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Metal speciation in salt marsh sediments: Influence of halophyte vegetation in salt marshes with different morphology

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A B S T R A C T

Salt marshes provide environmental conditions that are known to affect metal speciation in sediments. The elevational gradient along the marsh and consequent differential flooding are some of the major factors influencing halophytic species distribution and coverage due to their differential tolerance to salinity and submersion. Different species, in turn, also have distinct influences on the sediment's metal speciation, and its metal accumulation abilities. The present work aimed to evaluate how different halophyte species in two different salt marshes could influence metal partitioning in the sediment at root depth and how that could differ from bare sediments. Metal speciation in sediments around the roots (rhizosediments) of *Halimione portulacoides*, *Sarcocornia fruticosa* and *Spartina maritima* was determined by sequentially extracting operationally defined fractions with solutions of increasing strength and acidity. Rosário salt marsh generally showed higher concentrations of all metals in the rhizosediments. Metal partitioning was primarily related to the type of metal, with the elements' chemistry overriding the environment's influence on fractionation schemes. The most mobile elements were Cd and Zn, with greater availability being found in non-vegetated sediments. Immobilization in rhizosediments was predominantly influenced by the presence of Fe and Mn oxides, as well as organic complexes. In the more mature of both salt marshes, the differences between vegetated and non-vegetated sediments were more evident regarding *S. fruticosa*, while in the younger system all halophytes presented significantly different metal partitioning when compared to that of mudflats.

1. Introduction

Salt marshes play important roles in the estuarine ecosystem, like nutrient cycling or shoreline stabilizers. They are considered natural sinks for pollutants transported in the ecosystem (Caçador et al., 1993, 2000; Doyle and Otte, 1997), functioning as buffers. The usual proximity to densely populated and/or heavily industrialized areas leaves salt marshes facing important discharges of such pollutants. The idea that estuaries had the ability to dilute and disperse pollutants led to urban and industrial discharges into estuarine waters without pretreatment of wastes. Together with agricultural and road runoff, urban and industrial discharges added up to increase the pollutant load in these environments, namely metals (Williams et al., 1994). Metals are not naturally removed or broken down, and end up accumulating in the estuarine environment, of which salt marshes are a part (Doyle and Otte, 1997). Halophytes influence the concentration of metals in salt marsh sediments, with increasing concentrations in the sediment between roots when compared to bulk sediments (Caçador et al., 1996a; Doyle and Otte, 1997; Reboreda and Caçador, 2007b). Species distribution in salt marshes is influenced by the typical elevational gradient along the marsh and consequent differential inundation periods (Sanchez et al., 1996). The differential plant zonation will in turn influence a variety of physical, chemical and biological processes (Williams et al., 1994) and ultimately affect the sediment's metal accumulation capacity (Reboreda and Caçador, 2007b). Plants promote these changes by several ways. The pumping of atmospheric oxygen by the root system (Koop-Jakobsen and Wenzhöfer, 2014), for example, is responsible for oxidizing the sediment, causing shifts in the sediment redox potential, thus potentially affecting mobility and availability of metals (Williams et al., 1994). Another example

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involves plant detritus: plant litter actively draw metals from the water, which can immobilize metals in the salt marsh sediments, making them less available to surface waters (Lyngby and Brix, 1989). Metal uptake by plants does not usually reflect total metal concentrations in sediments (Caçador et al., 2009). Instead, it is the form of metals, i.e., the geochemical fraction to which they are bound, that will influence their bioavailability for plant uptake (Reboreda and Caçador, 2007b). Exchangeable and water-soluble forms are more bioavailable, while metals associated to the crystalline lattice of minerals are potentially unavailable to biota (Weis and Weis, 2004). Parameters such as soil texture or organic matter content combine to increase availability or immobilize metals (Greger, 2004). Plants themselves not only change the sediment's ability to accumulate metals, as mentioned above, but also exert influence on metal speciation, and consequently in metal mobility (Caçador et al., 1996b; Reboreda and Caçador, 2007a; Reboreda et al., 2008).

A detailed fractionation scheme was used in the sediments from two salt marshes with distinct morphologies (young and mature *cf.* Valiela et al., 2000) and their adjacent areas of intertidal mudflats. Three of the most abundant halophytes in Mediterranean salt marshes were chosen to investigate the influence of vegetation (and its absence) on metal mobility and availability in salt marsh sediments.

2. Material and methods

2.1. Study area and sampling

Sampling occurred in two salt marshes in the left margin of the Tagus estuary (Fig. 1), in the spring of 2010. Hortas salt marsh (38° 45.571′ N; 8° 54.451′ W) is located in the vicinity of Alcochete, in the middle estuary, next to an area that comprises the Tagus Estuary Natural Reserve. Rosário saltmarsh (38° 40.161′ N, 9° 00.198′ W) is located in the lower estuary, next to an area with higher urban and industrial pressures, in the surroundings of densely populated cities (e.g. Montijo). Rosário is a mature marsh with dense and well established vegetation, while Hortas is a young marsh still accreting and presenting the typical sparse vegetation stands of a young marsh (Duarte et al., 2013a).

Both salt marshes are dominated by three halophyte species: *Spartina maritima* Fernald (Poales, Poaceae) in the lower marsh, followed by *Halimione portulacoides* (L.) Aellen (Caryophyllalles, Chenopodiaceae) in the mid-upper marsh, and *Sarcocornia fruticosa* (L.) A.J. Scott (Caryophyllalles, Chenopodiaceae) in the upper marsh (Caçador et al., 1996a, 2013). Sediment cores were sampled beneath pure stands of each species, and in the adjacent non-vegetated area (*Mud*). Samples from 5 to 8 cm deep (higher root density) were sliced from the sediment cores for further analysis. All samples (3 replicates per type of vegetation cover, per site; n = 24) were quickly transported to the laboratory in plastic bags within refrigerated boxes. Rhizosediments (sediments beneath vegetation cover at root depth) were cleared from plant material and debris with the aid of tweezers.

2.2. Organic matter content and particle size distribution

Samples were used to determine total organic matter (TOM) content as loss on ignition (LOI), by ashing 1.0–5.0 g of sediment (dry weight), at 550 °C for 4 h. For particle size distribution, samples with 5.0–100.0 g were dried to constant weight in an oven at 60 °C for 72–120 h, after being washed through a 63 μm sieve to remove all silt and clay particles. The remaining fractions (>63 μm) were determined by sieving sediment samples through an AFNOR type column of sieves with calibrated mesh size, using mechanic shaking to completely separate the different size particles. A total of three size classes were considered: gravel (>2000 μm), sand (63–2000 μm), and silt/clay particles (<63 μm).

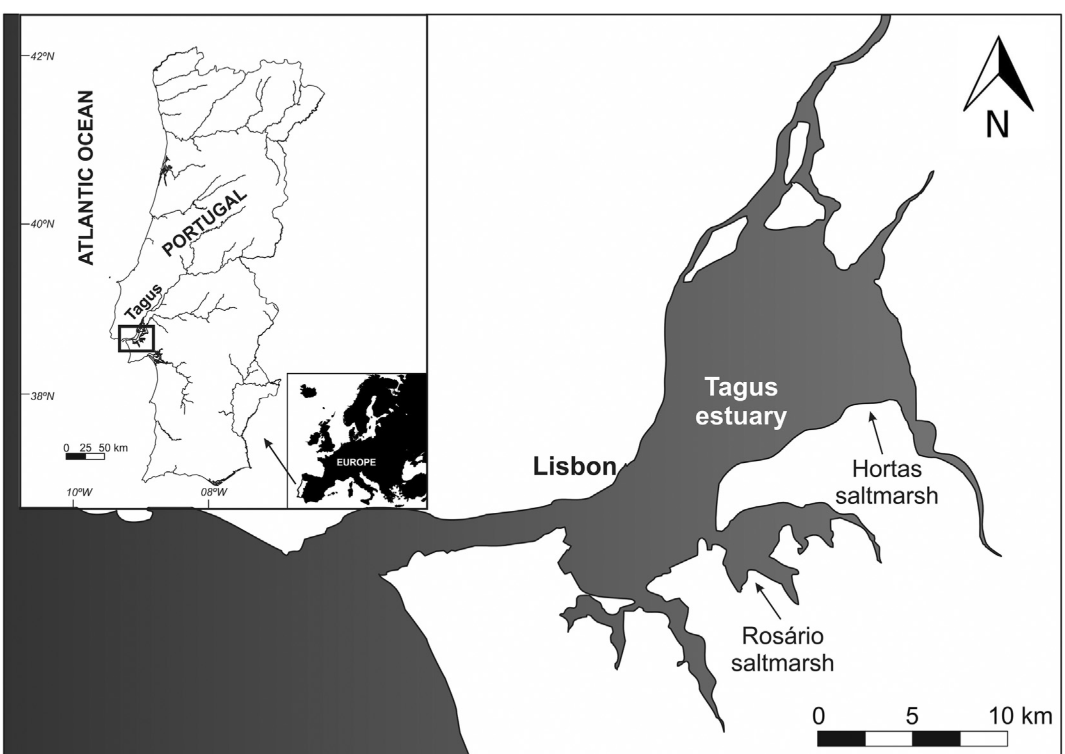

Fig. 1. Tagus estuary and sampling sites (Hortas and Rosário salt marshes).