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Platinum in salt marsh sediments: Behavior and plant uptake

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A B S T R A C T

Platinum is one of the least abundant elements in the earth crust with an average concentration of 0.51 ng g^{-1}, but its use in several human activities (mainly automobile catalytic converters) is leading its enrichment in surface sediments. Whereas, previous studies have assessed the Pt behavior in soils from urban areas, natural systems are still poorly studied.

Accordingly, this study is aimed to characterize the behavior of the Pt released to coastal environments in sediments, ascertain the role of vegetation on the biogeochemistry of this element and assess the transference of Pt into the biological compartments. Several sediment cores were sampled in salt marshes (in unvegetated and vegetated areas) of the Tagus Estuary under different traffic pressure. Platinum concentration was analyzed in solid sediment, interstitial water and roots, leaves and stems of *Sarcocornia fruticosa*, a typical plant in south European salt marshes. In addition, interpretative parameters (e.g. redox potential, dissolved oxygen, pH, total reduced sulfur species, salinity and dissolved Fe and Mn in interstitial waters) were determined to better understand the biogeochemical cycle of Pt in salt marsh sediments.

Although surface enrichment of Pt exists in the sediments at Low Traffic Station (2.8 ng g^{-1}), the highest enrichment was found at High Traffic Station where concentration was, in some cases, up to 40 ng g^{-1}, linked to traffic emissions. However, dissolved Pt in interstitial waters (from 0.14 to 0.70 ng L^{-1}) did not show this superficial maximum. This dissimilarity points out the unreactivity of traffic-borne Pt and the dissolution/precipitation cycle of natural Pt linked to Mn and O_2 cycle, depending on the redox conditions, highly controlled by the vegetation. Platinum concentration in roots (0.9 ± 0.6 ng g^{-1}) is reflecting the Pt concentration in the interstitial waters in each moment, even though at the two peaks of dissolved Pt (up to 2.5 ng L^{-1}) found at deeper layers, reflecting a low bioaccumulation. However, results pointed that a different Pt species (with different bioavailability) may exist in both stations. Besides, Pt mean value in stems and leaves (0.04 ± 0.05 ng g^{-1}) indicates a low translocation of Pt from the roots to aerial parts.

Therefore, the role of vegetation is fundamental on the geochemical behavior of Pt in sediments, due to the control of the redox conditions by roots in the surrounding sediments (between the O_2 release and the organic matter degradation) and leading to Pt species of varying bioavailability.

1. Introduction

Platinum (Pt) is one of the least abundant elements is the earth crust, due to its extreme affinity to the core (Rauch and Morrison, 2008) where Pt concentration is about 4 orders of magnitude higher than in the upper continental crust (5.5 μg g^{-1} and 0.51 ng g^{-1} respectively; Lorand et al., 2008; Peucker-Ehrenbrink and Jahn, 2001).

Platinum has been used in several different industrial activities like chemical, biomedical or jewelry, but automobile industry with the production of catalytic converters for engine gas emission reduction, currently represents 40–45% of the world Pt demand (Brenan, 2008; Johnson Matthey, 2013). Since the 80s, when cars started to use catalytic converters in Europe, 70% of the European Pt demand was for the manufacturing of catalytic converters (Johnson Matthey, 2013). Previous studies have reported an enrichment in superficial sediments and deposits linked to human activities in urban areas (Fritsche and Meisel, 2004; Rauch et al., 2004a; Schäfer and Puchelt, 1998; Sutherland et al., 2007; Tuit et al., 2000; Whiteley and Murray, 2005) – almost all traffic-borne Pt settles in the first 2 m away from the road (Fritsche and Meisel, 2004; Helmers and Mergel, 1998; Schäfer and Puchelt, 1998; Zereini et al., 2001), although wind or runoff may vary this dispersion (Schäfer and Puchelt, 1998) – although small fractions

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of Pt can be transported through the atmosphere to remote environments (Rauch et al., 2004b; Rauch and Morrison, 2008; Sen et al., 2013; Soyol-Erdene et al., 2011). However, some authors revealed that only the 1% of the anthropogenic Pt is soluble (Ravindra et al., 2004), but the post-depositional reactivity of natural Pt is unknown, and assessing its potential uptake, accumulation, toxicity to living organisms and transfer through the food web is vital to evaluate it potential risk.

Some studies have analyzed Pt concentration in biological natural samples (Alt et al., 1988, 1997; Beinrohr et al., 1993; Hodge et al., 1986; Pino et al., 2010) or food (Alt et al., 1997; Fragnière et al., 2005; Hoppstock et al., 1989) to ascertain concentrations in different matrices. Others have advanced in the research of the Pt uptake, designing tests where different organisms are grown in model Pt-rich environments (Cosden et al., 2003; Moldovan et al., 2001; Schäfer et al., 1998; Zimmermann et al., 2004) or in natural contaminated ones (Haus et al., 2007; Moldovan et al., 2001; Orecchio and Amorello, 2010; Rauch and Morrison, 1999). Experimental investigations revealed that Pt is effectively accumulated by terrestrial and aquatic plants and other organisms (Zimmermann and Sures, 2004), reflecting an environmental increase in this element concentration (Cosden et al., 2003; Helmers and Mergel, 1998; Neira et al., 2015; Schäfer et al., 1998). Nevertheless, there is a lack of studies dealing with the long-term accumulation of Pt by plants under natural conditions.

The characteristics of salt marshes and, specially, of their dominant halophytic plant species, which have a strong capability to accumulate contaminants in belowground biomass (e.g. Pb, Cr, Zn, Ni, Cu, As, Cd, Co), have been well studied improving the understanding of the biogeochemical cycle of several trace elements (Caçador et al., 1996, 2009; Caetano et al., 2007, 2008; Duarte et al., 2010; Santos-Echeandía et al., 2010; Sundby et al., 2003, 2005; Tanackovic et al., 2008). The ability of these plants to phytostabilize contaminants by uptake is due to their high biomass production (Duarte et al., 2010), and this has entailed their use for phytoremediation purposes (Caçador et al., 2009; González-Alcaraz et al., 2011). Therefore salt marsh vegetation was selected as an incomparable environment to assess the Pt bioaccumulation or transfer to the biological compartments.

The Pt behavior in the sediments of salt marshes is poorly known. Only two previous studies, also in the Tagus estuary salt marshes, reported a high input of traffic-borne Pt in surface sediments (Almécija et al., 2015; Cobelo-García et al., 2011). Thus, sediments, rhizoconcretions, interstitial waters and roots, stems and leaves of *Sarcocornia fruticosa* (the halophytic specie with the highest biomass; Caçador et al., 2009) were collected from the salt marshes of the Tagus Estuary (SW Europe) at two different sites, with daily extremely different traffic densities. The main objectives of this work are, therefore, to study the Pt behavior and its biological uptake in salt marshes and to investigate the role of the salt marsh plants in the biogeochemical cycle of Pt and its post-depositional mobility.

2. Study area

Tagus Estuary (Fig. 1), with a extension of 320 km^2 (40% are salt marshes), is one of the largest estuaries in Europe. The city of Lisbon (Portugal), with 3 million inhabitants, is located in the north bank of the Estuary (Valentim et al., 2013). Salt marsh areas are colonized mainly by *S. fruticosa* (Caryophyllales, Chenopodiaceae), *Sarcocornia perennis* (Caryophyllales, Chenopodiaceae), *Halimione portulacoides* (Caryophyllales, Chenopodiaceae) and *Sarcocornia maritima* (Poales, Poaceae). A typical zonation with homogeneous stands of *S. maritima* as a pioneer species, colonizing bare mud in the lower marsh areas, is found all over the estuary. Across the elevation (20–50 cm) transect, pure stands of *H. portulacoides* follow *S. maritima*, while *S. fruticosa* and *S. perennis* are found in the upper salt marsh. Although the abundance of each changes seasonally or annually due to ecological status, in general the highest biomass corresponds to *S. fruticosa* (Caçador et al., 2009). Marshes are fully inundated twice a day by tidal action (2–4 m of tidal amplitude) through a highly branched system of channels that cross the elevation transect. These channels have 0.5–1.5 m depth promoting the inundation of the higher marsh even at low amplitude tides. During the ebb tide water is drained into the channels due to the water table difference.

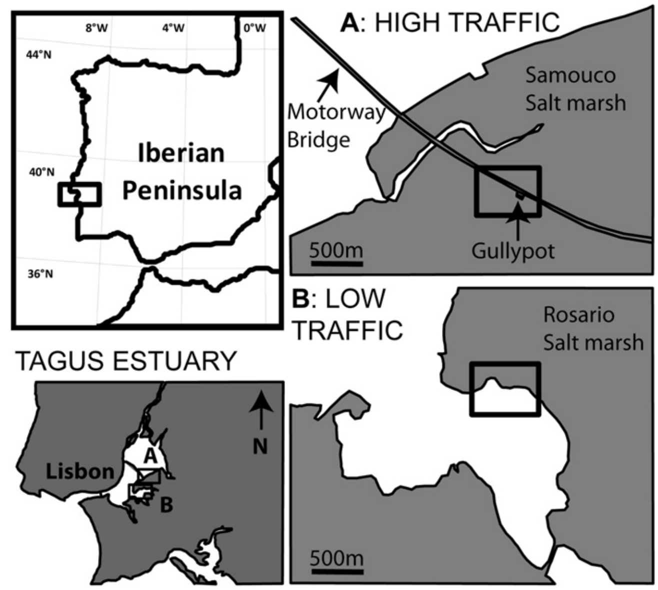

Fig. 1. Map of the study area in the Tagus Estuary (Lisbon, SW Europe). Two sampling points were chosen: (A) High Traffic Station (Samouco), under a motorway highway bridge; and (B) Low Traffic Station (Rosario).

Two stations, under different traffic pressures, were chosen for sampling: *Samouco* Salt Marsh or High Traffic Station (Fig. 1A) and *Rosario* Salt Marsh or Low Traffic Station (Fig. 1B). High Traffic Station is located under a motorway bridge with a traffic density of 50,000 vehicles per day (Instituto de Intraestructuras Rodoviárias IP de Portugal, 2013). Before the bridge was opened in 1998 the human activities in the area were restricted to local fishing. Conversely, the Low Traffic Station is located in the proximity of a heavy industrialized area that includes several chemical plants. During past decades, these industries had discharged effluents enriched in several contaminants directly into the estuary (Caetano et al., 2007; Mil-Homens et al., 2013), especially As, Pb, Zn, Cu or Hg (Vale et al., 2008). Several studies have characterized these inputs into the salt marshes and evaluate how plants behave (Caçador et al., 1996, 2009; Caetano et al., 2007, 2008; Duarte et al., 2010).

3. Materials and methods

3.1. Sampling and treatment of samples

Sediment cores were sampled in the intertidal salt marsh area of the Tagus Estuary in March (spring) and September (summer) 2011. At High Traffic Station (Fig. 1A) cores were collected in two different points, one colonized by *S. fruticosa*, and the other without vegetation. At Low Traffic Station cores were taken only where *S. fruticosa* grows (Fig. 1B). Leaves and stems were also sampled at both stations and seasons. Furthermore, some rhizoconcretions that surrounded the roots of *S. fruticosa*, formed by precipitation of Fe oxides in the pores of the sediment grains (Sundby et al., 1998; Vale, 1990), were collected at Low Traffic Station, while in High Traffic Station rhizoconcretions were not found. These structures may account for 4% of the sediment in the rhizosphere (Vale et al., 2003). Each core was sliced in situ and stored in acid-clean high-density polyethylene bottles, avoiding the air presence inside to minimize oxidation processes in sediments (every 2 cm from 0