Baseline

Trace metal concentrations in *Spartina densiflora* and associated soil from a Patagonian salt marsh

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ABSTRACT

The objectives of this study were to (i) assess *in situ* trace metal concentrations in soil and in *Spartina densiflora* in a Patagonian salt marsh (Rawson, Chubut, Argentina) and (ii) investigate the relationship between trace metal concentrations in soils and in plants to improve our knowledge regarding the ability of *S. densiflora* to take up and accumulate trace metals from the soil within its native region. Our results indicate that the soil and *S. densiflora* exhibit low metal concentrations in the Rawson salt marsh. *S. densiflora* accumulates Zn in below- and above-ground plant structures and Cr in below-ground parts. These results suggest at the time of this study there is scarce human impact associated with metals in the Rawson salt marsh.

The impact on coastal and estuarine environments of different pollutants such as trace metals, oil, pesticides, and fertilizers is an issue of great concern to ecologists and environmentalists (Mendelssohn et al., 2001; Marcovecchio and Ferrer, 2005). Although trace metals are natural elements in the environment, they may be enriched to toxic levels by human activities. Moreover, their concentration, behaviour and partitioning can be affected by different soil features such as pH, redox potential, salinity, texture, and organic matter content (Kabata-Pendias, 2011). Intertidal environments are subject to the input of contaminants discharged into seas or rivers and carried in water by the action of the tides. Salt marshes are coastal ecosystems characterized by the presence of vascular halophytes that have an important role in the dynamics of pollutants (Adam, 1990; Weis and Weis, 2004). In these environments, contaminants can be trapped in soils, remaining in biologically unusable forms (Hung and Chmura, 2007; Botté et al., 2010) or may be absorbed by vegetation (Reboreda and Caçador, 2007a,b; Hempel et al., 2008; Redondo-Gómez et al., 2009; Caçador et al., 2009; Duarte et al., 2010; Almeida et al., 2011). Furthermore, the physical and chemical soil conditions can be altered by plants that are able to produce micro-environmental changes, affecting metal mobility, speciation, bioavailability and in consequence their potential toxicity (Reboreda and Caçador, 2007a,b). Plants have different mechanisms for regulating the uptake of metals (Greger, 2004). For example, some plants species can depress the uptake of metals increasing the pH in the rhizosphere, which decreases the mobility of the metals (Greger, 2004). Conversely, the acidification of the rhizosphere through the release of H+ or exudates (which can act as complexing agents) may favour metal mobility, thus increasing their bioavailability (Mucha et al., 2005). Plants living in environments subject to submerged periods, such as *Juncus maritimus* and *Spartina alterniflora*, can transport oxygen through the aerenchyma to the rhizosphere zone (Justin and Armstrong, 1987; Maricle and Lee, 2002), thus increasing oxygenation, creating a gradient that forces the metals to be concentrated toward the roots (Burke et al., 2000).

When metals are absorbed by the plants, they can be retained in their roots or rhizomes (Reboreda and Caçador, 2007b; Hempel et al., 2008; Duarte et al., 2010) or translocated to their shoots or leaves (Burke et al., 2000; Weis et al., 2003); depending on the physicochemical soil parameters, the plant species, and the metal (Weis and Weis, 2004). By absorbing metals, plants can act as a conduit, mobilizing them from the soil to the food web, either to be consumed directly by herbivores, or through plant debris that are incorporated in basal level of the food chain. The decomposition rate and the contribution of detritus are different among the plant species; therefore the recycling of metals and their return to the aquatic environment also depends on the species (Duarte et al., 2010). Thus, salt marshes can act as sink or source of metals for the surrounding aquatic environment.

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It is widely accepted that salt marshes are highly productive ecosystems critical to the maintenance of the regional integrity for both terrestrial and marine communities (Mitsch and Gosselink, 2000). Anyway, most studies evaluating the concentration of trace metals in salt marshes have been conducted in highly populated or highly industrialized areas (Redondo-Gómez et al., 2009). Thus, pristine or scarcely impacted environments have been poorly studied, despite the importance of having a reference study, which may permit early diagnosis of pollution and achievement of low cost environmental recovery practices, both economic as ecological and logistical.

The Argentinean Patagonia is usually considered an area with low human impact (Bortolus and Schwindt, 2007), considering its low urbanization and low port and industrial activities in relation to large cities. Although there are some studies in Patagonian intertidal environments (Gil et al., 1999; Vázquez et al., 2007; Marinho et al., 2013), to date there is no research evaluating the levels of trace metals in salt marshes. The objectives of this study were to (i) assess *in situ* trace metal concentrations in soils and in *Spartina densiflora* in a Patagonian salt marsh (Rawson, Chubut, Argentina) and (ii) investigate the relationship between trace metal concentrations in soils and in plants to improve our knowledge regarding the ability of *S. densiflora* to take up and accumulate trace metals from the soil within its native region.

The present study was conducted in "Rawson salt marsh", the *Spartina*-marsh located on the mouth of the Chubut River, Chubut Province, Argentina (65°04′S, 43°20′W, Fig. 1). This salt marsh is mostly inhabited by the cordgrass *S. densiflora*, accompanied by *Sarcocornia perennis* in a very low proportion (Bortolus et al., 2009). The Chubut River arises in the Andes mountains, crosses from west to east of Chubut Province, and discharges its waters into the Atlantic Ocean at "Bahía Engaño" near a fishing port. In its lower course the river flows through the most populated area, where the largest riverside cities (Trelew: ~90,000 inhabitants and Rawson: ~34,000 inhabitants) and urban, agricultural, and industrial wastewaters are discharged. At the same time, the river is the principal source of water for several neighbouring cities of Chubut Province. Previous studies show moderate levels of pollution with Zn, Cu, and Pb in Bahía Engaño (Gil et al., 1999; Mohamed, 2008).

Two sampling sites were chosen in the Rawson salt marsh along a linear transect (running from east to west) to detect any contamination gradient: one named the 'RC' site, placed on the mouth of Chubut River, located nearest to Rawson City, and the second called 'RP' site located closest to the Rawson Port at the outlet of the river into the Atlantic ocean. In the spring of 2012, at each site, five core samples were collected at low tide from *S. densiflora* stands, all spaced 1 m from each other. Each sample (15-cm-diameter and 15-cm-depth) consisted of a block of soil with tillers, rhizomes and roots of *S. densiflora*. The redox potential (Eh) and pH of the soil in the root zone (0–10 cm) were determined in the field using a portable pH/Eh (ORP) meter and an electrode system Termo/pH meter Altronix TPA-IV. Samples were stored in polyethylene bags, transported to the laboratory, and frozen to −20 °C until analyzed.

The soil from the root zone (0–10 cm) was removed from the roots and rhizomes of each plant were dried at 85 °C until constant weight, and sieved through a 2 mm mesh to remove large stones and dead plant material. Electrical conductivity (EC) was measured with a conductivity meter after diluting 10 g of dried and sieved
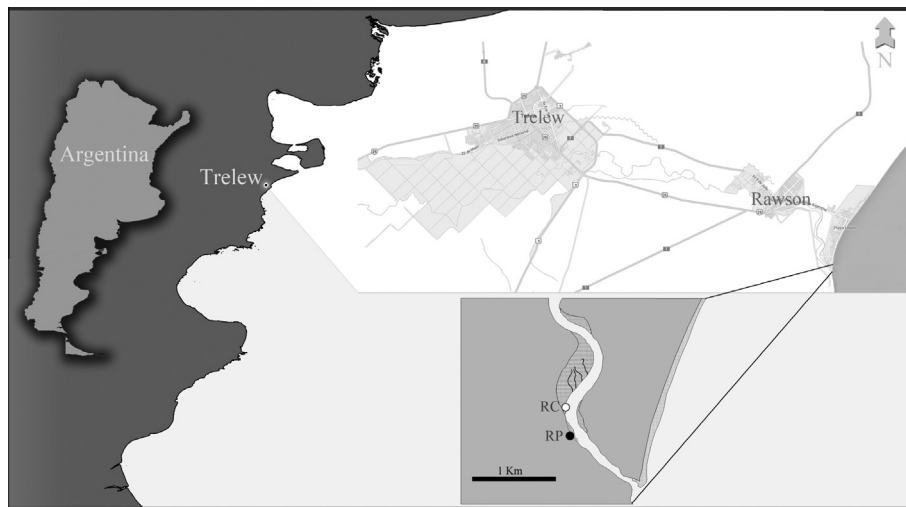

Fig. 1. Location of the sampling sites in the Rawson salt marsh.

Table 1
Trace metal concentrations in Reference Material and Recovery Percent.

Element	PACS-2			BCR-060		
	Media ± SD (n = 5)	% R	LD ($\mu g\,g^{-1}$)	Media ± SD (n = 5)	% R	LD ($\mu g\,g^{-1}$)
Cd ($\mu g\,g^{-1}$)	1.8 ± 0.1	88	0.25	2.1 ± 0.2	93	0.1
Cr ($\mu g\,g^{-1}$)	55.7 ± 5.1	61	2.50	31.6 ± 0.9[a]	122	1.0
Cu ($\mu g\,g^{-1}$)	275.6 ± 10.1	89	1.25	46.2 ± 1.3	90	0.5
Pb ($\mu g\,g^{-1}$)	158.0 ± 9.3	86	5.00	54.1 ± 4.9	84	2.0
Ni ($\mu g\,g^{-1}$)	33.1 ± 1.4	84	2.50	40.3 ± 1.2[a]	101	1.0
Zn ($\mu g\,g^{-1}$)	327 ± 14	90	0.25	441.7 ± 34.1[a]	141	0.1
Fe ($mg\,g^{-1}$)	3.29 ± 0.14	81	2.50	0.23 ± 0.03[b]	99	1.0

[a] Values no certified.
[b] Fe as Fe_2O_3.