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Mercury and selenium in tropical marine plankton and their trophic successors

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HIGHLIGHTS

- Feeding habit influenced on the accumulation of Hg, MeHg and Se by marine species.
- Pelagic food chain has higher MeHg biomagnification potential than benthic food chain.
- Different MeHg detoxification strategies were found in the liver of organisms.
- An antagonistic effect of selenium on MeHg was observed in dolphin liver.
- The MeHg to Hg ratios did not change with increasing Se:Hg in liver of fish.

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ABSTRACT

Selenium (Se), mercury (Hg) and methylmercury (MeHg) were determined in microplankton (⩾25 μm), crustacean muscle tissue, in the muscle and liver of two fish species and tissues of a dolphin from a bay in the Brazilian Southeast coast. Differences were found between the fish and dolphin muscle and hepatic concentrations. Liver showed the highest concentrations of Se and Hg. Positive biotransference of MeHg from source to consumer was observed for all interactions, demonstrating that MeHg biomagnified along the food web. The pelagic food chain has the highest biomagnification potential when compared to the benthic system. A large excess of Se in relation to Hg was observed in all tissues. The muscle and liver of the predator species, the dolphin and the carnivorous fish, presented similar MeHg. The predator species presented similar MeHg to Hg (% MeHg) ratios in muscle tissues (~100%), whereas dolphin showed lower hepatic% MeHg (18) than the carnivorous fish (69%). Iliophagous fish presented the lowest % MeHg in tissues. Fish showed a positive relationship between hepatic MeHg and Se, whereas % MeHg did not change with increasing Se:Hg molar ratios in liver. Dolphins showed a significant inverse relationship between hepatic MeHg and Se and the % MeHg and Se:Hg ratios. This suggests a strong antagonistic effect of Se on MeHg assimilation and accumulation in this species. Probably, the differences observed among Hg as MeHg and Se and on the effect of Se on MeHg assimilation and accumulation in all marine species are related to the physiological differences between dolphins and fish.

1. Introduction

The trophic transfer of trace elements along marine food chains has been recognized as an important pathway for metal and metalloid bioaccumulation in aquatic organisms (Fisher and Reinfelder, 1995). The analysis of different trophic levels can give information regarding the bioaccumulation and biomagnification processes that may occur (Costa et al., 2004).

The presence and behavior of mercury in marine systems is of great interest and importance, since this is the only metal that bioaccumulates and biomagnifies over the entire marine food web (Agusa et al., 2007). Methylmercury, the most abundant organic form of mercury in the environment, is largely responsible for the accumulation of mercury in organisms (bioaccumulation) and the transfer of mercury from one trophic level to another (biomagnification) (Kehrig et al., 2009a). This toxic form of mercury can affect the productivity, reproduction and survival of coastal and

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marine organisms, and can eventually be hazardous to human health (WHO, 1989). For these reasons, methylmercury has been recognized as a serious pollutant of aquatic ecosystems.

In the marine environment, almost all mercury present in fish and mammal muscle tissue is methylated (Joiris et al., 2001; Kehrig et al., 2010). However, the major portion of mercury accumulated in their internal organs, especially in liver, exists as inorganic mercury, suggesting that demethylation of methylmercury is possible (Wagemann et al., 2000; Kehrig et al., 2008; Seixas et al., 2008).

Selenium is an important essential trace element for metabolic activity of all life forms that have nervous systems. This micronutrient acts as a protective agent against the toxicity of exogenous metals, such as mercury (Feroci et al., 2005). Some studies have shown that selenium may be effective in reducing the availability of mercury, as methylmercury, blocking it in insoluble compounds (Feroci et al., 2005), consequently decreasing methylmercury toxicity (Wagemann et al., 2000; Kehrig et al., 2008).

Marine fish generally contain far more selenium (Se) than mercury (Hg), and Se:Hg molar ratios exceeding 1:1 are thought to provide Se-dependent health benefits, but Se:Hg molar ratios approaching 1:1 would not necessarily be similarly protective since that set of fish would necessarily include those with mercury present in molar excess of selenium (Ganther et al., 1972). The information available is even more limited regarding the manner in which mercury and selenium interact through tropical estuarine and marine food chains (Kehrig et al., 2009a, 2013b).

The present study evaluated the concentrations of selenium, mercury and methylmercury (MeHg), the MeHg to Hg (% MeHg) ratios and selenium–mercury molar ratios (Se:Hg) in microplankton ($\geqslant$25 μm), in crustacean muscle tissue muscle, in the muscle and liver of two fish species and tissues of a coastal dolphin (top-predator) from an important area in the Brazilian Southeastern coast, Ilha Grande Bay (Fig. 1). This study assessed the inter-element relationships in marine species and their possible influence on Se and MeHg bioaccumulation and biomagnification along the food web.

2. Materials and methods

2.1. Sampling area

Ilha Grande Bay (total area: 3100 km^2, 22°50′S and 23°20′S), in the Rio de Janeiro state, can be considered an important water body concerning economic and ecological purposes on the South-eastern Brazilian coast, as it is a biodiversity hotspot and includes a high number of protected areas (Creed et al., 2007). Ilha Grande Bay has an important shipyard, an oil terminal and two nuclear power plants. Despite the presence of these potential pollution sources, this bay presents a typically oligotrophic aquatic environment (Seixas et al., 2012, 2013) and low levels of trace elements in water, biota and sediments (Lacerda et al., 1981; Kehrig et al., 1998; Cardoso et al., 2001).

2.2. Sample collection

Planktonic organisms were sampled from the superficial water layer (0.2–1.0 m in depth) at Ilha Grande Bay, on May 2011, using a planktonic conical net of 25 μm mesh size (microplankton). Plankton samples were stored in pre-cleaned Teflon bottles, separated per site and identified. Microplankton was composed mainly of Chlorococcales (chlorophyceae), diatoms and cyanobacteria. At the laboratory these samples were freeze-dried and stored in hermetic vessels until the chemical analyses. Crustaceans and fish were collected with the help of local fishermen between 2009 and 2011 at Ilha Grande Bay. Dolphin individuals were collected by Dr. Salvatore Siciliano. Table 1 shows the common names, number of individuals, feeding habits, habitat and length of the sampled marine biota.

After sampling, the biological characteristics of each individual were obtained, and sub-samples of dorso-lateral muscle and liver were removed, except for crustacean that had whole tissues removed. All samples were then freeze-dried and sheltered from light until analysis. After the lyophilization procedure the samples lost around 75% of their water content.

2.3. Trace elements and methylmercury analyses

For the mercury analyses, dried samples (0.05 g) were digested in a sulfuric–nitric acid mixture. Mercury was determined by cold vapor atomic absorption spectrometry, using $NaBH_4$ as the reducing agent (Kehrig et al., 2008). For selenium, the samples (0.05 g) were digested in nitric acid and selenium content was determined by graphite furnace atomic absorption spectrometry, using $Pd(NO_3)_2$ as chemical modifier (Seixas et al., 2008).

The methylmercury analyses were conducted by digesting samples with an alcoholic KOH solution, followed by dithizone–toluene

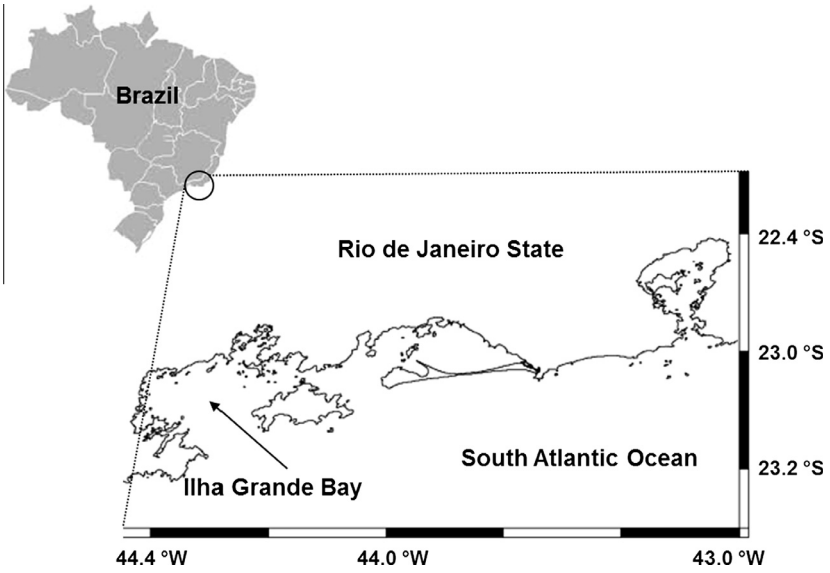

Fig. 1. Sampling area in the Rio de Janeiro coast, South-eastern Brazil.