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Mercury methylation in sediments of a Brazilian mangrove under different vegetation covers and salinities

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HIGHLIGHTS

- Methylmercury (MMHg) formation is poorly studied in mangrove ecosystems.
- Sediments (various depths, zones and salinities), roots and litter all formed MMHg.
- Hg methylation was high in intertidal sediments and low in infralittoral ones.
- MMHg formation in sediments under *R. mangle* was lower than under other trees.
- MMHg formation in sediment tended to increase with salinity.

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ABSTRACT

The presence and formation of methylmercury (MMHg), a highly toxic form of Hg, in mangrove ecosystems is poorly studied. Therefore the aim of this study was to evaluate mercury methylation potentials in sediment, litter and root samples (*Avicennia shaueriana* and *Spartina alterniflora*) from different regions of a mangrove ecosystem, as well as the influence of salinity on methylation. Sediment was sampled under different depths and in mangrove regions with different plant covers and salinities. All samples were incubated with ^{203}Hg and MM^{203}Hg was extracted and measured by liquid scintillation. MMHg was formed in all samples and sites tested including plant roots and litter. Higher Hg methylation was found in the superficial fraction of sediments (0.47–7.82%). Infralittoral sandy sediment had low MMHg formation (0.44–1.61%). Sediment under *Rhizophora mangle* had lower MMHg formation (0.018–2.23%) than under *A. shaueriana* (0.2–4.63%) and *Laguncularia racemosa* (0.08–7.82). MMHg formation in sediment tended to increase with salinity but the differences were not significant. Therefore, MMHg formation occurs in different sites of mangrove ecosystems and may be an important threat that requires further study.

1. Introduction

Mercury (Hg) behavior in aquatic environments, especially the production of methylmercury (MMHg), is influenced by a diversity of environmental factors that form a complex system with synergistic and antagonistic effects. Methylation is mostly mediated by microorganisms such as sulfate reducing bacteria (SRB) and its efficiency commonly depends on factors like microbial activity and composition, which are in turn affected by factors like pH, Eh and the presence of organic and inorganic complexing agents in the medium (Mauro et al., 1999; Ullrich et al., 2001).

Mercury biogeochemistry has been intensively studied in the last decades on land, atmospheric and freshwater systems and more recently on coastal ecosystems (Hammerschmidt et al., 2004; Sonke et al., 2013). Coastal ecosystems have an important role in the global mercury cycle, not only as sinks of mercury from the land environment, but also as potential Hg sources to the ocean (Fitzgerald et al., 2007). It is estimated that human exposure to MMHg, a highly toxic form of mercury, occurs mainly by fish

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consumption, of which >60% is composed of marine species (Hammerschmidt et al., 2004).

Mangroves occupy 8% of the world's coast line, representing a total of 181.077 km^2 distributed in tropical and subtropical regions. Brazil possesses the second largest mangrove area in the world, approximately 13.400 km^2, the first being Indonesia, with 42.550 km^2 (Filho, 2005). This ecosystem is of great ecological importance since it constitutes a nursery and refuge for a variety of marine species, which can pass all their life cycle or part of it inside the mangrove. It also has economic importance due to the extraction of crabs and oysters for sale and consumption and is usually located in areas of high anthropic pressure and pollution (Suhogusoff and Piliackas, 2007). Although mercury pollution generates environmental and health concerns, there are few studies regarding its accumulation and behavior in this ecosystem. A search for the words mercury and mangrove in the Web of Science search engine (March, 2014) returns 69 articles and this number drops to 13 when searching for MMHg instead.

Most of the articles published so far deal with the distribution of total mercury and MMHg and possible correlations with geochemical parameters as in Liang et al. (2013) and Wu et al. (2011); and a smaller number of articles study this metal concentration in local fauna and flora as in Ding et al. (2011). Studies in the Sepetiba Bay mangrove, where our research was done, showed a higher total Hg accumulation in surface layers of mudflat and tidal creek sediments whereas mangrove forest sediments showed higher Hg accumulation in root-rich subsurface layers (Silva et al., 2003). In the same region, studies showed that tidally driven export from the mangrove represent a significant potential source of MMHg to nearby coastal waters (Paraquetti et al., 2007). A recent paper showed the same results for Hg and MMHg in the Everglades, USA (Bergamaschi et al., 2012).

The use of radiotracer techniques offers unique possibility to better understand Hg methylation in various sites and environmental conditions. This approach is less expensive and time consuming when compared to competing technologies such as the use of enriched stable isotopes and mass spectrometry (Loveland et al., 2006). The use of the ^{203}Hg radiotracer has helped the study of Hg methylation in a variety of ecosystems and matrices (Langer et al., 2001; Desrosiers et al., 2006; Correia et al., 2013). Briefly, trace amounts of ^{203}Hg are added to the sample and methylation is estimated by the conversion of $^{203}Hg^{2+}$ into $MM^{203}Hg$. Since ^{203}Hg is not found in the environment, any $MM^{203}Hg$ found in samples is the product of biotic and/or abiotic ^{203}Hg methylation, depending on experimental set-up. This technique has the limitation of not measuring methylation and demethylation rates simultaneously, expressing only potential net Hg methylation rates.

Even though Hg methylation potentials have been studied in similar ecosystems such as saltmarshes (Gilmour et al. 1998; Marvin-Dipasquale, 1998), we did not find any study concerning this subject in mangroves. Knowing the potential methylmercury formation in this ecosystem is of great importance to predict the effects to the local biota and to humans that may consume the exposed organisms.

Mangroves have a number of specific features that can influence MMHg formation, such as tidal-driven oxygen, sulfate and salinity gradients, as well as a restless activity of burrowing animals. Mangrove trees, on the other hand, have developed different strategies to deal with anoxic substrates and their root systems modify redox potentials of surrounding sediments.

The objective of the present work was to determine Hg methylation potentials in: (1) mangrove sediments of a sea-land transect under different depths, vegetation covers, incubation times and salinities; (2) sediments associated to the rhizospheres of the mangrove trees *A. schaueriana*, *Laguncularia racemosa* and *Rhizophora mangle*; (3) their roots and litter.

2. Methodology

2.1. Sampling area

The study was conducted in Coroa Grande mangrove, Sepetiba Bay, located in Rio de Janeiro, Brazil. Despite the growth of urban and industrial activities installed around the bay contributing to its pollution, the Coroa Grande mangrove forest is moderately preserved. (Lacerda et al., 2001; Molisani et al., 2004). Total Hg concentrations in these mangrove sediments (22–184 ng g^{-1}) are considerably lower than in the adjacent Guanabara bay (50–3000 ng g^{-1}, Wasserman et al., 2000; Silva et al., 2003).

Avicennia schaueriana Stapf and Leech, *L. racemosa* Gaertn. and *R. mangle* L. trees are abundant and the mangrove is fringed by a *Spartina* sp. Zone (Lacerda et al., 2001) as shown in Fig. 1. All experiments were conducted in 2009.

2.2. Concentration of nutrients in the sediment

In order to better characterize the sediments used in the experiments described in later sections, Carbon (C), Nitrogen (N) and Phosphorus (P) were determined in three different mangrove regions: (1) unvegetated infrallitoral region exposed by the low tide, (2) a *Spartina* sp. stand, and (3) region rich in *Avicennia* roots (pneumatophores). For the determination of C, N and P, sediment samples were dried at 50 °C until constant weight. After maceration, the total nitrogen content was determined according to Allen et al. (1974) and total phosphorus according to Fassbender (1973). For total carbon determination, we used the solid unit of a 5000 TOC Analyzer (Shimadzu Co., Japan). C, N and P data are shown in Table 1.

2.3. Experiments

2.3.1. Mangrove transect

Since there is virtually no information on Hg methylation potentials in this ecosystem, the main objective of this first

Table 1
Concentrations of Nitrogen, Phosphorus and Carbon in the sediment of the three sampling stations in the Coroa Grande mangrove.

Stations	*N* (μmol g^{-1})	*P* (μmol g^{-1})	*C* (μmol g^{-1})
Roots (Pneumatophores)	500 ± 60	2.51 ± 0.16	8000 ± 1930
Spartina sp. stand	521 ± 12	3.14 ± 0.08	5480 ± 495
Infralittoral	351 ± 54	2.33 ± 1.09	3353 ± 180

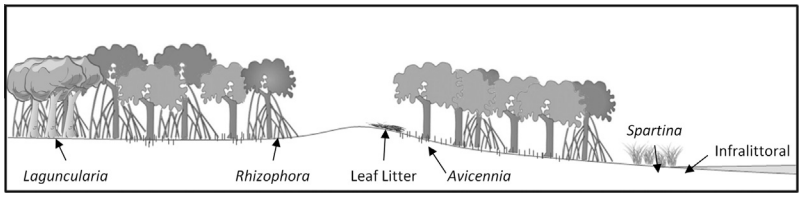

Fig. 1. Scheme of sampling area in Coroa Grande mangrove.