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Mercury mobility in a salt marsh colonised by *Halimione portulacoides*

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ABSTRACT

The present study intends to increase the knowledge on the mobility of mercury in a salt marsh colonised by *Halimione portulacoides*. Mercury distribution in the sediment layers and its incorporation into the plant biomass were assessed, as well as the potential export of mercury from the contaminated area to the adjacent environment. Mercury pools in the sediments ranged from 560 to 943 mg m^{-2} and are largely associated with the solid fraction, with just a small amount being associated with the pore waters. Estimated diffusive fluxes of reactive mercury ranged from 1.3 to 103 ng m^{-2} d^{-1}. Despite the above ground biomass values being comparatively higher than below ground biomass values, the mercury pools were much higher in the root system (0.06–0.16 mg m^{-2} and 29–102 mg m^{-2}, respectively). The annual bioaccumulation of mercury in above ground tissues was estimated in 0.11 mg m^{-2} y^{-1}, while in below ground biomass the values were higher (72 mg m^{-2} y^{-1}). The turnover rates of *H. portulacoides* biomass suggest higher mercury mobility within the plant rhizosphere. Taking into account the pools of mercury in above ground biomass, the export of mercury by macro-detritus following the "outwelling hypothesis" is not significant for the mercury balance in the studied ecosystem. The mercury accumulated in the below ground part of the plant is quite mobile, being able to return to the sediment pool throughout the mineralisation process.

1. Introduction

The vital importance of salt marshes is recognised worldwide. Biological productivity, hydrologic flux regulation, biogeochemical cycling of metals and nutrients and habitat for fish and wildlife, are among the several essential ecological functions supported by these ecosystems. (Richardson, 1999; Mitsch and Gosselink, 2000; Caçador et al., 2007; Lillebø et al., 2007; Reboreda and Caçador, 2007). Due to strategic and economical reasons, most of the large cities around the world are located along or nearby estuaries and, as a consequence, and until recently, salt marshes have become subjected to large inputs of contaminants, namely metals derived from urban and industrial effluents which contribute to their vulnerability.

Salt marshes play a significant role in metal recycling in the coastal ecosystems, as they may act as sources, sinks or transformers of chemicals, depending on the wetland type, hydrologic conditions and the time of exposure to the chemical loading (Mitsch and Gosselink, 2000). Some salt marshes may act as sinks for nutrients and contaminants (e.g. Hung and Chmura, 2006; Hwang et al., 2006; Caçador et al., 2007), yet salt marshes can be classified as open systems exporting organic matter (Bouchard and Lefeuvre, 2000) and nutrients which support estuarine and terrestrial food webs, but they can also export metals (Montague, 1999). The outwelling hypothesis was first introduced by Odum in 1968 and states that marsh-estuarine systems produce more material than can be degraded or stored within the systems, and that the excess material is being exported to the coastal ocean supporting near-coastal ocean productivity (Dame and Allen, 1996).

Over recent decades, the anthropogenic sources of mercury (e.g. chlor-alkali plants) in aquatic systems have been reduced, due to the high number of restrictive rules and yet mercury is still one of the most hazardous contaminants present in the aquatic environment and it is included in the list of high priority environmental pollutants within the scope of the European Water Framework Directive (WFD). Once released into the aquatic environment, inorganic mercury salts can be converted into more toxic forms, such as organic mercury compounds, particularly methylmercury. The toxicity of organic mercury compounds is higher due to the higher solubility in lipids, which increases the potential for biological uptake and bio-concentration. Methylmercury can be effectively taken up by aquatic organisms with bio-concentration factors of 10^4–10^7 (Wiener et al., 2003) and is considered to be the major source of mercury to humans, via the ingestion of fish and seafood (Costley et al., 2000). The organic compounds of mercury in the environment result from methylation processes that are mostly mediated by bacterial activity (biotic processes) (Ullrich et al.,

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2001), but can also result from abiotic processes. Physicochemical and biological processes (e.g. erosion, dredging, early-diagenesis, bioturbation) may enhance the presence of organic mercury compounds in the overlying water column affecting the environment on a local/regional scale, particularly in areas highly dependent on fishery activities, endangering the system ecologically, economically and also in terms of human health. The primary way for humans to be exposed to mercury is through the consumption of contaminated fish and shellfish, and therefore knowledge of mercury biogeochemistry in the different compartments of the salt marsh environment is extremely important. As stated before, inputs of mercury into the aquatic systems has been reduced during recent decades although mercury pools in sediments are still a worrying problem due to its potential release into other environmental compartments, such as the overlying water column and biota. The number of studies highlighting the potential role of salt marshes as sinks for several heavy metals, namely mercury (Weis and Weis, 2004; Hung and Chmura, 2006; Kongchum et al., 2006; Válega et al., 2008) has been increasing over recent years; however, most of these studies report only the potential role of vegetation in metal speciation and availability, especially when this is due to root activity (Alloway, 1995; Mendelssohn et al., 1995).

The present study intends to increase the knowledge on the mobility of mercury in a salt marsh colonised by *H. portulacoides* (L.) Aellen (Caryophyllales: Chenopodiaceae), its redistribution in the sediment layers containing plants and its incorporation into below ground biomass. *H. portulacoides* plays an important role in the floristic coverage of the European salt marshes; in fact this species is noted as being one of the most abundant in European salt marshes and one of the most productive species (Bouchard et al., 1998). For these purposes, mercury pools in *H. portulacoides* biomass and in sediments were assessed, as well the potential export of mercury from the contaminated salt marsh to the adjacent areas. Thus, this study provides important data about the dynamic of mercury inside the salt marsh, comprising the below ground and the above ground system.

2. Material and methods

2.1. Study area

The Ria de Aveiro is a temperate, shallow and well-mixed coastal lagoon located along the Atlantic Ocean (approximately 45 km long and 10 km wide) on the northwest coast of Portugal (40°38′N 08°44′W) (Fig. 1). With an extensive area of wetlands (83 km^2-high tide and 66 km^2-low tide), it is a mesotidal system, where tides are semi-diurnal and propagate from the mouth to the inner lagoon areas. Minimum tidal range is 0.6 m (neap tides) and the maximum tidal range is about 3.2 m (spring tides). The Ria de Aveiro is one of the most mercury-contaminated systems in Europe, due to the continuous mercury discharges of a chlor-alkali plant during more than four decades (1950–1994), into an inner bay of 1.5 km^2 called Laranjo Bay (Pereira et al., 1998). Laranjo Bay has a salt marsh area where *H. portulacoides* plays an important role in the floristic coverage throughout the year. The Laranjo salt marsh is inundated by tidal action twice a day, which contributes to high detritus exportation to the main system.

2.2. Sampling

Samples were collected bi-monthly during a one-year period between April 2003 and April 2004 at the highly contaminated area of Laranjo Bay salt marsh (Fig. 1) during low tide. *H. portulacoides* biomass (above and below ground biomass), sediments and water samples from intertidal water pools were collected in monotypic stands, uniform in size and in density of stems. Above ground material was collected at ground level in squares of 50 cm ($n = 3$) and, after cutting the above ground material, three sediment *corers* of Ø 7 cm and 15 cm depth were taken. Below ground biomass of *H. portulacoides* is more abundant in upper layers (<15 cm), since the effect of root-sediment interactions in the first 15 cm layers can be more clearly observed. Sediment cores were sliced into 5 cm layers and one of the cores was preserved

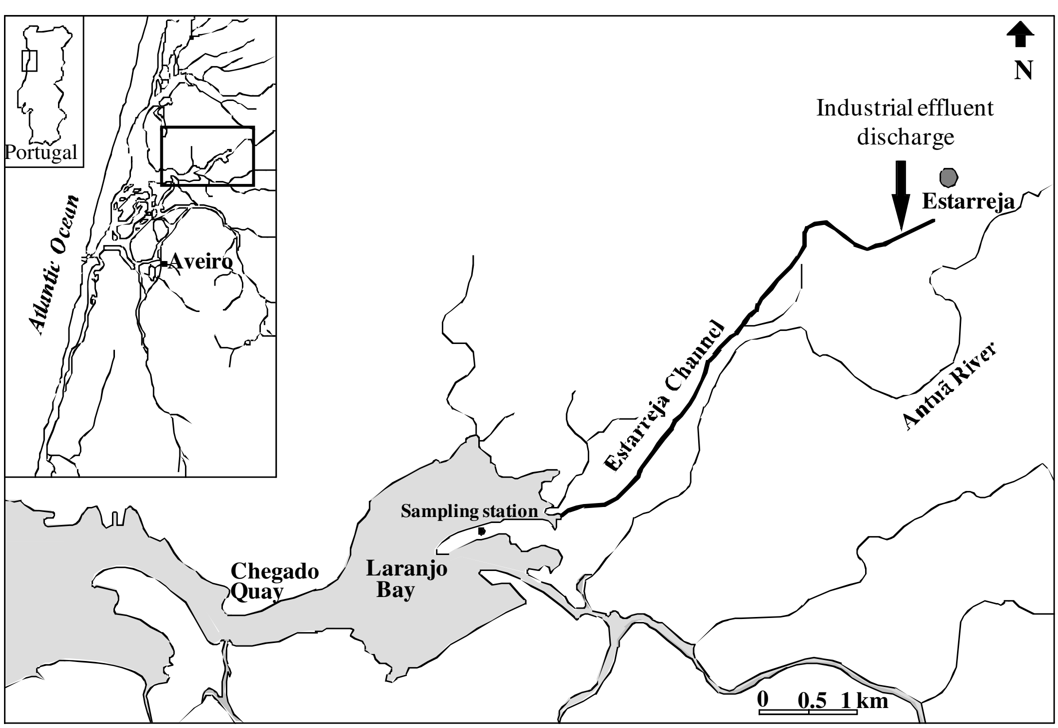

Fig. 1. Location of the Laranjo Bay with the sampling station.