Mercury in litterfall and sediment using elemental and isotopic composition of carbon and nitrogen in the mangrove of Southeastern Brazil

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A B S T R A C T

Mercury and elemental and isotopic compositions of carbon and nitrogen were determined in litterfall and sediments from the mangrove of the Paraíba do Sul River, Rio de Janeiro, Brazil. Total mercury (THg) and monomethylmercury (MMHg) concentrations in sediment ranged from 33 to 123 ng g^{-1} and 0.20 −1.38 ng g^{-1}, respectively. The δ^{13}C in sediment varied from −29.4 to −26.5‰ and from 2.4 to 5.8‰ in δ^{15}N. The THg concentration in litterfall and its annual input to the mangrove was 21 ± 2 ng g^{-1} and 16 ± 4 µg m^{-2} for the species *Laguncularia racemosa*, 18 ± 1 ng g^{-1} and 17 ± 3 µg m^{-2} for *Rhizophora mangle*, and 53 ± 4 ng g^{-1} and 33 ± 4 µg m^{-2} for *Avicennia germinans*, respectively. The isotopic composition of leaf litter ranged from −28.6 to −26.9‰ for δ^{13}C and 4.5–7.2‰ for δ^{15}N. Both the highest annual Hg input via litterfall and highest sediment Hg concentration were observed in areas dominated by *A. germinans*. These results suggest that the rate of litterfall of plant species and the atmospheric deposition have played an important role in the Hg biogeochemical cycle in the mangrove ecosystem.

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1. Introduction

Mercury (Hg) is a global contaminant, and the atmosphere is its means of transport (Gustin et al., 2015; Travnikov et al., 2017). Thus, anthropic and natural Hg releases in the various atmospheric deposition routes of terrestrial and aquatic ecosystems (Zhang et al., 2009; Wang et al., 2016) are causes of concern. The inventory of global Hg emissions into the atmosphere estimated that anthropic releases into the global cycle account for 2000 tons per year, and Brazil was reported to be the country with the seventh highest Hg emissions in the world (UNEP, 2013).

In the atmosphere, Hg exists mainly in three forms: gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) (or gaseous oxidized Hg - GOM), and particulate bound mercury (PBM) (Driscoll et al., 2013; Wright et al., 2016). Transfers of these Hg forms to vegetation surfaces have been reported as an important pathway of Hg input to the forest ecosystems, which are estimated through litterfall production data (Wang et al., 2016; Risch et al., 2017). In forest canopies, dry deposition of RGM on the leaf surface can be the main source of Hg in litterfall, although GEM is also retained (likely in oxidized form) in foliage by stomatal uptake (Graydon et al., 2009; Stamenkovic and Gustin, 2009; Wang et al., 2016). The RGM and PBM also adsorb on leaf surfaces, where the Hg may either be photoreduced or re-emitted to the atmosphere (Graydon et al., 2009; Demers et al., 2013). Once in vegetation, Hg can be leached by precipitation and transferred to sediments via atmospheric deposition (e.g., throughfall) and through litterfall decomposition (Pokharel and Obrist, 2011; Wright et al., 2016). However, the relevance of the role of vegetation in the Hg biogeochemical cycle is not well understood (Wang et al., 2016); this is a fact highlighting the need for studies using frameworks that integrate different areas and processes related to the dynamics of Hg in marine coastal regions.

In mangrove ecosystems, litterfall can account for approximately one-third of the total productivity (Robertson et al., 1992).

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Some studies have been published in temperate and boreal forest ecosystems that relate Hg in litterfall with dry and wet deposition (Larsen et al., 2008; Fisher &Wolfe, 2012; Risch et al., 2017). However, in tropical Brazilian forest ecosystems, such data has been insufficient and concentrated in the Amazon (e.g., Fostier et al., 2000, 2015; Silva et al., 2009) and Atlantic Forest regions (Oliveira et al., 2005; Silva-Filho et al., 2006; Teixeira *et al.*, 2012), with few published studies on litterfall from mangroves (Oliveira et al., 2015).

Beginning in the 1980s, intense gold mining activities began in the Brazilian Amazon region, which employed Hg in the amalgamation of alluvial gold (Lacerda and Salomons, 1998). In the lower basin of the Paraíba do Sul River, where the present study was carried out, there are registers of the historic use of Hg. Beginning in the 1970s, Hg was used in organomercurial fungicides against pests in sugarcane plantations, which is the main agricultural product of the region (Câmara et al., 1986). Later, in the early 1980s, Hg began to be used in gold mining activities (Lacerda et al., 1993; Almeida and Souza, 2008). Though such activities were short-lived, estimates have put the annual release of Hg into rivers of the region at approximately 150 kg (Lacerda et al., 1993). Despite legal prohibitions, sporadic gold mining with Hg occurs even today. The studies carried out in the region have consistently reported Hg biomagnification along the estuarine food web (Di Beneditto et al., 2011; Di Beneditto et al., 2012). Moreover, Hg concentrations in mangrove sediments are higher than in estuarine, fluvial and coastal sediments (Araújo et al., 2015).

Elemental and isotopic compositions of carbon and nitrogen have been used in ecological studies to evaluate the sources, fate and quality of organic matter (OM) in estuarine and marine ecosystems (Thornton and McManus, 1994; Graham et al., 2001; Bouillon et al., 2008; Ohkouchi et al., 2015). They have also been utilized for tracing the mangrove OM transfer through the estuarine food web (Bouillon et al., 2000; Aita et al., 2011) and in association with other tracers recognized in the mangrove OM export to the coastal ecosystem (Cifuentes et al., 1996; Dittmar et al., 2001). The stable carbon isotopes (δ^{13}C) are commonly used to differentiate C_3 and C_4 plants and infer the OM cycling in the ecosystem (Wooller et al., 2003b; Bouillon et al., 2008; Ohkouchi et al., 2015). The nitrogen isotopes analysis (δ^{15}N) and (C/N)$_a$ ratio in plants and sediment must be interpreted with caution because they can be influenced by many processes, including biological N fixation, ammonification, nitrification and denitrification (Wooller et al., 2003a; Gonneea et al., 2004; Muzuka and Shunula, 2006). In addition, these data from the primary producers in mangroves are relevant to other studies for investigating trophic links and biogeochemical cycling in this coastal ecosystem.

Therefore, in the present study, an investigation of Hg accumulation and distribution patterns in the leaf litter of three common mangrove forest species and in the sediment of the mangrove was completed. The elemental and isotopic analysis of carbon and nitrogen were used as tools for characterization of organic matter in the ecosystem.

2. Materials and methods

2.1. Study area and sampling

Sampling was carried out in the estuary of the Paraíba do Sul River in the São Francisco do Itabapoana City (21° 36′ 00″ S and 41° 03′ 00″ W), in the Rio de Janeiro State, Southeastern Brazil (Fig. 1). Three study sites with limited anthropic influence (i.e., absence of trash, sewage and industrial discharges) were previously selected based on the study by Bernini and Rezende (2011). Site 1 was
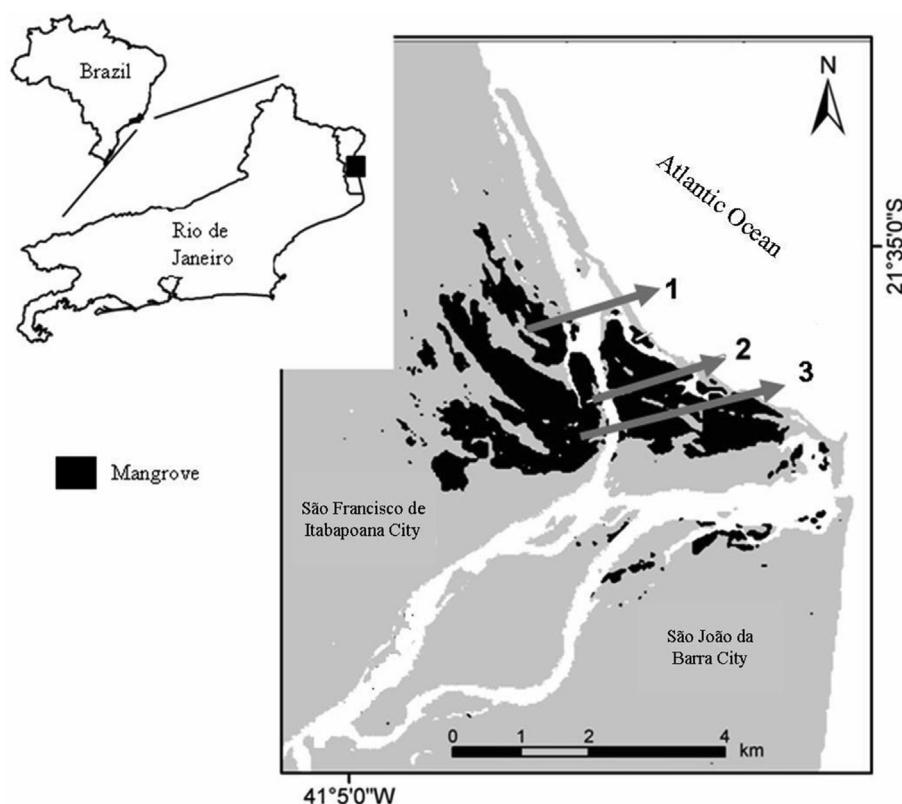

Fig. 1. Location of the sampling sites in the mangrove forest of the Paraíba do Sul River, Rio de Janeiro.