,485	23,832	nd	nd	nd	nd	nd	nd

AHWL Argentinean Hazardous Waste Law 24.051 (1992), *CEQG* Canadian Environmental Quality Guidelines (CCME 2001), *nd* no available data

Bonuccelli et al. 2004; Vázquez et al. 2007). Fine particles, which are known to provide a larger relative surface area and thus high cation exchange capacity for contaminants (Zhang et al. 2014), may be easily spread out by wind. In addition, acid drainage may produce metal leaching from the Pile to the Encerrado channel (Bonuccelli et al. 2004).

Considering children exposition, HQ indexes were higher than the unity for all metals (Cd = 1.2, Pb = 58.7, Cu = 16.8, Zn = 2.6, and Fe = 13.3) and the HI index was 92.7, which suggests a high risk for this sector of the population. For adults instead, risk would be lower (HQ Cd = 0.1, Pb = 5.5, Cu = 1.6, Zn = 0.2 and Fe = 1.2; HI = 8.7). It is interesting to note that the greatest contribution to HI corresponded to Pb in both cases. This highlights the hazard that this deposit represents for people living near the Pile.

Actual concentrations of metals in sediments from the mudflat and the salt marsh

All the studied sediments were impoverished in fine particles (<9%) and OM (0.7–3.0%), thus suggesting a limited affinity for metal retention. The pH ranged from 5.8 to 7.2 in the mudflat and from 7.1 to 8.0 in the salt marsh, while the redox potential was above −100 mV in most cases. Less oxidized conditions were found in sediments nearby *S. alterniflora* than *S. densiflora*, probably influenced by their different locations (low and medium-high salt marsh, respectively) (Table 3).

Results of metal analysis performed on bulk sediments (pseudototal and labile concentrations) and on silt-clay particles (labile concentration) are shown in Fig. 2. Pseudototal metal concentrations in bulk sediments showed the following general pattern: Fe (0.8–21.3%) > Zn (15.1–211.9 mg kg^{-1}) > Pb (<5.0–41.2 mg kg^{-1}) > Cu (2.4–22.9 mg kg^{-1}) > Cd (undetectable). As expected, labile concentrations in the bulk sediments (Fig. 2) were lower than that in pseudototal contents. For Cu and Zn, the former accounted for around 80% of the pseudototal concentration in site 1 and 20% in the remaining sites. For Pb, percentages varied between 70 and 95% within the Encerrado channel and in the East Harbor (7) and below 10% in the other sites. Finally, Fe yielded the least lability (10–20% in all sites). Considering the importance of the labile fraction as an index of potential mobility and bioavailability of the total load, it is clear that sediments from the innermost site of the channel and from its adjacent *Spartina* salt marsh (sites 1 and 1sd) should be considered as risky, not only due to Pb but also due to Cu and Zn. This is in agreement with our findings of excessive pseudototal concentrations compared to safety guidelines in these sites.

Table 3 General characteristics of the sediments from SAB (mudflat $N = 1$ and salt marsh $N = 3$, mean ± SD)

Site	Zone	Plant species	%OM	% sand	% silt-clay	Eh	pH
Pile	Soil		8.8	88.7	11.3		
1	Mudflat		3.0	92.5	7.5	−100 ± 16	7.0 ± 0.1
2	Mudflat		0.9	98.1	1.9	−69 ± 11	7.0 ± 0.1
3	Mudflat		1.4	96.6	3.4	−214 ± 21	6.2 ± 0.1
4	Mudflat		1.0	97.7	2.3	50 ± 8	6.9 ± 0.2
5	Mudflat		1.2	98.7	1.3	133 ± 13	7.4 ± 0.1
6	Mudflat		0.8	99.3	0.7	55 ± 6	5.8 ± 0.3
7	Mudflat		3.0	95.9	4.1	77 ± 10	7.2 ± 0.1
8	Mudflat		0.7	99.4	0.6	98 ± 13	6.6 ± 0.1
1sd	Salt marsh	*S. densiflora*	2.0 ± 0.2	91.7 ± 0.2	8.3 ± 0.2	238 ± 9	8.0 ± 0.2
3sd	Salt marsh	*S. densiflora*	1.7 ± 0.2	97.6 ± 0.4	2.4 ± 0.4	193 ± 12	8.0 ± 0.2
5sd	Salt marsh	*S. densiflora*	0.9 ± 0.2	98.9 ± 0.3	1.1 ± 0.3	156 ± 9	8.0 ± 0.1
5sa	Salt marsh	*S. alterniflora*	1.5 ± 0.4	96.6 ± 0.6	3.4 ± 0.6	−59 ± 14	7.1 ± 0.1
8sa	Salt marsh	*S. alterniflora*	2.0 ± 0.7	95.7 ± 1.3	4.3 ± 1.3	−217 ± 13	7.2 ± 0.3

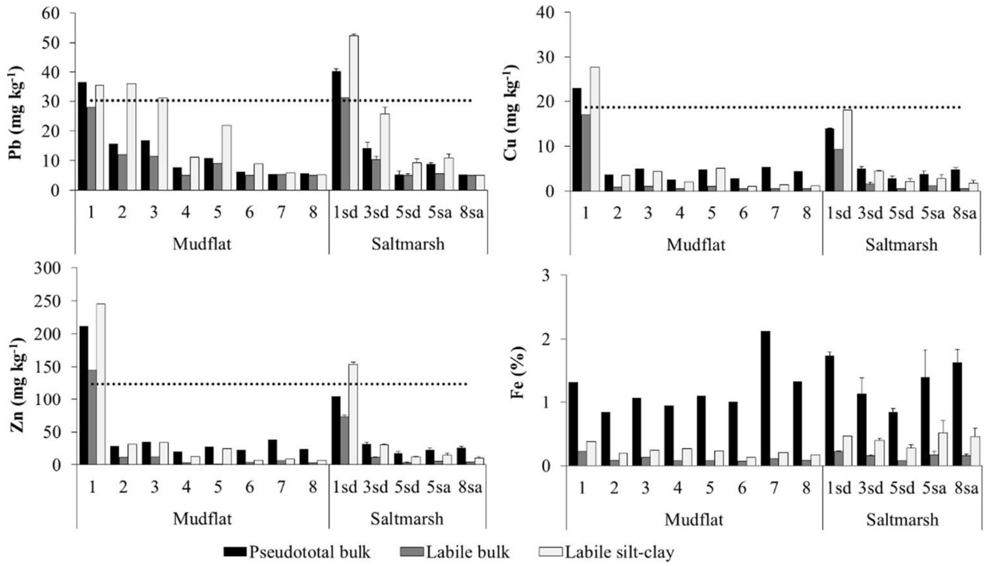


Fig. 2 Mean metal concentrations in sediments for the study site (mudflats: $N = 1$; salt marsh: mean ± SD, $N = 3$). *Dotted line* represents the Interim Sediment Quality Guidelines (ISQG) Canadian (CCME 2001)

Labile concentrations in silt-clay were higher than in bulk sediments, where sandy particles produce a dilution effect. The following ranges were obtained: Fe 0.13–0.52%, Zn 6.8–245.5 mg kg^{-1}, Cu <1.0–27.7 mg kg^{-1}, Pb < 5.0–52.3 mg kg^{-1} (Fig. 2). It is observed that Canadian guideline values for protection of aquatic life (CCME 2001) were exceeded by Pb, Cu, and Zn inside the Encerrado channel (Fig. 2). The highest values were registered in site 1 (close to the Pile), both mudflat and salt marsh, except for Fe, which was maximum in site 7 (eastern harbor).

In order to compare pollution status of mudflat sediments inside and outside the Encerrado channel, sampling sites in the mudflat were separated in two groups: sites 1, 2, 3, and 4 and sites 5, 6, 7, and 8, respectively. The same was done for sites in the salt marsh: sites 1sd and 3sd for inside and sites 5sd, 5sa, and 8sa for outside. In the mudflat, Pb was significantly higher inside the channel for pseudototal concentrations in bulk sediments (*t* test, gl 6, $p = 0.047$) and for labile concentrations in silt-clay (*t* test, gl 6, $p = 0.045$). In the salt marsh, pseudototal concentrations of Pb, Cu, and Zn in bulk sediments were higher inside than outside the channel (*t* test, gl 13, $p_{Pb} < 0.001$, $p_{Cu} = 0.002$, and $p_{Zn} = 0.016$). The same was observed for labile concentrations in bulk sediments (*t* test, gl 13, $p_{Pb} = 0.004$, $p_{Cu} = 0.009$, and $p_{Zn} = 0.007$) and for labile concentrations in silt-clay (*t* test, gl 13, $p_{Pb} < 0.001$, $p_{Cu} = 0.005$, and $p_{Zn} = 0.005$).

In comparison with available historical data, the potentially bioavailable metal concentrations in silt-clay particles seem to have decreased; however, levels in the Pile still remain high compared to values of previous studies (Gil et al. 1999; Vázquez et al. 2007; Lo Russo 2012) (Fig. 3). Although the metals in the slag seem to be stabilized, any physical or chemical alteration of the soil may remobilize them, with a high environmental risk.

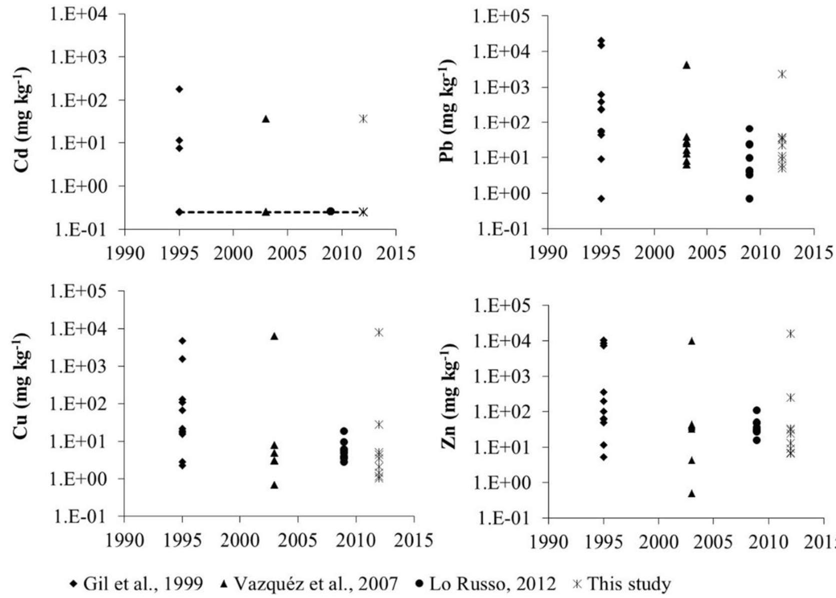
Integration of environmental and metal results in sediments through a PCA, allowed extracting two new variables (PC1 and PC2) that explained 88% of the total variance (57 and 31%, respectively) (Table 4). PC1 exhibited high positive relationships with Zn, Cu, and Pb (both pseudototal and labile contents in the bulk sediments as well as labile contents in silt-clay particles), while PC2 was positively associated to the percentage of silt-clay particles, OM contents, and Fe concentrations.

Position of factor scores (Fig. 4) shows that sites located closer to the Pile (1, 2, 3, 1sd, and 3sd) are positioned towards the positive PC1 axis (most metal-polluted sediments) with the highest score for site 1, whereas negative signs were scored for all the other cases (less-polluted sediments) with the highest negative score corresponding to the site 8sa.

In relation to PC2, positions towards the positive axis are occupied by sites 1, 7, 1sd, 5sa, and 8sa (the most enriched in silt-clay, OM, and Fe). Sediments nearby *S. alterniflora* (sites 5sa and 8sa) notably exhibited higher PC2 scores than their adjacent mudflat sediments (sites 5 and 8, respectively). In coexisting *S. alterniflora* and *S. densiflora* sediments (sites 5sa and 5sd), higher PC2 scores were observed for the former as expected in sediments related to lower salt marsh plants.

This integrative analysis shows that sediment metal pollution in SAB is actually restricted to the Encerrado channel, being the Pile the principal source. Metal retention capacity of sediments from the salt marsh does not seem to be different from adjacent mudflat sediments. Furthermore, general distribution of metals within the bay would not strongly depend on fine particles and OM distribution. In this sense, physical process (such as wind and ebb currents) would be critical factors that contribute to the dispersion of particles enriched with metals, since they set a net transport of material out of the bay (Aliotta et al. 2000).

Fig. 3 Labile metal concentrations in silt-clay particles (mg kg^{-1}) from sediments in SAB at different years. *Dotted line* in Cd indicates detection limit (0.25 mg kg^{-1})



Metal concentrations in shoot and root tissues of *Spartina* spp.

Metal results in plant tissues showed that roots from the five sites are capable of absorbing all the metals detected in the sediments, with the essentials in higher levels than non-essential ones (Fe > Zn > Cu > Pb > Cd). Cadmium, which was not detected in either sediment sample, was found in roots of *S. alterniflora* (0.15–0.16 mg kg^{-1}). Low salt marsh is subject to daily tidal flooding, determining fluctuations in the oxidation-reduction conditions. Under anaerobic conditions, Cd could be retained as sulfide in the rhizosphere, and eventually be oxidized by oxygen released by the roots themselves, favoring its absorption by plants (Sundby et al. 1998; Burke et al. 2000). Pb was detected in plants located closest to the Pile in root (7.0 ± 4.5 mg kg^{-1}) and shoot (3.0 ± 1.8 mg kg^{-1}), while in others sites, it was measured only in roots tissues near or under the detection limit (Table 5). It was observed that Cu, Zn, and Fe were higher in root than in shoot.

Inside the Encerrado channel, metal concentrations in *S. densiflora* were compared among sites and tissues (two-way ANOVA) (Table 6), obtaining a significant interaction for the three metals. Post hoc comparisons showed that differences between shoot-root were higher in site 1sd than in sites 3sd and 5sd for Cu and Fe (Tukey, $p < 0.05$). For Zn, the differences were higher in sites 1sd and 5sd than in site 3sd (Tukey, $p < 0.05$).

Comparison between species was only possible in site 5 (5sd and 5sa). No significant differences were found for Zn, while Cu ($p = 0.035$) and Fe ($p = 0.016$) were higher in *S. alterniflora* than in *S. densiflora*. Comparing between tissues, Cu ($p = 0.001$) and Zn ($p < 0.001$) were higher in root than in shoot for both species and Fe showed no differences (Table 6).

As reported in the literature, the metal levels in tissues were below phytotoxic levels (Table 7) (Prassad et al. 2006; Kabata-Pendias 2011). Compared to other salt marshes, the results obtained for *S. densiflora* in this study were similar to those reported for *S. densiflora* from Rawson (Chubut Province, Argentina), which has been considered as non-polluted (Idaszkin et al. 2014). The only exception was site 1sd, where concentrations of Pb, Zn, and Fe in roots were twice as Rawson records. A recent study in SAB in

Table 4 Factor loadings for PCA

	PC1	PC2
OM%	0.264	*0.871*
Silt-clay%	0.494	*0.800*
Pb pc	*0.955*	0.211
Cu pc	*0.777*	0.531
Zn pc	*0.846*	0.421
Fe pc	0.042	*0.882*
Pb lc	*0.955*	0.216
Cu lc	*0.913*	0.336
Zn lc	*0.887*	0.384
Fe lc	0.474	*0.825*
Pb lf	*0.934*	−0.057
Cu lf	*0.923*	0.277
Zn lf	*0.960*	0.237
Fe lf	0.156	*0.777*
Expl. var	7.975	4.408
Prp. total	0.70	0.315

Significant values are indicated in italics

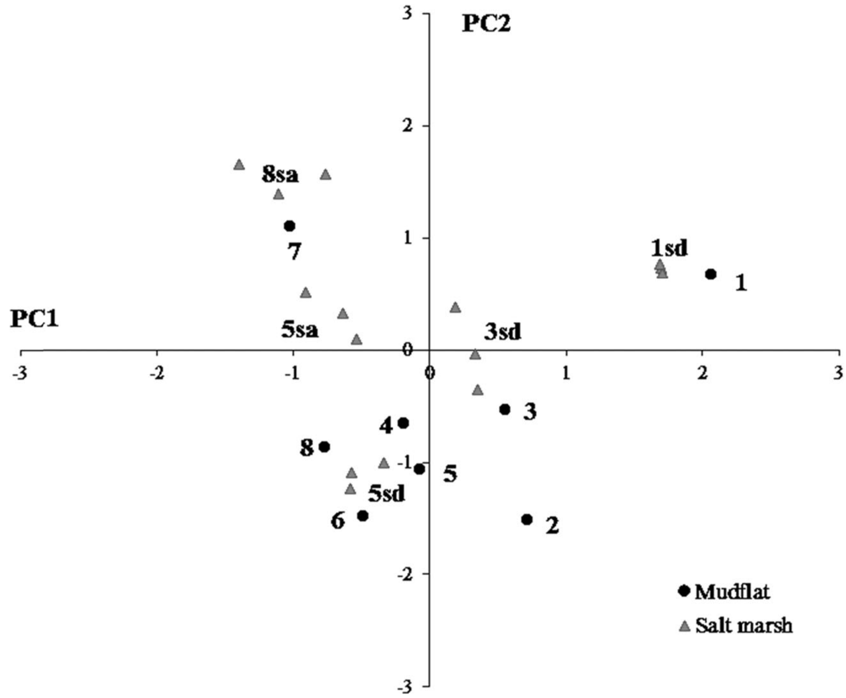


Fig. 4 Principal component analysis with PC1 (Pb, Cu, and Zn contents) and PC2 (fine particles, OM, and Fe content)

S. densiflora showed a similar level in shoots and roots (Idaszkin et al. 2015). In the case of *S. alterniflora*, the values found in SAB were in the same order of magnitude than those reported by Hempel et al. (2008) for the salt marsh of Villa del Mar (Buenos Aires Province, Argentina), which is subjected to several sources of pollution. On the other hand, results in SAB are lower than those reported in *S. maritima* and *S. densiflora* from highly metal-polluted places like estuary of the Odiel and Tinto rivers (Spain) (Cambrollé et al. 2008; Curado et al. 2014), *S. alterniflora* from Hackensack Meadowlands in New Jersey (Burke et al. 2000; Windham et al. 2003) and *S. maritima* from Swartkops estuary in South Africa (Phillips et al. 2015), among others (Table 7).

Overall, the BCF was above the unit for Cu and Zn and below the unit for Pb and Fe (Table 8). Due to levels below detection limit, BCF for Cd could not be calculated; nevertheless, Cd was uptaken for roots of *S. alterniflora*. It is known that mechanisms of metal uptake differ with each metal. Essential elements like Cu and Zn are actively absorbed, while non-essential elements like Pb and Cd are passively absorbed with a reduced uptake rate (Kabata-Pendias 2011). Zn and Cd have similar chemical properties. Compounds released by the plant for facilitating Zn uptake may promote Cd uptake too (Almeida et al. 2011). The geochemistry of Fe plays an important role controlling its own uptake, as well as those of other elements. In this sense, low BCF for Fe was in accordance with the high concentrations found in the sediments surrounding roots, probably as Fe oxyhydroxide. Low BCF for Fe is expected in plants capable to release oxygen from roots, like *Spartina* spp. (Vale et al. 1990; Williams et al.

Table 5 Metal concentrations in *Spartina* tissues ($N = 3$, mean ± SD, mg kg^{-1})

Species	Site	Tissue	Cd	Pb	Cu	Zn	Fe
S. densiflora	1sd	Shoot	nd	3.0 ± 1.8	2.2 ± 0.8	20.7 ± 3.4	476 ± 174
		Root	nd	7.0 ± 4.5	8.4 ± 1.0	81.0 ± 13.3	2274 ± 556
	3sd	Shoot	nd	nd	2.6 ± 0.9	34.1 ± 17.5	519 ± 115
		Root	nd	1.2 ± 0.3	4.3 ± 0.6	50.8 ± 6.6	605 ± 376
	5sd	Shoot	nd	nd	1.7 ± 0.6	17.1 ± 3.0	158 ± 23
		Root	nd	nd	2.7 ± 0.1	60.6 ± 9.6	250 ± 86
S. alterniflora	5sa	Shoot	nd	nd	1.9 ± 0.5	19.9 ± 2.6	351 ± 104
		Root	0.16 ± 0.05	1.4 ± 0.2	4.5 ± 0.5	55.6 ± 18.9	303 ± 84
	8sa	Shoot	nd	nd	2.8 ± 1.2	10.4 ± 3.0	556 ± 78
		Root	0.15 ± 0.04	nd	5.2 ± 0.6	24.1 ± 10.0	1300 ± 759

nd no detected

Table 6 Two-way ANOVA results for metal concentrations in plants

Comparisons among sites and tissues for *S. densiflora*		Cu		Zn		Fe	
	df	*F*	*p*	*F*	*p*	*F*	*p*
Site	2	11.64	*0.002*	1.89	0.193	31.38	*<0.001*
Tissue	1	45.54	*<0.001*	82.19	*<0.001*	15.93	*0.002*
Site*tissue	2	5.45	*0.021*	6.13	*0.015*	7.42	*0.008*
Error	12						
Comparisons between species and tissues for site 5							
Species	1	6.48	*0.035*	0.03	0.868	9.22	*0.016*
Tissue	1	28.07	*0.001*	78.85	*<0.001*	0.75	0.412
Species*tissue	1	1.63	0.237	1.19	0.307	3.09	0.117
Error	8						

$p < 0.05$; significant differences are indicated in italics

1994). In addition, the rhizoconcretions formed on the roots have a large capacity to retain other metals, thus could be limiting their uptake into the tissue (Vale et al. 1990; Otte et al. 1991; De Lacerda et al. 1993).

With respect to TF, it was below the unit for all elements in all sites, except for Fe in site 5sa (Table 8). This pattern suggests an avoidance of metal translocation, keeping the metals in roots and surrounding sediments, accordingly to previous studies performed in different *Spartina* species (Windham et al. 2003; Duarte et al. 2009; Cambrollé et al. 2011; Almeida et al. 2011). Possible physiological mechanisms responsible for restricted uptake and translocation within plants include cell wall immobilization, complexation with substances such as phytochelatins, and barriers at the root endodermis (Vale et al. 1990; Clements et al. 2002; Mucha et al. 2005; Anjum et al. 2013). Even when this pattern explains a low upward transport, excretion mechanisms through leaves

Table 7 Metal concentrations in *Spartina* genus from different sites (mg kg^{-1})

Species Phytotoxic range (1, 2)	Tissue Leaves	Cd 5–30	Pb 30–300	Cu 20–100	Zn 100–400	Fe
S. densiflora (3)	Shoot	<1	<2	6	18–22	0.75%
	Root	<1	<2	4–6	20–25	1–1.5%
S. densiflora (4)	Shoot	<0.1	2–12	1–3	10–60	200–500
	Root	<0.1	6–18	3–17	20–120	500–2800
S. densiflora (5)	Leaf		25–40	100–500	100–200	
	Root		100–150	500–2000	500–1000	
S. alterniflora (6)	Shoot	0.10–0.8	<0.12	5–13	19–27	199–365
	Root	<0.01–0.1	<0.12–2.0	12–37	46–63	239–510
S. alterniflora (7)	Leaves		1.6 ± 1.1	3.7–6.5	4.2–26.5	
	Stems		0.9 ± 0.8	0.9–7.1	12.9–32.2	
	Root		120.6 ± 54.8	100.8–212.3	236–898	
	Rhizome		19.7 ± 20.8	6.3–52.8	29.5–168.0	
S. alterniflora (8)	Shoot		0.9	6.8	29.77	
S. alterniflora (9)	Leaves			4.2–6.3	6–14	128–385
	Stem			4.3–7.7	6–47	39–372
	Root			4.7–13.5	16–173	417–3030
S. alterniflora (10)	Shoot		2–10	5–30	25–80	
	Root		5–25	20–100	25–200	
S. maritima (5)	Leaf		30–60	100–800	100–400	
	Root		50–175	400–4500	400–1500	
S. maritima (11)	Leaves	0.4 ± 0.0	4.5 ± 0.7	83 ± 5	102 ± 9	1513 ± 137
	Stems	0.7 ± 0.2	<LD	36 ± 4	33 ± 11	270 ± 22
	Root	2.4 ± 0.5	6.0 ± 2.4	348 ± 58	193 ± 54	4160 ± 945
	Rhizome	1.0 ± 0.2	0.4 ± 0.1	74 ± 10	48 ± 14	636 ± 83
S. maritima (12)	Leaves	0.60–0.79	2.7–5.2	6.7–10.1	22.0–30.3	
	Stems	0.73–0.74	0.9–5.2	6.2–7.0	13.3–34.0	
	Root	1.36–1.79	8.1–37.3	18.1–25.8	48.7–57.2	
S. maritima (13)	Shoot	0.02–0.03		2.8–3.8	17–21	0.00–0.01%
	Root	2.5–19		48–287	743–4185	2.2–14%
S. maritima (13)	Shoot	0.00–0.01		3.4–6.1	17.0–20	0.01–0.04%
	Root	0.19–1.9		17–105	14–174	2.5–7.8%
S. maritima (14)	Shoot	1–5	5–20	10–20	10–50	
	Root	1–5	10–50	10–50	50–150	
S. anglica (15)	Shoot	0.1–1.1		2–6	24–50	
	Root	0.5–16		3–37	40–190	

References: 1—Prassad et al. 2006; 2—Kabata-Pendias 2011; 3—Idaszkin et al. 2014; 4—Idaszkin et al. 2015; 5—Cambrollé et al. 2008; 6—Hempel et al. 2008; 7—Windham et al. 2003; 8—Burke et al. 2000; 9—Alberts et al. 1990; 10—Quan et al. 2007; 11—Curado et al. 2014; 12—Phillips et al. 2015; 13—Caetano et al. 2008; 14—Couto et al. 2013; 15—Otte et al. 1991

Table 8 Bioconcentration (BCF) and translocation (TF) factors for *Spartina* spp. ($N = 3$, mean ± SD)

		BCF				TF			
Specie	Site	Pb	Cu	Zn	Fe	Pb	Cu	Zn	Fe
S. densiflora	1sd	0.2 ± 0.1	0.9 ± 0.1	1.1 ± 0.1	1.0 ± 0.2	0.5 ± 0.3	0.3 ± 0.1	0.3 ± 0.0	0.2 ± 0.0
	3sd	0.1 ± 0.0	2.9 ± 0.3	5.3 ± 0.8	0.4 ± 0.2	–	0.6 ± 0.2	0.7 ± 0.3	1.0 ± 0.4
	5sd	–	4.6 ± 0.2	19.6 ± 2.5	0.3 ± 0.1	–	0.6 ± 0.2	0.3 ± 0.1	0.7 ± 0.2
S. alterniflora	5sa	0.3 ± 0.0	6.2 ± 2.2	10.5 ± 1.3	0.2 ± 0.1	–	0.4 ± 0.1	0.4 ± 0.2	1.3 ± 0.6
	8sa	–	8.7 ± 1.0	5.5 ± 1.3	0.9 ± 0.5	–	0.5 ± 0.2	0.5 ± 0.1	0.5 ± 0.2

– not calculated due to values below the detection limit

and subsequent metal return through senescent leaves to sediments should be taken into account. *S. alterniflora* can release large quantities of metals into the salt marsh environment through both excretion and deposition of leaves. In fact, it has been reported that salt-tolerant plants can excrete large amount of metals in salt crystals produced by salt glands of leaves (Burke et al. 2000; Weis and Weis 2004).

According to these results, metal distributions in tissues of plants from SAB are in agreement with the expected patterns reported in the literature for *Spartina* genus, showing higher metal concentrations in below-ground structures such as rhizomes and roots than shoots as a consequence of reduced metal translocation (Quan et al. 2007; Caetano et al. 2008; Cambrollé et al. 2008; Caçador et al. 2009; Almeida et al. 2011; Redondo Gómez 2013). However, their influence on the global distribution of metals within the bay would not be relevant, due to the following facts: the most metal enriched area (inside the Encerrado channel) is dominated by high salt marsh (Isacch et al. 2006), where metal retention is less likely to occur than in the low salt marsh (Otte et al. 1991; Luque et al. 1999; Weis and Weis 2004). In oxidized sediment, as in high salt marsh, metals are exposed to air and they are present in oxyhydroxide form. Whereas in low salt marsh, the time of inundation is longer and the anoxic sediment favors the formation of insoluble sulfur and less bioavailable forms of metals (Weis and Weis 2004). On the other hand, the area of the bay where large low salt marsh is developed (outside the Encerrado channel) is subject to a very low level of contamination.

Conclusions

For the first time a screening-level risk-assessment approach has been conducted in the protected area of the San Antonio Bay. Comparisons of values with environmental guidelines and with natural concentrations help us to conclude that hazardous metal levels would be restricted to the innermost area of the Encerrado channel. Concentrations decrease rapidly with increasing distance to the Pile and, regarding historical evolution, a decline has been observed at the scale of the complete bay. This shows a clear washing of the system probably influenced by its hydrological characteristics.

Given the remobilization and resuspension of sediments and their distribution due to the tidal hydrodynamics, all organisms could be affected, regardless of their location in the studied area. Furthermore, the use of different extraction procedures showed that Zn, Cu, and particularly Pb in sediments from the Encerrado channel were associated to the more unstable fraction. Thus, under physical and chemical changes, they would be susceptible to increase their potential for remobilization and pass into the water column.

Nevertheless, plants located within the Encerrado channel seem to be able to deal with pollution, probably because of its high location, where oxidized conditions favored mobility of metals. Under these conditions, the metals could be dispersed into the bay by seawater instead of being retained in the sediment. High concentrations of metals in salt marsh sediments not necessarily lead to elevated concentrations in plant tissues, maybe because of its high position in the contaminated channel (*S. densiflora* inside the channel) or due to growth in the area less polluted (*S. densiflora* as well as *S. alterniflora* outside the channel). Studies on other substrates such as water, atmospheric dust, and biota would help to understand the cycle of metals in this ecosystem.

In contrast, trace metal concentrations in the soils from Pile were the highest. These soils contain concentrations of Cd, Pb, Cu, and Zn that exceed the values for agricultural, residential, and industrial land uses and represent a human health risk. It is noteworthy that the mining wastes still coexist with the population of San Antonio Oeste. Only recently, a remediation strategy has been initiated. A containment cell will be built, far from the urban zone, to hold the contaminated mining wastes from the Pile. The removal and transport of contaminated material must be carefully done to avoid releasing the contaminated particles.

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