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Temporal characterization of mercury accumulation at different trophic levels and implications for metal biomagnification along a coastal food web

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ABSTRACT

The main goal of this study was to assess temporal mercury variations along an estuarine food web to evaluate the mercury contamination level of the system and the risks that humans are exposed to, due to mercury biomagnification. The highest mercury concentrations in the sediments and primary producers (macrophytes) were observed during winter sampling. Instead, the highest mercury concentrations in the water, suspended particulate matter as well as in the zooplanktonic and suprabenthic communities were observed during summer sampling. Evidences of mercury biomagnification along the food web were corroborated by the positive biomagnification factors, particularly for omnivorous macrobenthic species. Comparing the mercury levels at distinct components with several environmental quality criteria it suggests that sediments, water and edible species (e.g., bivalve *Scrobicularia plana* and the crustacean *Carcinus maenas*) presented higher mercury levels than the values accepted by legislation which represent a matter of concern for the environment and human health.

1. Introduction

For several decades, contamination by mercury (Hg) has become a worldwide concern since this metal is recognized as a severe pollutant due to the significant inputs into the environment, its mobility and persistence in the ecosystems and toxicity to living organisms (Boening, 2000). In addition, organic forms of mercury biomagnify in estuarine food chains becoming concentrated in species consumed by humans (Díaz-Jaramillo et al., 2013). A legal framework for controlling global mercury pollution is being developed by the United Nations Environment Program (UNEP) to protect human health and the global environment from the release of mercury and its compounds by minimizing and, where feasible, ultimately eliminating global, anthropogenic mercury releases to air, water and land (UNEP, 2011).

Despite the reduction in total mercury emissions in the last decades, contaminated sediments are still a cause for concern due to the potential release of mercury into other components, such as the overlying water column and biota. In order to better understand the biomagnification of mercury within a food web, its quantification in biological tissues of multiple species is needed (Lillebø et al., 2011). The metals determination in abiotic and biotic samples is very important in order to monitor the levels of contamination and potential risks that humans are exposed to.

Mercury pollution varies across multiple time scales, reflecting a range of processes. Temporal variation likely reflects patterns in net mercury methylation in the sediment or water column (Greenfield et al., 2013). This variability in habitat and biological factors may influence the bioavailability of pollutants in the estuarine food webs (Greenfield et al., 2005; Díaz-Jaramillo et al., 2013). As a result, delineating temporal patterns in mercury biomagnification rates in food webs can contribute to minimize the monitoring efforts contributing to decrease human and ecological risk from mercury exposure (Zhang et al., 2012).

Several studies have already been performed in order to evaluate the impact of mercury contamination in different biotic groups, like suprabenthos (Cardoso et al., 2013a), macrobenthos (Raftopoulou and Dimiatris, 2011; Cardoso et al., 2013b), zooplankton (Cardoso et al., 2013c), fishes (Abreu et al., 2000; Gehringer et al., 2013), salt marsh vegetation (Válega et al., 2008a, 2008b) and macroalgae (Coelho et al., 2005). Despite the

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existent literature on the assessment of mercury concentrations from different trophic levels (Dietz et al., 2000; Dehn et al., 2006; Chouvelon et al., 2009), most of those studies focus only in one or two biotic groups isolated (e.g., macrobenthic organisms and/or fishes) (e.g., Coulibaly et al., 2012; Díaz-Jaramillo et al., 2013). So, there is still a lack of information regarding a temporal variability on metal concentrations, considering a longer food web (including several biotic groups). Is there any temporal variation in mercury contamination at the different trophic levels? How does a temporal variation may affect the mercury biomagnification process along the food web? How is the quality of edible fauna and surrounding environment for the human health? These are the central questions that are addressed in this paper. Therefore, the main objective of this study is to evaluate the temporal trends in mercury concentrations at distinct ecosystem compartments (abiotic: sediments, water and SPM and biotic: primary producers, zooplankton, suprabenthos and macrobenthos) along a mercury gradient in a temperate coastal lagoon and infer about the risks of mercury biomagnification along the food web.

2. Materials and methods

2.1. Study site

Ria de Aveiro is a shallow coastal lagoon located in the northwestern coast of Portugal (40°38′N, 8°45W) with a single connection to the sea (Fig. 1) (see details in Pereira et al., 2009). From the 1950s until 1994, the Ria de Aveiro has received a highly contaminated effluent discharged from a mercury cell chlor-alkali plant located in Estarreja industrial complex (indicated in Fig. 1 as "Hg source"). The discharges resulted in an accumulation of about 33 tons of mercury in the lagoon, much of which is known to be sediment-associated in a small basin named Laranjo Bay (Pereira et al., 2009). In the last two decades, the mercury discharge diminished considerably, however, mercury concentrations in the surface sediments of that area are still high, ranging from 20 to 200 μg g^{-1} (Cardoso et al., 2013a).

Three sampling stations were selected in the Laranjo Bay along a transect defined by the distance from the mercury point source (the point at which the freshwater input with mercury load enters the lagoon). Station 1 (St1) is located at the mercury point source in the lagoon, and the other stations are located at 600 m (station 2 – St2) and 3000 m (station 3 – St3) from this one (Fig. 1). All the stations were located at similar depths (≈2 m) and presented analogous sediment granulometry (Cardoso et al., 2013d).

2.2. Sampling procedure

The zooplanktonic, suprabenthic and macrobenthic assemblages as well as the primary producers (macroalgae and rooted macrophytes) were sampled during the day, at two periods (January 2012 – winter sampling point and August 2012 – summer sampling point). At each sampling station and occasion, *in situ* measurements of water temperature, salinity, dissolved oxygen and pH were taken and water was collected in two distinct conditions (low tide *versus* high tide).

Sediments ($n = 3$) from each site were also collected with a syringe from the first 5–10 cm, for total mercury content quantification. They were homogenized and freeze-dried for posterior mercury analysis.

Zooplanktonic samples ($n = 3$) were collected with a plankton net equipped with 200 μm mesh net, at flood tide, and transported in a cool box (a detailed description can be seen in Cardoso et al., 2013c). Later, samples for mercury determination were cleaned from the excess of organic matter and immediately frozen being afterwards freeze-dried. In addition, during high tide, water ($n = 3$) from the first 30 cm of the water column (high tide condition) was also collected for mercury determination in suspended particulate matter and total dissolved mercury. They were transported in thermic boxes until the laboratory.

Suprabenthic community (i.e., faunal element of the benthic boundary layer, corresponding to the animals living in the lowest strata of the water column and dependent on the proximity of the bottom) (Cardoso et al., 2013a) was sampled at flood tide by means of a modified suprabenthic sledge, consisting of a heavy metal frame with a rectangular 50 cm high × 40 cm wide opening equipped with a 500 μm mesh net. The sledge samples the water column between 0.01 and 0.5 m above the bottom, and was trawled at ca. 1.5 knots for about 1.5 min to avoid the clogging during the tows (a detailed description can be seen in Cardoso et al., 2013a). The collected specimens for total mercury quantification were transported in a cool box and later were separated under a dissecting microscope, identified to the lowest possible taxon, frozen and later freeze-dried for total mercury analyses.

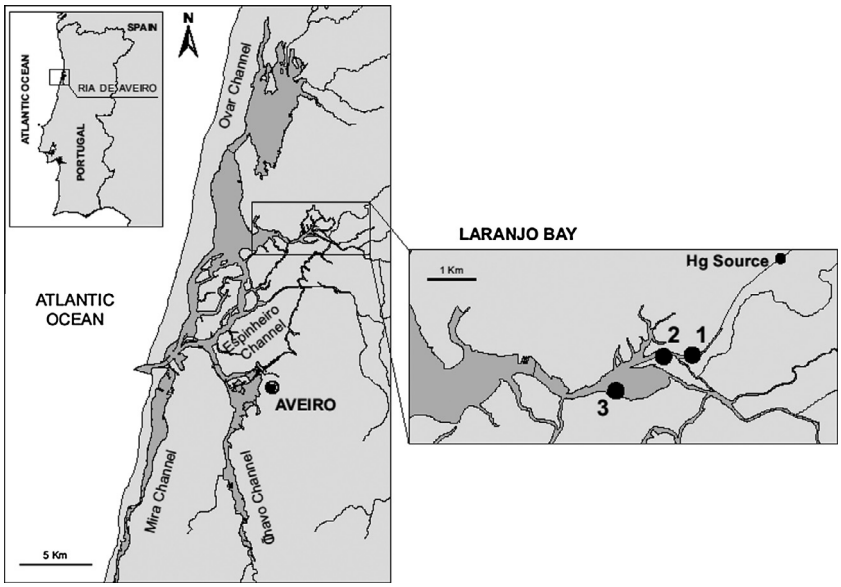

Fig. 1. Location of the sampling stations in the Laranjo Bay (Ria de Aveiro).