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Uptake and accumulation of metals in *Spartina alterniflora* salt marshes from a South American estuary

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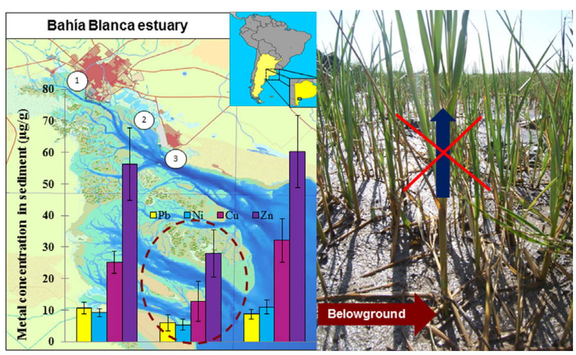
HIGHLIGHTS

- Metal concentrations in sediments and plants were always in this order: Zn > Cu > Pb ≥ Ni > Cd.
- Site 2 achieved the lowest values for OM, fine sediments and all metals in sediments.
- All metals were in higher concentrations in belowground than in aboveground tissues.
- Bioconcentration factors for all metals were higher in site 2.
- Belowground pools were usually higher than aboveground pools for all metals.

GRAPHICAL ABSTRACT



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ABSTRACT

Salt marshes are capable of reducing metal pollution in coastal waters, but this capacity is highly dependent on the metal, the physico-chemical characteristics of the sediment, the plant species, the production of biomass, the time of the year, etc. The aim of this study was to assess the uptake and accumulation of Pb, Ni, Cu and Zn in *Spartina alterniflora* from three salt marshes within the Bahía Blanca estuary (BBE), a human-impacted Argentinean system. Metal concentrations in sediments and plants showed the same order at all sites: Zn > Cu > Pb ≥ Ni. The site with lower organic matter and fine sediment content had lower metal concentrations in the sediments, but not a lower metal content in the plant tissues, meaning that the sediment characteristics influenced the metal concentrations in the sediment and their uptake by plants. Despite differences in sediment characteristics between sites, metals were always higher in the belowground tissues than in aboveground ones and, in general, higher in dead than in live tissues. Some metals were accumulated in plant tissues, but not others, and this is dependent on the metal and the sediment characteristics. Allocation patterns of metals in tissues of *S. alterniflora* were mainly dependent on metal concentrations, determining higher belowground pools, but the aboveground pools were important in some cases due to higher biomass. Partitioning of metals in above or belowground pools determines their fate within the estuarine system, since tissues can decompose in situ (belowground) or be exported (aboveground). Seasonal dynamics were important for some variables but were less noticeable than the differences between sites and tissues. Our results indicate that *S. alterniflora* from the BBE is efficient in

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accumulating some metals, despite usually low metal concentrations in sediments and plants. This accumulation capacity has implications for the whole system through the fate of the tissues.

1. Introduction

Salt marshes are recognized worldwide for the various ecosystem services they provide (Barbier et al., 2011). One of these services is the reduction of metal pollution in coastal waters due to the capacity of halophytes to sequester metals in their tissues, although this capacity is highly variable (Anjum et al., 2014). Halophytes uptake metals during growth at a rate that is dependent on metal mobility and availability in the sediment, which is in turn determined by the physico-chemical characteristics of the sediment (redox potential, pH, organic matter content, grain size, etc.) (Kabata-Pendias, 2010). The uptake of metals also depends on the metal, the plant species and the tidal energy, among others (e.g., Weis and Weis, 2004).

Once metals are absorbed by halophytes, they can be retained in the belowground tissues or be translocated to the shoots and leaves, depending on the metal, the plant species, the time of the year, etc. (Weis and Weis, 2004; Anjum et al., 2014; Phillips et al., 2015; Petranich et al., 2017). The allocation of metals in the below or aboveground tissues determines whether metals are retained within the salt marsh (belowground) or whether they are likely to be exported to other areas of the coastal system through the action of tides and waves (aboveground) (Windham et al., 2003; Caçador et al., 2009; Duarte et al., 2010; Duarte et al., 2017). In addition, the differential metal distribution in live and senescent aboveground tissues and the biomass production of each type of tissues are critical factors that control the amount and rate of release of metals (Caçador et al., 2009; Duarte et al., 2010; Couto et al., 2013; Song and Sun, 2014; Chen et al., 2017). The release of metals back to the environment through decomposition varies with the plant species, the chemical composition of the tissues and environmental factors (Liao et al., 2008; Negrin et al., 2012a; Song and Sun, 2014; Chen et al., 2017). Moreover, detritus produced from senescent aboveground tissues is the base for most marine food webs, resulting in the introduction of metals to higher trophic levels (Moore et al., 2004; Weis and Weis, 2004; Bergamino and Richoux, 2015). Hence, the partitioning of metals between different tissues ultimately determines their fate within the coastal environment.

One of the most studied halophytic species regarding metal accumulation is *Spartina alterniflora* Loisel., including both field and experimental laboratory studies (Redondo-Gómez, 2013). *S. alterniflora* is a perennial C_4 grass which reproduces mainly by rhizomes and is native of the Atlantic coast of North America but has been introduced worldwide, mainly for erosion control (Mobberley, 1956; Bortolus et al., 2015; Global Invasive Species Database, 2018). *S. alterniflora* usually accumulates metals in belowground tissues (Alberts et al., 1990; Windham et al., 2003; Quan et al., 2007; Marinho et al., 2017; Chen et al., 2017), as most salt marsh plants (e.g., Caetano et al., 2008; Caçador et al., 2009; Couto et al., 2013; Idaszkin et al., 2014; Song and Sun, 2014; Phillips et al., 2015; Petranich et al., 2017), although some authors have found the opposite pattern (Pang et al., 2017). Despite the importance of this species in salt marshes throughout the world, most of the information comes from studies in North America and, more recently, in Asia (Redondo-Gómez, 2013). In the Southern Hemisphere, *S. alterniflora* is usually the dominant species from southern Brazil to the northern coasts of Argentina (Isacch et al., 2006), but only a few studies deal with metal accumulation in its tissues. To the best of our knowledge, there are only two studies on the topic from Argentina, both from the Bahía Blanca estuary (BBE; Botté, 2005; Hempel et al., 2008), and two reviews partially based on them (Negrin et al., 2016; Marcovecchio et al., 2016). However, the importance of the sediment characteristics and the seasonal dynamics of metals and biomass production were not evaluated in these previous studies.

The aim of this study was to assess the uptake and accumulation of Pb, Ni, Cu and Zn in *S. alterniflora* in three salt marshes within the BBE, a human-impacted Argentinean coastal system. We conducted seasonal sampling and evaluated the concentration of these metals in the sediment and plant tissues together with the biomass production and the physico-chemical characteristics of the sediment at each site. We hypothesized that: 1) sediment characteristics greatly influence the concentration of metals in sediment, which in turn determine different accumulation and distribution patterns in the different populations of *S. alterniflora*; 2) seasonal dynamics in plant growth and the uptake of metals influence metal distribution within salt marsh compartments.

2. Materials and methods

2.1. Study area

The BBE (Fig. 1) is a mesotidal shallow system that extends over 2300 km^2 and is formed by a series of northwest to southeast oriented tidal channels separated by extensive tidal flats, salt marshes and islands. It has a main navigation channel, the Canal Principal, of 60 km long (Piccolo et al., 2008). Tides and winds are the main inputs of energy to the estuarine circulation. Tidal energy is provided by a quasi-stationary semidiurnal tidal wave (Perillo and Piccolo, 1991). Winds are persistent all year round and their annual mean velocity is 22.5 km/h. The climate of the region is temperate (mean temperature is 15 °C), with a large spatial and temporal variability in the precipitation, but usually higher in spring and summer (Piccolo, 2008). Rainfall patterns affect the freshwater input to the BBE, which is usually low (mean discharge of 241,000 m^3/day) due to the scarce discharge of the only two permanent tributaries: the Sauce Chico and the Napostá Grande streams (Limbozzi and Leitão, 2008).

The water column of the BBE is characterized by high salinity and turbidity, and high levels of nutrients and particulate organic matter are found most of the year (Freije et al., 2008). Dissolved metal concentrations are usually low, but the particulate forms of some metals are in higher concentrations than in other polluted estuaries (Botté et al., 2007; La Colla et al., 2015; Fernandez Severini et al., 2017; La Colla et al., 2018). Regarding metals in sediments, the concentrations in tidal flats were lower than those reported for other estuarine systems (Botté et al., 2010; Serra et al., 2017; Simonetti et al., 2017). The anthropogenic impact depends on different local pressures: cities, industries, cattle production and cropping. The most important deep-water port system of Argentina (Ingeniero White) is located in association with these industries. Due to the circulation of big ships, the Canal Principal is regularly dredged with a considerable removal of sediments.

Salt marshes are distributed along the margins of the channels and islands of the BBE, and *S. alterniflora* is one of the most abundant species (Isacch et al., 2006). Pure stands of *S. alterniflora*, which cover an area of 196 km^2, are commonly restricted to marshes in the middle and outer zones of the BBE, and rarely appear in the inner area (Piovan, 2016). *S. alterniflora* marshes are expanding their cover in the estuary in a process that involves sedimentation –which is mainly related to dredging activities- and mudflat colonization by plants (Pratolongo et al., 2010, 2013). The present study was conducted in three natural salt marshes within the BBE: Maldonado (hereafter site 1), Villa del Mar (hereafter site 2) and Puerto Rosales (hereafter site 3) (Fig. 1). The intertidal zones from the chosen sites are mainly covered by *S. alterniflora*, which can be up to 1.50 m in height (Lamberto et al., 1997).