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Mercury cycling between the water column and surface sediments in a contaminated area

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A B S T R A C T

Mercury cycling in the water column and upper sediments of a contaminated area, the Largo do Laranjo, Aveiro (Portugal), was evaluated after determination of reactive and non-reactive mercury concentrations in the water column and pore waters of sediments, collected in several places of this bay. In the water column, reactive mercury concentrations varied between 10 and 37 pmol dm^{-3}, the highest values being observed near the mercury anthropogenic source. However, reactive mercury was a narrowly constrained fraction of the total mercury, making up only 4–16% of the total, showing evidence of the importance of dissolved organic matter on mercury transport.

In sediments, higher concentrations of mercury were also determined near industrial discharges. Results indicate the existence of an equilibrium between solid and liquid phases, determined by solid sediment/pore water distribution coefficients. Much of the mercury present in the solid fraction is associated with organic matter ($r = 0.837$) and iron oxyhydroxides ($r = 0.919$), but as oxides begin to dissolve in reduced sediments and organic matter decays, the adsorbed mercury is released. In fact, the mercury concentrations in pore waters of those contaminated sediments largely exceeded the values determined in the water column. As molecular diffusion may contribute to the dissolved mercury distribution in the overlying water column, this phenomenon was evaluated. However, the pore waters of Largo do Laranjo do not enrich the water column substantially in terms of reactive and non-reactive mercury. In fact, pore waters can contribute only to 0.2% and 0.5% of the reactive and non-reactive mercury present in the water column, respectively, showing that as long as mercury is being incorporated in sediments, it stays in stable forms.

1. Introduction

The fate and reactivity of anthropogenic mercury in the aquatic environment are of major concern owing to their toxicity for most organisms and humans. Trace metals are particle reactive (Paraquetti et al., 2004) and quickly sorbed to the suspended particulate matter (SPM) (Kennish, 1998) or to the particulates in the sediment–water interface. Once they reach the sediment, the major fraction of anthropogenic mercury is ultimately retained (Kennish, 1998). In many situations, the vertical profiles of total mercury in sediments record the historical contamination of the area under study

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(Kennish, 1998; Bellucci et al., 2002). However, the coastal sediments are highly dynamic and the conditions existing in the upper layers influence the sediment–water exchanges and have a strong effect on the distribution of trace elements (Sundby, 1994). The remobilisation due to the resuspension of metal enriched on fine bed sediments may increase the dissolved metal content in the overlying water column (Martino et al., 2002), as well as maintain large amounts of particulate mercury (Lacerda and Gonçalves, 2001). The types and the extension of the reactions that take place between the solid sediments and the aqueous phase can be evaluated by the pore water composition (Hong et al., 1994). This may be enriched in mercury in comparison to the water column (Cossa and Gobeil, 2000). This mercury present in the pore waters may escape to the water column and deleteriously affect the biota.

Since decades, a chlor-alkali plant has been discharging mercury into one of the most remote branches of Ria de Aveiro, which is a coastal lagoon with a permanent connection to the sea. Most of the discharged mercury settles in Largo do Laranjo, an inner bay of 1.5 km^2. Since the 1980s, high mercury concentrations in sediments, SPM and water have been detected and reported in several studies (Lucas et al., 1986, Pereira et al., 1998a b, Ramalhosa et al., 2001a). Generally, the highest mercury concentrations in sediments (maximum 35 μg g^{-1}) were found at 30–40 cm depth, corresponding to the period of maximum industrial production (Pereira et al., 1998a). However, particulate mercury escapes when the surface sediments are resuspended and transported by the tide to the rest of the lagoon (Pereira et al., 1998b). The contribution of the dissolved mercury was not evaluated due to the low concentrations found (Pereira et al., 1998b). In posterior works, the pore water profiles indicated that mercury is being remobilised in the anoxic sediments and these may constitute internal sources of mercury to the water column (Ramalhosa et al., 2001a).

This study presents the distributions of total and reactive mercury in solid sediments, pore waters and water column, as well as iron and organic matter, in Largo do Laranjo. On the basis of these data, associations of mercury in sediments and water column are evaluated and mercury cycling between both compartments is assessed by considering molecular diffusion.

2. Materials and methods

2.1. Sampling

Surface sediments (0–0.5 cm layers) were collected with a grab sampler at 20 sites in Largo do Laranjo contaminated area in February 2000 (Fig. 1). The fluvial flow rate was high in this

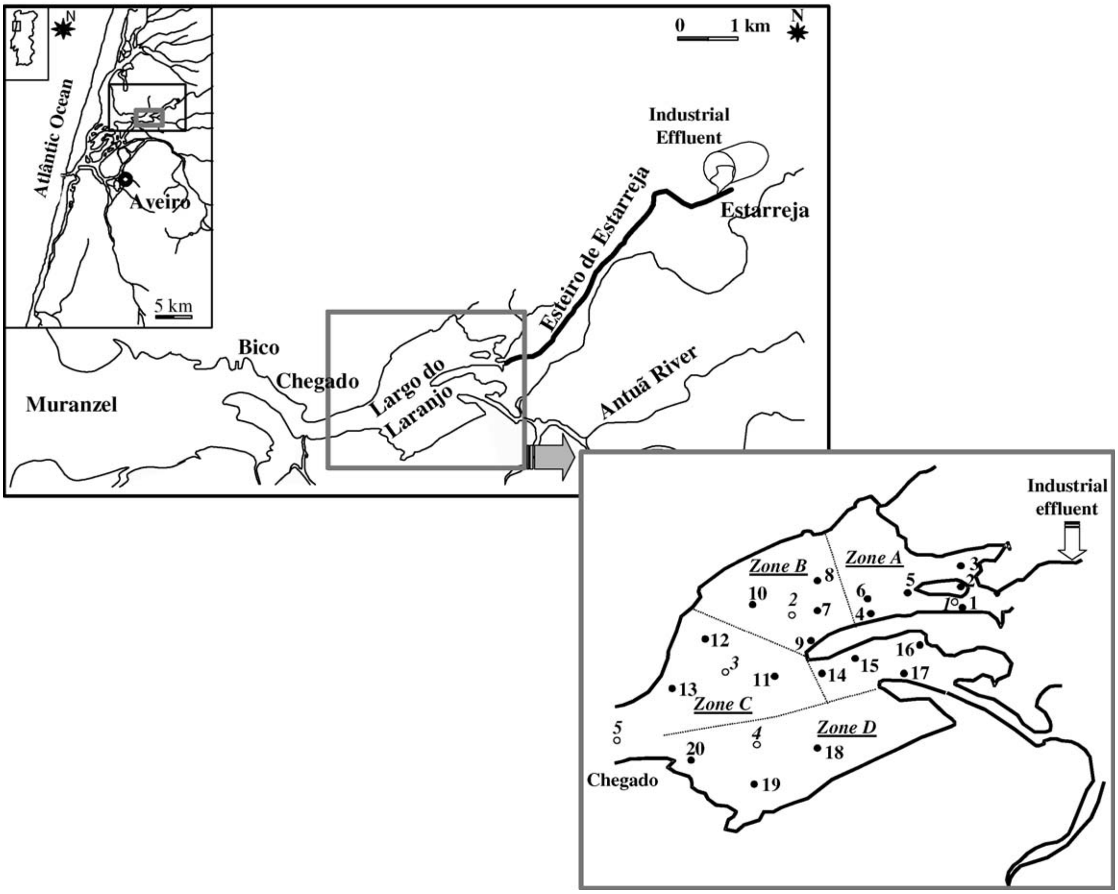

Fig. 1 – Detailed maps of Ria de Aveiro and Largo do Laranjo, showing the location of the sediment (●) and water (○) sampling stations. The mercury industrial discharge is also marked.