Estuarine, Coastal and Shelf Science 85 (2009) 36–44

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

Trophic transfer of methylmercury and trace elements by tropical estuarine seston and plankton

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ARTICLE INFO

Article history:
Received 3 December 2008
Accepted 26 May 2009
Available online 6 June 2009

Keywords:
bioaccumulation
Brazil
microbial loop
eutrophic estuary
microorganism size classes

ABSTRACT

Methylmercury (MeHg) and trace elements (TE), mercury, selenium, cadmium, lead and copper, were determined in a microbial loop composed by three size classes of autotrophic and heterotrophic microorganism samples, 1.2–70 μm (seston, SPM), 70–290 μm (microplankton) and ≥290 μm (mesoplankton) from five sampling stations within a polluted eutrophic estuary in the Brazilian Southeast coast and one external point under the influence of the bay. TE concentrations were within the range reported for marine microorganisms from uncontaminated locations. Microplankton was primarily composed of proto-zooplankton and diatoms (>90%) while approximately 50% of mesoplankton was composed mainly of copepods. MeHg and TE in samples did not differ among the five sampling stations within the bay. Cd, Pb and Cu in seston were higher in the stations sampled inside Guanabara Bay (0.67 μg Cd g^{-1}, 9.26 μg Pb g^{-1}, 8.03 μg Cu g^{-1}) than in the external one (0.17 μg Cd g^{-1}, 3.98 μg Pb g^{-1} and 2.09 μg Cu g^{-1}). Hg, MeHg and Se did not differ among the five points within the more eutrophic waters of the estuary and the external sampling station. The trophic transfer of MeHg and Se was observed between trophic levels from prey (seston and microplankton) to predator (mesoplankton). The successive amplification of the ratios of MeHg to Hg with increasing trophic levels from seston (43%), to microplankton (59%) and mesoplankton (77%) indicate that biomagnification may be occurring along the microbial food web. Selenium, that is efficiently accumulated by organisms through trophic transference, was biomagnified along the microbial food web, while Hg, Cd, Pb, Cu did not present the same behavior. Concentrations differed between the three size classes, indicating that MeHg and TE accumulation were size-dependent. MeHg and TE concentrations were not related to the taxonomic groups' composition of the planktonic microorganisms. Results suggest the importance of the role of the trophic level and microorganism size in regulating element transfers. Eutrophication dilution may provide a process-oriented explanation for lower MeHg and TE accumulation by the three size classes of microorganisms collected at the five sampling stations within the bay.

1. Introduction

Estuaries act as a transitional ecosystem between terrestrial and oceanic environments, and present a high accumulation capability of continental and marine originated materials. They are extremely productive and are home to large numbers of organisms, many of which are of commercial importance. Estuaries also provide vital breeding and feeding grounds for many birds, fishes, shrimps and larvae of several animals (Castro and Huber, 2007).

Coastal systems in urbanized areas throughout the world are becoming eutrophic as a result of substantial anthropogenic nutrient inputs from human activities. This increased nutrient loading stimulates phytoplankton production, and has flow-on effects to biogeochemical processes and food webs (Burford et al., 2008). A major functional change in eutrophied coastal systems is increased water column and benthic respiration relative to production. High respiration rates have caused widespread and recurrent hypoxia and anoxia along urbanized coasts (Nezlin et al., 2009). Indeed, eutrophication often adversely affects oxygen balance in aquatic environments (Nezlin et al., 2009), resulting in a depletion of oxygen concentration to critical levels, inducing hypoxia and anoxia of the water column and subsequent mortality of benthic communities (Meyer-Reil and Köster, 2000).

These coastal areas, particularly near high population density centers, are of special concern, as they receive the largest exposure

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doi:10.1016/j.ecss.2009.05.027

to chemical contamination and anthropogenic nutrient inputs due to source proximity. Due to its singular geographical situation, Guanabara Bay, located in Rio de Janeiro State, Brazil, receives an expressive amount of organic and inorganic pollution generated by the domestic and industrial park of the metropolitan Rio de Janeiro region (Kjerfve et al., 1997).

Autotrophic and heterotrophic microorganism in the "microbial loop" are key steps in the transfer of carbon and trace elements through marine food webs (Fenchel, 2008), influencing the biogeochemical cycling of the aquatic ecosystem, as well as being major contributors to elemental cycling and vertical fluxes (Fisher et al., 2000). The term "microbial loop" was originally coined by Azam et al. (1983), and includes several trophic levels of the microbial food web and a large fraction of the organic carbon particulate. The main effect of the microbial loop on element cycling in the water column is the acceleration of organic matter mineralization and thus regenerates the nutrients for primary production (Fenchel, 2008). A large fraction of the organic matter that is synthesized by primary producers becomes dissolved organic matter (DOM) and is taken up almost exclusively by bacteria. Most of the DOM is respired to carbon dioxide and a fraction is assimilated and re-introduced into the classical food chain (phytoplankton to zooplankton to fish) (Fenchel, 2008). The dynamics of toxic chemicals through the microbial food web are influenced by the microbial loop.

Phytoplankton are primary producers that play a significant role in nutrient cycling, water quality and as a food source for heterotrophic organisms, that are the primary consumers such as zooplankton and filter-feeder mussels (Okay et al., 2000; Anandraj et al., 2008). Reduction of primary production can affect the amount of food available to organisms of other trophic levels, especially aquatic herbivores in the same marine ecosystem (Yap et al., 2004). Zooplankton has the ability to accumulate both essential and non-essential trace elements from the aquatic environment in which they live, from ingested food and/or directly from the dissolved phase (Wang and Fisher, 1998).

Trophic transfer of trace elements along marine food webs has been recognized as an important process influencing bioaccumulation and geochemical cycling of many elements (Fisher and Reinfelder, 1995). However, bioavailability and chemical species, especially free ions, influence trace element toxicity and their bioaccumulation by organisms in the estuarine environment (Wang and Rainbow, 2005).

The study of mercury, mainly as methylmercury, and trace element bioaccumulation by marine autotrophic and heterotrophic microorganisms is of great significance. Therefore, it is of great importance to obtain a better understanding of the estuarine processes concerning these trace elements' accumulation and their possible biomagnification throughout the base of the estuarine food web. However, few data is available for comparative purposes on coastal waters (Faganeli et al., 2003; Blackmore and Wang, 2004; Stewart et al., 2004; Kehrig et al., 2009).

Furthermore, tropical coastal waters are less monitored than marine environments from the Temperate and Polar Regions, in particular the South Atlantic Ocean, which is often considered as less contaminated then the northern ocean. Accordingly, the western South Atlantic Ocean has, until now, received little attention from researchers regarding levels of trace elements in marine organisms, especially in autotrophic and heterotrophic microorganisms (De Marco et al., 2006; Friedrich et al., 2006; Kehrig et al., 2006, 2009; Molisani et al., 2007).

In this study, mercury, methylmercury, selenium, cadmium, lead and copper were determined in a microbial loop composed by three size classes of autotrophic and heterotrophic microorganisms, 1.2–70 μm (seston, SPM), 70–290 μm (microplankton) and ≥290 μm (mesoplankton) collected at five sampling stations within Guanabara Bay, and one external point under the influence of the bay, used as a control area. The aims were to compare the possible differences in the bioaccumulation and trophic transfer of methylmercury and trace elements among all sampling points, as well as along the base of the estuarine food web. The composition of taxonomic groups of planktonic community was also examined to verify the possible influence of this biological parameter in the bioaccumulation and transfer of the contaminants.

2. Materials and methods

2.1. Study site

Guanabara Bay (22°S, 43°W, 384 km^2) in the Southeastern Brazilian coast (Fig. 1), is one of the most eutrophic tropical systems in the world (Valentin et al., 1999), receiving large loads of untreated domestic and industrial sewage from a drainage basin affected by over 7.8 million inhabitants, 10 000 industrial plants, two harbors, shipyards and oil terminals. In some areas of the bay, the ecosystem is heavily impacted by organic matter, oil and heavy metals, including cadmium, copper, mercury and lead, whose main consequences are high concentrations of toxic metals (Rebello et al., 1986; Kehrig et al., 2003) and hydrocarbons (Silva et al., 2007) in sediments and changes in the pelagic and benthonic communities (Valentin et al., 1999). The bay is among the most productive marine ecosystems in the Rio de Janeiro State, presenting a high phytoplankton density, as well as high nutrient concentrations (Kjerfve et al., 1997; Valentin et al., 1999; Kehrig et al., 2009) that result in high primary production waters, with an average net primary production (NPP) of 0.17 mol C m^{-2} day^{-1} (Carreira et al., 2002). However, the half-life of its water turn-over ($T_{50\%}$) is relatively short, of 11.4 days (Kjerfve et al., 1997), and exemplified by the good water quality of the deep central channel, which connects the bay to the Atlantic Ocean, in a north – south direction. Tides at Guanabara Bay are mainly semidiurnal with a period of approximately 12 h (Guenther et al., 2008). Its hydrobiology exhibits seasonal trends as well as spatial patterns associated with tidal currents, which create typical horizontal and vertical gradients (Kjerfve et al., 1997). The local climate is tropical humid, characterized by a dry season in winter and a rainy one in summer. Despite the intense pollution, habitat degradation and the reduced number of species available in commercial quantities, Guanabara Bay is the most important estuary for fish production on the Southeastern Brazilian coast (Jablonski et al., 2006).

2.2. Sampling procedures

Water and planktonic organisms were sampled from the superficial water layer (depth of 0.2–1.0 m) of Guanabara Bay, on 11 August 2005. Sampling was performed at neap tide cycle during the day, at a tide amplitude of 0.1 m in the New Moon phase. The experimental design was based on the tide chart from the Brazilian Navy's *Diretoria de Hidrografia e Navegação* – DHN (http://www.mar.mil.br/dhn/chm/tabuas/index.htm). Microorganisms were collected at five sampling stations along the lower estuary (points 1–5) and one external point under the influence of the bay (point 6), used as a control area (see Fig. 1). The sampling stations were chosen according to natural hydrodynamic characteristics of Guanabara Bay and pollution intensity established in previous studies (Francione et al., 2004; Kehrig et al., 2006, 2009).

At each sampling station, water samples were collected using 5 L Van Dorn bottles, which were then stored in plastic bottles at −10 °C. Plastic bottles were previously washed with phosphorous free detergent and cleaned with diluted hydrochloric acid (10%) in