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Mercury and selenium in seston, marine plankton and fish (*Sardinella brasiliensis*) as a tool for understanding a tropical food web

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ABSTRACT

Mercury (Hg) and selenium (Se) concentrations were evaluated in a planktivorous fish and four size classes of organisms (FSCO), collected at an oligotrophic bay in the Southeastern Brazilian coast. No significant spatial differences between Hg and Se were found in the FSCO within the five sampling points in the bay. Hg and Se concentrations increased with successive increases in the size class of the analyzed plankton, i.e. approximately 3- and 2-fold, respectively, from microplankton to macroplankton. Hg and Se biomagnified throughout the planktonic food web. The smallest size class of organism, seston, composed of both biotic and abiotic portions, and fish showed the highest Hg concentrations. This indicates that Hg is not biomagnifying in the base of the bay food web. Selenium concentrations in fish were approximately 5.9 times higher than those in seston. Hg and Se concentrations in fish were approximately 3.5 and 14.6 times higher than those found in the plankton, respectively.

Estuaries are of great ecological importance due to their biological productivity that makes them important and vital breeding and feeding grounds sites for fishes, shrimps and the larvae of several animals of high commercial importance (Höfling et al., 2000). In the last centuries, increasing anthropogenic activities have degraded the coastal ecosystems, mainly through the release of pollutants such as mercury (Hg) and selenium (Se) (Srogi, 2008).

Mercury is an exogenous and harmful metal that accumulates in the tissues of aquatic organisms as they grow, and biomagnifies through food webs from the base (autotrophic and heterotrophic organisms) to the top, made up of predatory fish and aquatic mammals (Kehrig et al., 2013; Seixas et al., 2014; Bisi et al., 2012). Conversely, selenium (Se) is an important micronutrient for the metabolic activity of all life forms that have nervous systems, acting as a protective agent against mercury toxicity (Feroci et al., 2005).

Trace elements enter the food web via cell adsorption in autotrophic and heterotrophic organisms, i.e. organisms that form the microbial loop (bacterioplankton, phytoplankton and zooplankton) (Kehrig et al., 2009a). The term 'microbial loop' was originally coined by Azam et al. (1983), and includes several trophic levels of the microbial food chain and a large fraction of the organic carbon particulate.

Studies on the microbial food chain can be considered essential for the understanding of the nutrient cycling and trace elements flow loading in coastal ecosystems (Burford et al., 2008). These processes can influence the bioaccumulation of trace elements by organisms at the base of the food web (Fenchel, 2008). However, studies on the bioaccumulation and trophic transfer of Hg and Se in Brazilian estuarine microbial loops are still scarce (Kehrig et al., 2009a).

In this context, the present study appraised the accumulation of mercury and selenium in a microbial loop consisting of four autotrophic and heterotrophic organism size classes (1.2–70 μm, seston, suspended particulate material, SPM; 70–290 μm, microplankton; 290–500 μm, mesoplankton, and ≥500 μm, macroplankton) collected at five sampling points within an important estuarine complex located in the Southeastern Brazilian coast, Ilha Grande Bay (Fig. 1). Mercury and selenium were also evaluated in the muscle of a planktivorous fish, *Sardinella brasiliensis*, as a model to investigate the behavior of these trace elements in a superior trophic level of the studied food web. Thus, mercury and selenium could be used as a tool for understanding a tropical food web.

Ilha Grande Bay (total area: 3100 km^2, 22°50′S and 23°20′S) presents 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) and low levels of trace elements (Lacerda et al., 1981; Kehrig et al., 1998; Cardoso et al., 2001).

Water samples were taken at five sampling points on May 2011 according to USEPA method 1669 (USEPA, 1997). Some physico-chemical parameters of surface water (temperature, salinity, pH and Eh) from each sampling point were measured in the field. In the laboratory, the

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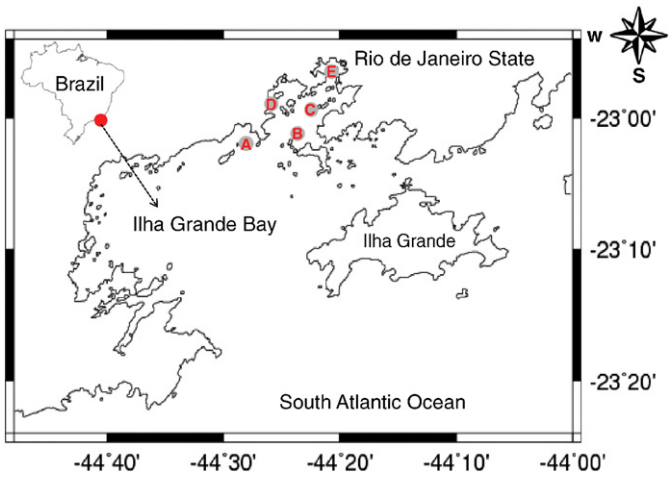

Fig. 1. Sampling points of seston and plankton at Ilha Grande Bay, Southeastern Brazilian coast.

water samples were filtered through 1.2 μm Millipore fiberglass filters, previously calcined at 450 °C for 24 h with a vacuum pump. The filters were then freeze-dried. Eight filters from each sampling point were used to obtain total suspended solids (TSS), total organic carbon (TOC), mercury (Hg) and selenium (Se) concentrations. TSS were determined by a gravimetric method, measuring the initial and the final dry weight of each filter before and after filtration, using an analytical balance of ±0.1 mg precision with known volume of water. Subsequently, the filters were subjected to an acidic atmosphere for 24 h to eliminate carbonates were then used for TOC determinations by an elemental Perkin Elmer 2400 Series II CHNS/O analyzer. The filters used to determine chlorophyll *a* were stored in the dark covered by aluminum foil. Chlorophyll *a* (Chlor *a*) was determined fluorimetrically in triplicate (Designs® Turner TD-700) after extraction in 90% acetone for 18 h at 4 °C, according to the procedures described by Parsons et al. (1984). Total soluble phosphorus was determined by the ascorbic acid/persulfate method followed by colorimetric determination on a spectrophotometer (APHA, 2005). Ammoniacal nitrogen ($N\text{-}NH_3$ + $N\text{-}NH_4^+$), referred to herein simply as ammonia, was determined by the indophenol blue method (Parsons et al., 1984). Nitrite was determined by the diazotisation method (Grasshof et al., 1999). Nitrate was determined by reduction on a Cd-Cu column followed by diazotization (Grasshof et al., 1999) and determined via flow injection analysis (FIA).

At the same time and in the same sampling points used for the water sampling at Ilha Grande Bay, plankton samples were collected by horizontal hauls at the water surface, using planktonic conical nets of 70, 290 and 500 μm mesh size in order to separate microplankton, mesoplankton and macroplankton. After each trawl, the plankton samples were stored in plastic bottles previously decontaminated with a dilute HNO_3 solution and identified by size class. These bottles were kept protected from the sun and heat in an insulated box containing ice throughout the sampling process and then transported to the laboratory. Plankton samples were freeze-dried and homogenized with a mortar and pestle for the trace elements analyses. Sub-plankton samples were also preserved in a 4% (v/v) formalin solution for taxonomic group identification. The qualitative and quantitative plankton analyses were conducted through a Sedgewick-Rafter cell counter, employing an electron microscope (BX-Olympus) (Kehrig et al., 2009a).

S. brasiliensis (Steindachner, 1879) (Orangespot sardine or Brazilian *Sardinella*), a planktivorous fish (N = 26) were collected at Ilha Grande Bay in 2011 with the help of the local fishing colony. After the identification of each individual, total weight and body length were measured (Table 2), and the left dorso-lateral muscle tissue was removed and kept frozen at −20 °C until the freeze-drying process. The freeze-dried muscle samples lost around 75% of moisture content.

S. brasiliensis is a pelagic fish from the Southeastern Brazilian coast found in large shoals and is the main species exploited at Ilha Grande Bay. The sardine is one of the most important fishery resources of the Brazilian coast, contributing to 25% of total annual marine resources caught in the Brazilian waters (IBAMA, 2004).

For the total mercury and selenium analyses, two aliquots of approximately 200 mg of dry plankton and muscle fish samples, as well as two SPM filters from each sampling point, were digested with an acid solution. Mercury was determined using a portable atomic absorption spectrometer, (Lumex apparatus), and selenium was determined by GF-AAS (Seixas et al., 2009), using iridium (Ir) as a permanent chemical modifier.

Quality control was performed by a strict blank control and the analysis of replicates and certified reference material (CRM). Accuracy was assessed throughout the analysis of DORM-2 certified reference material (Hg: 4.64 ± 0.26 μg g^{-1}; Se: 1.40 ± 0.09 μg g^{-1}) from the National Research Council—Canada. Mean recovery values varied between 85–107% and 80–90% for Hg and Se, respectively. Reproducibility was evaluated using the coefficient of variation of the replicates, which was always lower than 10%.

Statistical analyses were performed using STATISTICA® 7.0 for Windows (StatSoft, Inc. 1984–2004, USA). Data were tested for normal distributions and non-parametric tests were then applied. Descriptive statistics were used to determine the means of the duplicates for each sample (analytical blank, CRM, seston, plankton, fish), as well the standard deviation and the coefficient of variation for each analyzed batch. The analysis of variance was conducted by the Kruskal–Wallis test-ANOVA followed by a post-hoc test (Mann–Whitney U-test) in order to define significant differences in trace element concentrations among the seston, different size plankton classes and fish, and the physico-chemical parameters and nutrients of surface water from all sampling points. The Spearman correlation test (r) was performed to determine the relationships between physico-chemical parameters, dissolved nutrient concentrations, Chlor *a* concentrations and the number of cyanobacteria present in the plankton composition.

Seston samples (1.2–70 μm mesh) were primarily composed of nanoplankton, unicellular phytoplankton, bacterioplankton, and cellular and inorganic debris. The smallest size class of plankton, microplankton (70–290 μm mesh), was mostly composed of Chlorococcales (chlorophyceae), diatoms and cyanobacteria. Mesoplankton (290–500 μm mesh) and the largest class size, macroplankton (≥500 μm mesh), were composed of microcrustaceans, primarily copepod nauplii, copepods and Cladocerans, and eggs and larval fish.

Thus, the Ilha Grande Bay microbial loop can be defined as: seston (nanoplankton and bacterioplankton), primary producers (Chlorococcales, diatoms and cyanobacteria) and consumers, constituted by copepod nauplii, copepods and cladocerans that feed on primary producers and seston.

The physical and chemical characterization of surface water is presented in Table 1.

Little variability in salinity and pH was observed, with the coefficient of variation (CV) ranging between 4.0% and 5.0%, respectively. The values for these parameters indicated a clear contribution from the South Atlantic Ocean in this area (Table 1). A positive correlation between salinity and dissolved nitrate concentrations was also observed, indicating that nitrification must be occurring, due to the influence of oxygenated ocean waters (Paranhos et al., 1998).

No significant difference ($p > 0.05$) was observed in the total organic carbon (TOC %) content of the suspended particulate matter between all sampling points. On the other hand, the total particulate material suspended solid (TSS) concentrations presented significant difference ($p < 0.05$) among the sampling points within the bay (Table 1).

The most external sampling point of the bay, i.e. point A (Fig. 1) presented the highest salinity (34 psu), pH (8.1) and dissolved nitrate concentrations (2.29 μM) in superficial water. This sampling point also presented the lowest total dissolved phosphorus (0.02 μM), Chlor *a*