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

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ABSTRACT

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 $\delta^{13}C$ in sediment varied from −29.4 to −26.5‰ and from 2.4 to 5.8‰ in $\delta^{15}N$. 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 $\delta^{13}C$ and 4.5–7.2‰ for $\delta^{15}N$. 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.

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 ($\delta^{13}C$) 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 ($\delta^{15}N$) 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

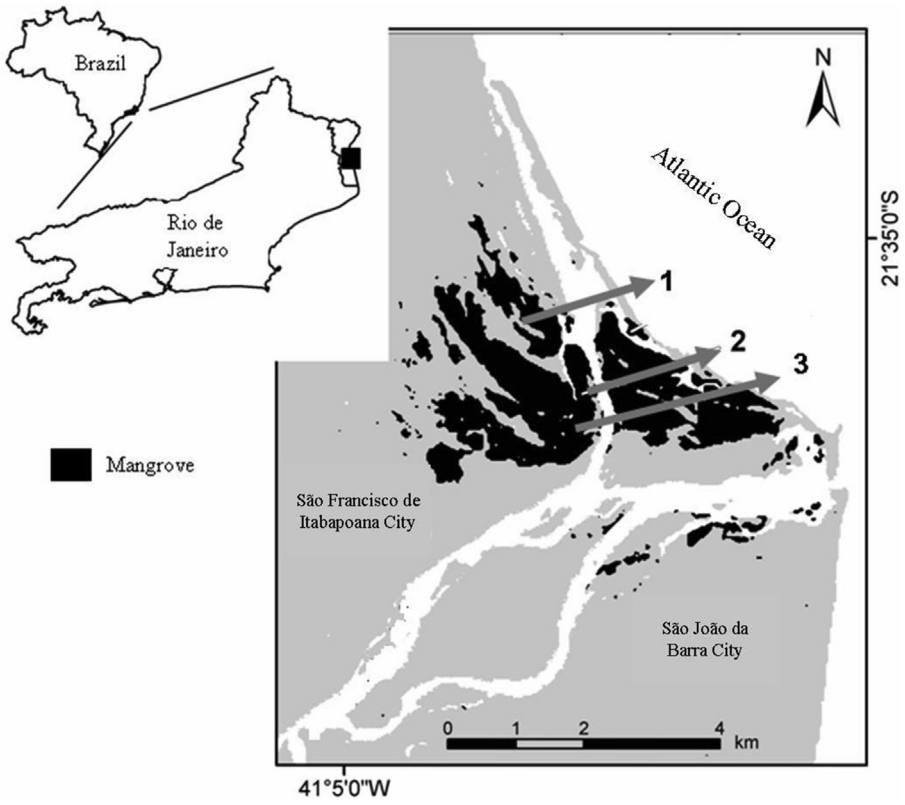

Fig. 1. Location of the sampling sites in the mangrove forest of the Paraíba do Sul River, Rio de Janeiro.

composed of *Laguncularia racemosa* (100% relative dominance and relative density), Site 2 of *Rhizophora mangle* (75% relative dominance and 97% relative density), and Site 3 of *Avicennia germinans* (99% relative dominance and 98% relative density) (Fig. 1). In a previous study conducted in the same area, there were no significant differences found between the edges and inner regions for the structural parameters (e.g., basal area and mean density for living and dead individuals, as well as mean diameter and height) (Bernini and Rezende, 2004).

The litterfall was collected at the sampling sites every fifteen days from January to December 2006. Seven litter traps (0.49 m^2 and 50 cm deep; 1.3 m above the sediment) were randomly distributed at each site. The biweekly (15 d) collections were grouped by month, with 21 samples/month and 252 samples/year for all species. The samples were dried in a circulation oven (60 °C for 72 h) without washing and subsequently separated into different litter fractions. The present study only made use of leaf fractions, as this was the most representative (52–66%) of the total litter composition according to Bernini and Rezende (2010). The leaves were crushed, homogenized and stored in a dry place until analyses were conducted in 2010.

In 2012, at each sampling site, four sediment samples were collected at different distances from the edge to the interior (5, 25, 45, and 75 m), except at Site 2, where sampling at the last point (75 m) could not be achieved due to logistical access. This sampling strategy was based on the size of each site and the phytosociology data reported by Bernini and Rezende (2011) in the same area, as well as the inundation features, considering the tidal range in the estuarine region. At each sampling point, 5 superficial sediment samples were collected (0–2 cm) for use as sample replicas. Thus, 20 samples were obtained from Sites 1 and 3, and 15 samples were obtained from Site 2. The sediments were separated into <2.0 mm fractions and lyophilized. A gross sub-sample was used for granulometric analysis, while homogenized samples in the ball mill (Fritsch model Pulverisette 6) were employed in the other analyses. The analyses were carried out in 2013, and all samples (plants and sediments) were stored in our clean laboratory and preserved in a well-sealed vial for Hg determinations.

2.2. Geochemical measurements and elemental and isotopic composition

The grain-size was measured with a particle analyzer (SALD 3101, *Laser Diffraction Particle Size Analyzer, Shimadzu*) with lyophilized sediments classified into three fractions: sand ($0.062 < d < 2$ mm), silt ($0.004 < d < 0.062$ mm) and clay ($d < 0.004$ mm), (d = diameter according to the Wentworth scale).

The elemental and isotopic composition (C and N) analysis in sediments was carried out in two stages. First, the determinations were performed on the bulk samples using 10 mg to obtain elemental and isotopic values for nitrogen. For isotopic and elemental organic carbon, decarbonated samples were used. The decarbonation procedure was performed by placing 10 mg of sample into a silver capsule, to which 1.0 M of HCl was added approximately 3 times (Kennedy et al., 2005). The litter leaf analysis was carried out using 3 mg of bulk samples.

Elemental concentrations and ($\delta^{13}C$ and $\delta^{15}N$) isotopic ratios were determined in a Finnigan Delta V Advantage Thermal Isotopic Mass Spectrometer with Conflo IV and Thermo Scientific Flash 2000 Organic Elemental Analyzer. Triplicate analysis was carried out for every 5 samples (95%). The detection limits for C and N were 0.05% and 0.02%, respectively. The $\delta^{13}C$ and $\delta^{15}N$ results were obtained according to the standards and were expressed in relation to the carbonate of the Pee Dee formation (Belemnite) for $\delta^{13}C$ and in relation to atmospheric N_2 for $\delta^{15}N$.

2.3. Total mercury (THg) analysis

The THg of the leaf litter was determined from 0.2 g of samples that were previously crushed and homogenized, then digested with H_2SO_4/HNO_3 (adapted from Silva-Filho et al., 2006). For the sediment, 0.3 g of dry and homogenized samples were subjected to acid extraction using HCl:HNO_3 (3:1) (adapted from Santos et al., 2005). The acid digestion was carried out in a Mars Xpress (CEM) microwave system, and the analytic determination of Hg was performed in a CETAC Quick Trace M-7500 H g Analyzer, with a detection limit of 1 ng g^{-1} for the method. Triplicates were analyzed every 20 samples for the litterfall and every 5 samples for the sediment. THg determinations of certified reference materials (apple leaves – NIST 1515 and estuarine sediment - NIST 1646) were within 92% and 95% of the certified valued, respectively, and coefficients of the variation of triplicate analyses were below 10%.

2.4. Monomethylmercury analysis

Monomethylmercury (MMHg) was measured in sediments located on the edge (5 m) and interior (15 m) of the sampling sites. The analytical determination was based upon a distillation process in which 500 μL of H_2SO_4 9 M and 200 μL KCl (20%) were added to 0.5 g of sediment heated on a hot plate (130 °C) with N_2 flow for approximately 50 min (adapted from EPA 1630). Samples were prepared with 220 μL CH_3COONa and 30 μL of sodium tetraethyl borate ($NaBEt_4$). The determination was completed using a Tekran 2700 Methylmercury Analyzer System at Trent University in Ontario, Canada. The recoveries of certified standards (IAEA-405) were above 85%, and coefficients of variation of triplicate analyses were below 10%. The detection limit of the method was <0.04 pg g^{-1}.

2.5. Hg input through litterfall and statistical treatment

The THg flux to the ecosystem via litterfall was calculated through the Hg concentrations (ng g^{-1}) and litterfall production (g m^{-2}) for the same period (Bernini and Rezende, 2011). The monthly and annual input values were expressed in μg m^{-2} $month^{-1}$ and μg m^{-2} $year^{-1}$, respectively. Comparisons of the values between vegetal species and sample sites were performed using the Kruskal-Wallis and Dunn tests.

3. Results

3.1. Geochemical parameters of the sediments

The sediments from the Paraíba do Sul mangrove were predominantly composed of silt and clay (d < 63 μm), which composed more than 60% of the sediment in all areas. Site 3 represented the region with the highest level of these two granulometric fractions, with values varying from ~80 to 90%. At Site 1, silt and clay ranged from 73 to 86%, while Site 2 had values from 60 to 73%. In terms of distance, Sites 1 and 2 generally showed increasing silt and clay fractions moving from the edge of the sampling sites (5 m) toward the interior (75 m) (Table 1).

The organic carbon (OC) and total nitrogen (TN) at the edges of the sampling sites (5 m) presented lower values compared to the 25 m and 45 m locations of Sites 1 and 2, while the opposite occurred at Site 3. The average concentrations ranged from 2.7 to 32.7% for OC and from 0.14 to 1.22% for TN. For the atomic ratio $(C:N)_a$, lower values were observed at the edges of the sites (5 m), with values between 16.1 and 31.8 (Table 2).

The carbon isotope results ($\delta^{13}C$) varied from −29.4 to −26.5‰ and nitrogen ($\delta^{15}N$) varied from 2.4 to 5.8‰ (Table 2). Site 3 differed

Table 1
Granulometry values (%) of the sediments from the Paraíba do Sul River mangrove, Rio de Janeiro.

Sites		Distance			
		5 m	25 m	45 m	75 m
1	Sand	26.7 ± 5.5	22.0 ± 3.6	13.7 ± 0.5	14.2 ± 0.6
	Silt	61.6 ± 15.7	67.3 ± 10.4	73.8 ± 1.7	74.0 ± 1.5
	Clay	11.7 ± 4.6	10.7 ± 2.1	12.5 ± 0.2	11.8 ± 0.7
2	Sand	40.6 ± 2.1	26.6 ± 1.2	27.3 ± 3.0	x
	Silt	53.1 ± 5.7	63.6 ± 3.7	63.0 ± 9.5	x
	Clay	6.3 ± 1.9	9.8 ± 0.7	9.7 ± 1.8	x
3	Sand	10.2 ± 1.3	11.3 ± 0.4	14.7 ± 1.3	23.2 ± 1.1
	Silt	73.9 ± 2.5	73.2 ± 0.3	70.6 ± 2.5	65.4 ± 2.2
	Clay	15.9 ± 1.5	15.5 ± 1.0	14.7 ± 1.4	11.4 ± 1.2

statistically from the other regions for $\delta^{13}C$ (Kruskal-Wallis $H_{55} = 23.38$, $p < .0001$ and Dunn test), as well as $\delta^{15}N$ data (Kruskal-Wallis $H_{55} = 23.12$, $p < .0001$ and Dunn test).

The THg average concentrations ranged from 33 to 104 ng g^{-1} in the sediment of Site 1, from 50 to 66 ng g^{-1} for Site 2, and from 87 to 123 ng g^{-1} for Site 3. The THg values increased from the edges of the sampling sites (5 m) to the interiors (75 m), except for Site 3 (Table 2). This last site, which is dominated by *A. germinans*, showed the highest Hg concentrations and differed statistically from the other sites (Kruskal-Wallis $H_{55} = 23.67$, $p < .0001$ and Dunn test). The THg values in the sediment were associated with the silt-clay fraction of each site ($r_s = 0.645$, $n = 20$, $p < .05$ at Site 1; $r_s = 0.811$, $n = 15$, $p < .05$ at Site 2; $r_s = 0.717$, $n = 20$, $p < .05$ at Site 3) and with the OC level ($r_s = 0.932$, $n = 20$, $p < .05$ at Site 1; $r_s = 0.839$, $n = 15$, $p < .05$ at Site 2; $r_s = 0.628$, $n = 20$, $p < .05$ at Site 3).

Monomethylmercury (MMHg) in the sediments ranged from 0.20 to 1.38 ng g^{-1}, with an average of 0.73 ± 0.45 ng g^{-1} (Table 3). The highest values that registered were at Site 3. The concentrations of MMHg and the proportion in relation to THg (% MMHg) were higher in the interior of the sampling areas compared with the edges at Sites 2 and 3, whereas at Site 1, the opposite occurred.

3.2. Concentration and flux of THg and elemental and isotopic compositions in the litterfall

The average content of OC in the leaf litter presented values between 44.7 and 46.3%, while the TN data ranged from 0.56 to 0.98%. *A. germinans* exhibited the highest OC and TN values, while the atomic ratio $(C:N)_a$ was highest in *R. mangle*. For the OC data, the species *L. racemosa* was significantly different from the others, while *R. mangle* and *A. germinans* did not differ (Kruskal-Wallis $H_{252} = 64.4$ $p < .0001$ and Dunn test). However, for the TN and $(C:N)_a$ values, all species showed significant differences between them (Kruskal-Wallis $H_{252} = 148.4$ and $H_{252} = 148.1$ for TN and C:N, respectively; $p < .0001$ and Dunn test). The $\delta^{13}C$ data ranged from −28.6 to −26.9‰, and from 4.5 to 7.2‰ for $\delta^{15}N$ (Table 4). The $\delta^{13}C$ and $\delta^{15}N$ values differed among all three species (Kruskal-Wallis $H_{252} = 180.8$ for $\delta^{13}C$ and $H_{252} = 189.8$ for $\delta^{15}N$, $p < .0001$ and Dunn test).

The average Hg concentrations in the leaf litter varied from 13 to 34 ng g^{-1} (21 ± 2 ng g^{-1}) for *L. racemosa*, 7–26 ng g^{-1} (18 ± 1 ng g^{-1}) for *R. mangle*, and 36–66 ng g^{-1} (53 ± 4 ng g^{-1}) for *A. germinans* (Fig. 2). *A. germinans* showed the highest Hg values during the year and differed statistically from the other species. *L. racemosa* and *R. mangle*; however, it did not exhibit significant differences (Kruskal-Wallis $H_{252} = 135.56$ $p < .0001$ and Dunn test).

The monthly average Hg input for the litterfall was 1.4 μg m^{-2} $month^{-1}$ for *L. racemosa*, 1.4 μg m^{-2} $month^{-1}$ for *R. mangle*, and 2.7 μg m^{-2} $month^{-1}$ for *A. germinans* (Fig. 3). The annual Hg input values were 16 μg m^{-2} $year^{-1}$, 16 μg m^{-2} $year^{-1}$, and 32 μg m^{-2} $year^{-1}$ for species *L. racemosa*, *R. mangle*, and *A. germinans*, respectively. There was a significant difference between the annual

Table 2
Mean values of total Hg and of elemental and isotopic composition of carbon and nitrogen in sediment from the Paraíba do Sul River mangrove, Rio de Janeiro.

Sites		Distance			
		5 m	25 m	45 m	75 m
1	THg	33 ± 11	75 ± 24	104 ± 7	102 ± 8
2	(ng g^{-1})	50 ± 11	66 ± 13	61 ± 16	x
3		111 ± 14	123 ± 5	113 ± 13	87 ± 7
1	OC (%)	2.7 ± 1.3	9.8 ± 3.9	21.3 ± 3.9	32.7 ± 2.3
2		3.1 ± 1.2	13.5 ± 5.3	12.5 ± 4.9	x
3		10.6 ± 2.4	10.6 ± 0.9	9.1 ± 1.1	6.1 ± 0.8
1	TN (%)	0.14 ± 0.07	0.38 ± 0.17	0.84 ± 0.14	1.22 ± 0.06
2		0.15 ± 0.05	0.49 ± 0.17	0.46 ± 0.19	x
3		0.76 ± 0.14	0.69 ± 0.04	0.56 ± 0.08	0.34 ± 0.05
1	$(C:N)_a$	22.8 ± 1.5	30.9 ± 1.9	29.5 ± 1.3	31.3 ± 2.2
2		22.8 ± 2.3	31.8 ± 2.0	31.6 ± 1.5	x
3		16.1 ± 1.9	17.9 ± 1.3	18.9 ± 0.7	21.1 ± 1.3
1	$\delta^{13}C$	−29.4 ± 0.4	−28.2 ± 0.6	−28.9 ± 0.4	−27.8 ± 0.4
2		−28.8 ± 0.3	−28.1 ± 0.6	−28.6 ± 0.3	x
3		−26.6 ± 0.5	−26.5 ± 0.1	−27.1 ± 0.2	−28.4 ± 0.4
1	$\delta^{15}N$	3.8 ± 0.5	4.0 ± 0.5	4.4 ± 0.1	5.4 ± 0.3
2		4.6 ± 0.3	3.2 ± 1.1	2.4 ± 0.3	x
3		5.8 ± 0.2	5.5 ± 0.1	5.1 ± 0.1	4.5 ± 0.1

Table 3
Monomethylmercury concentrations in relation to total Hg values in the sediment from the Paraíba do Sul River mangrove, Rio de Janeiro.

Sites	Distance	THg (ng g^{-1})	MMHg (ng g^{-1})	% MMHg
1	5 m	34.1	0.38	1.1
	15 m	100.0	0.45	0.4
2	5 m	43.3	0.20	0.5
	15 m	56.9	1.26	2.2
3	5 m	119.2	0.75	0.6
	15 m	110.3	1.38	1.2

Table 4
Elemental and isotopic composition of carbon and nitrogen in the leaf litter of the species *Laguncularia racemosa*, *Rhizophora mangle*, and *Avicennia germinans*.

	Site 1	Site 2	Site 3
	(*L. racemosa*)	(*R. mangle*)	(*A. germinans*)
OC (%)	44.7 ± 0.8	45.9 ± 1.8	46.3 ± 1.3
TN (%)	0.71 ± 0.19	0.56 ± 0.11	0.98 ± 0.15
$(C:N)_a$	78.2 ± 18.3	98.2 ± 15.9	56.2 ± 7.8
$\delta^{13}C$	−28.6 ± 0.1	−28.1 ± 0.1	−26.9 ± 0.1
$\delta^{15}N$	4.5 ± 0.2	3.9 ± 0.2	7.2 ± 0.1

contribution of *A. germinans* compared with the other species, while *L. racemosa* and *R. mangle* did not differ (Kruskal-Wallis $H_{252} = 65.1$ $p < .0001$ and Dunn test).

4. Discussion

The OC content in the litterfall was similar between the plant species, while the TN values were greater in *A. germinans*. Consequently, the $(C/N)_a$ ratio was the lowest in this species. This association was observed in other studies of *Avicennia* sp. (Wooller et al., 2003b; Muzuka and Shunula, 2006). Nutrient analyses in the mangrove leaves from other studies also reported an elevated N content in *A. germinans* compared with *L. racemosa* and *R. mangle* (Cuzzuol & Campos, 2001; Medina et al., 2001). Mangroves can export most of the OC to adjacent coastal waters as DOC (dissolved organic carbon), POC (particulate organic carbon) and MD (macrodetritus, i.e., leaves, branches and reproductive parts of plants). According to Rezende et al. (2007), the different fractions of the total OC behave differently and are controlled by environmental variables, such as flooded area extension (mostly for DOC and POC) and external forces (e.g., wind, mostly MD). The authors estimated the amount of carbon exported as MD to be 0.99 kg over four tidal cycles in the mangroves of Sepetiba Bay, Rio de Janeiro. The MD is likely a significant source of OC to coastal marine sediments (Boto and Bunt, 1981; Jennerjahn and Ittekkot, 2002), and their transport is controlled by litterfall production and deposition, mangrove structure, crab activity, strong winds and tidal energy (Rezende et al., 2007; Bouillon et al., 2008).

The $\delta^{13}C$ values in the leaf litter were similar to the previous data reported for the C_3 plants, with the most frequent values around −27‰ (e.g., Rao et al., 1994; McKee et al., 2002; Muzuka and Shunula, 2006). The $\delta^{15}N$ data in mangrove plants have provided different results, with differences of up to 10‰ (e.g., Fry et al., 2000; McKee et al., 2002). These variations may be explained by the N source and/or differences in fractionation during uptake, or by other factors (Fry et al., 2000; Wooller et al., 2003b). Furthermore, products from anthropic activities such as urban sewage or fertilizers from agriculture systems can influence the N levels in the mangroves (Wooller et al., 2003b; Bouillon et al., 2008).

The carbon isotope results in the sediments indicates that the main source of organic matter to this compartment was the mangrove leaves, as reported by Muzuka and Shunula (2006) and

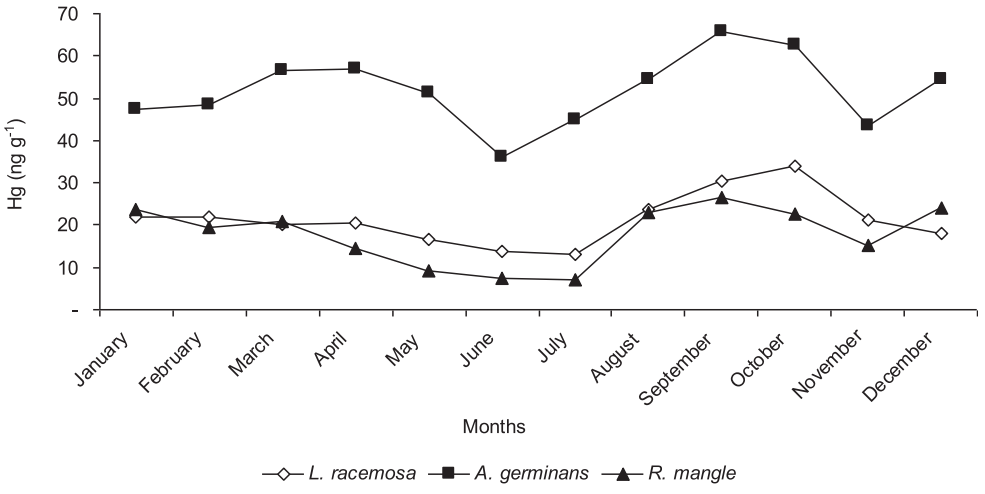

Fig. 2. Mean total Hg concentrations in the leaf litter of three dominant plant species of the Paraíba do Sul River mangrove, Rio de Janeiro.

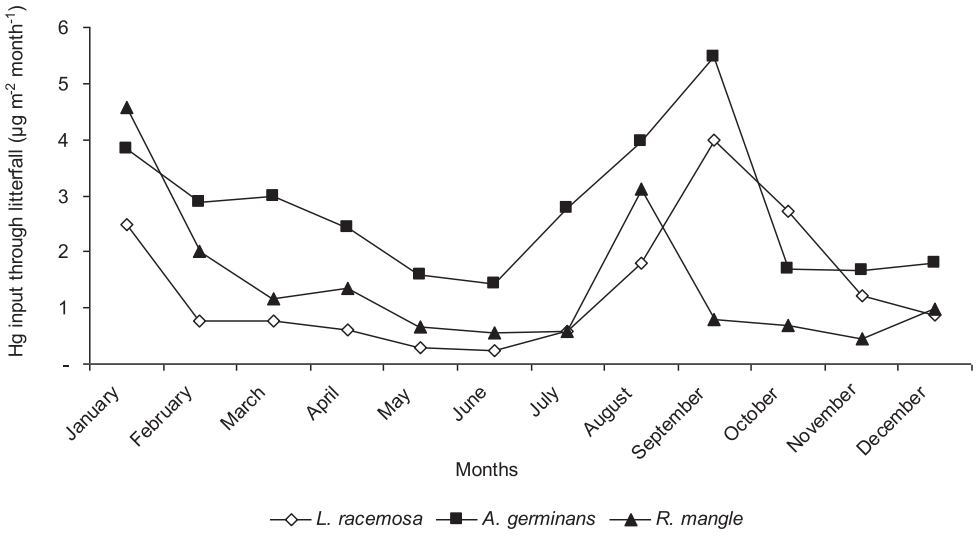

Fig. 3. Mean monthly total Hg input via litterfall from three dominant plant species of the Paraíba do Sul River mangrove, Rio de Janeiro.

Bouillon et al. (2008). At Site 3, both isotopic and elemental analyses showed different contents from the other sites. A previous study at the same sites found higher decomposition rates in the *A. germinans* leaf litter compared with the other species (Matos et al., 2012). Although the $(C/N)_a$ ratio of Site 3 presented lower values compared with Sites 1 and 2, these results are not sufficient to infer the digenetic process of the sedimentary OM, considering the high N values can be associated with other parameters, such as organic or inorganic N adsorption onto silicate clay surfaces and microbial N incorporation during OM decomposition, for example (Gonneea *et al.*, 2004).

The THg concentrations in the sediment ranged from 33 to 123 ng g^{-1}. These values were consistent with those reported in estuarine regions with limited anthropic influence, as described by Silva et al. (2003), Vilhena et al. (2003), and Sanders et al. (2008). The mean THg concentrations observed in the present study were above the background levels established for coastal sediments in Brazil, which were between 15 and 30 ng g^{-1} (Marins et al., 2004). Moreover, compared with the guidelines established by NOAA (National Oceanic Atmospheric Administration), our results were below both the TEL (threshold effect level) reference values of 174 ng g^{-1} for freshwater sediments and the PEL (probable effect level) of 486 ng g^{-1} (Buchman, 2008). The mangroves under the influence of industrial and port complexes, however, have demonstrated levels superior to those reported in the present study. Both Kehrig et al. (2003) and Covelli et al. (2012), for example, carried out studies in Guanabara Bay in the state of Rio de Janeiro.

The THg concentrations in sediments shows spatial variation at each site, which is probably associated with the silt-clay fraction and OC content. These positive and significant relations can indicate Hg retention in the fine sediments and signals the importance of organic matter as geochemical support in Hg accumulation and distribution in the sedimentary matrix of the mangrove. Several studies conducted in estuarine regions have found an association between Hg and the silt-clay fraction (Sanders et al., 2008; Araújo et al., 2015) and with OC values (Marchand et al., 2006; Almeida and Souza, 2008). According to Bernini and Rezende (2004), there is no structural difference between the edge and inner regions of the mangrove of the Paraíba do Sul River, as previously mentioned. However, the flood frequency is probably higher at the edge of the sampling sites than in the interior, which results in a higher transport of the organic matter associated with the low-density sedimentary material.

The MMHg mean concentrations obtained in the sediment were 0.73 ± 0.45 ng g^{-1}, ranging from 0.20 to 1.38 ng g^{-1}. In their studies of mangroves in China, Ding et al. (2011) reported similar concentrations to those observed in the present study, with mean values of 0.80 ± 0.60 ng g^{-1} (0.24–1.86 ng g^{-1}). However, when the THg levels in the sediment (225 ± 157 ng g^{-1}; 26–438 ng g^{-1}) and the MMHg proportion in relation to THg are compared, values from the Chinese study were higher than in the present study (0.1%–7.1%). Ding et al. (2011) reported that the high levels of atmospheric Hg in the Chinese region (72.5 ± 12.5 ng m^{-3}) and in plants of different species (THg: 1760 ± 1885 ng g^{-1}, MMHg: 0.72 ± 0.47 ng g^{-1}) are the factors responsible for these results. Furthermore, we emphasize that the process of methylation is sensitive to a variety of variables, which are dependent on the location and distinct area characteristics, such as the concentration of inorganic Hg (Hg^{2+}), sulfites and sulfates, and the physico-chemical conditions of the system (e.g., Eh, pH, temperature, salinity) and in addition to the level of microbial diversity and activity (Oliveira et al., 2015; Correia and Guimarães, 2017).

The highest MMHg values were observed at Site 3, which is an area covered by *Avicennia germinans*. A study conducted in a mangrove of Sepetiba Bay, Rio de Janeiro, Brazil reported a similar pattern (Oliveira et al., 2015). The authors investigated the methylation potential of Hg in sediments under different vegetation covers (*Avicennia schaueriana*, *Laguncularia racemosa*, and *Rhizophora mangle*). The superficial sediment (0–2 cm) associated with *Avicennia* showed higher methylation rates than the others. The elevated methylation rates in the superficial sediments is associated mainly with the elevated OC content caused by the litterfall decomposition that is easily utilized by anaerobic bacteria, such as sulfate reducers, iron-reducing bacteria and methanogens, which are considered important in the Hg methylation in this ecosystem (Correia and Guimarães, 2017). In the Sepetiba Mangrove, Lacerda et al. (1995) used amino acids and sugars analysis and suggested that the organic matter associated with *Avicennia* soils showed higher microbial activity and more degradable organic matter than the soils associated with *Rhizophora*. This fact corroborates with the enhanced recycling of nutrients and possibly the heightened formation of MMHg.

The THg distribution in litterfall from the three species

throughout the year showed an increase of the concentrations from August to October; in fact, the precipitation average in these months were higher (68 mm) in comparison to the previous marked dry period (from May to July – 17 mm) (INMET, 2006). This period represents the beginning of the rain and consequently the wet deposition of Hg from the atmosphere. On the other hand, in November, the precipitation rate was the highest (176 mm) and the Hg values decreased, suggesting a washing of the Hg from the litterfall.

The highest THg concentrations in leaf litter were observed in *A. germinans*. This species has elevated trichome density on its leaf surface, as described by Tomlinson (1986). This provides a larger surface area for atmospheric deposition, increasing the foliar adsorption of RGM and PBM. The association of trichome density and leaf surface were reported by Teixeira *et al.* (2012) in the plant species of the Atlantic Rainforest. A part of the Hg deposited may be rapidly photoreduced and re-emitted to the air, while a portion may be retained on foliage and deposited with litterfall, as demonstrated by some isotope spike experiments (Hintelmann et al., 2002; Mowat et al., 2011). Dry deposition of RGM and PBM are strongly related to emissions from local sources, due to their short lifespan in the air (Demers et al., 2013; Wright et al., 2016). In addition, *A. germinans* is a salt-excreting plant that can eliminate ions through specialized leaf glands (Scholander et al., 1962). Hg excretion by the salt gland was reported by Kraus et al. (1986) in the leaves of the salt marsh plant *Spartina alterniflora*, but this mechanism has not been described for *A. germinans* to justify the highest concentrations in its leaves. These facts suggest that litterfall rates and atmospheric deposition play an important role in the Hg cycle in mangroves, although more studies are needed to confirm the relevance of these processes in accumulation of Hg in leaves.

There are no reports in the literature regarding the Hg values in the leaves of species *L. racemosa*, *R. mangle*, or *A. germinans,* which were analyzed in the present study. Ding et al. (2011) studied the Hg concentration in the leaves of other plant species of Chinese mangroves and reported THg litterfall values of 385–2130 ng g^{-1}, which is above those obtained in the present study. The higher concentrations shown in the Chinese mangroves were attributed to the high atmospheric Hg content, as cited above for MMHg.

The atmosphere is believed to be the main source of Hg input into forest canopies (Fostier et al., 2015; Risch et al., 2017). The translocation of Hg between roots and leaves would not be significant (i.e., close to 10%) (Bishop et al., 1998; Graydon et al., 2009). Thus, atmospheric Hg concentrations that affect levels of Hg in foliage and canopies become more enriched along their lifetime (Rea et al., 2002; Wright et al., 2016). The atmospheric Hg deposition was measured in bulk precipitation by Lacerda et al. (2002) in the city of Campos dos Goytacazes (0.51 ng L^{-1}), which is approximately 30 km from the estuary of the Paraíba do Sul River. This value was lower than the Hg values in the bulk deposition in the Amazon region (Fostier et al., 2000; Fadini and Jardim, 2001) and in other studies around the world (e.g., Wright et al., 2016; Sprovieri et al., 2017). Although the concentrations are low, Lacerda et al. (2002) suggested that sugarcane plantations may contribute to the atmospheric Hg emissions in the region during pre-harvest burning activity (performed throughout the dry season – May to October). This fact was important due to the past use of organomercury fungicides in sugarcane, which may re-release the Hg into the atmosphere through vaporization.

On a global scale, Hg concentration in the litterfall of terrestrial forest ecosystems and its annual Hg deposition was estimated by Wang et al. (2016) at 168 sites around the world. The global mean Hg concentration in litterfall was 54 ± 22 ng g^{-1} (17–238 ng g^{-1}) and the Hg flux was 27 ± 36 μg m^{-2} yr^{-1} (2.7–219.9 μg m^{-2} yr^{-1}). In this global evaluation, Brazil showed both the highest Hg

Table 5
Mean total Hg concentrations and Hg input through litterfall in plants from different ecosystems.

Site	Forest Type	ng g^{-1}	μg m^{-2} yr^{-1}	Reference	Comments
São Francisco do itabapoana Rio de Janeiro, Brazil	Mangrove	31 ± 2	24	This study	Mean value of leaf litter all fraction of the three species
Amazonian rainforest, Brazil	Amazon rainforest	60.5	49	Fostier et al., 2015	Calculated from 10 datasets
Negro River Basin, Manaus, Brazil	Amazon rainforest	48 ± 10	43	Silva et al., 2009	Collected monthly for 1 year
French Guiana	Amazon rainforest	64 ± 14	45	Mélières et al., 2003	Leaves collected from the canopy
Rio de Janeiro, Brazil	Atlantic Forest	238 ± 52	184	Teixeira *et al.*, 2012	Collected monthly for 1 year
Ilha Grande, Rio de Janeiro, Brazil	Atlantic Forest	131 ± 74	122	Silva-Filho et al., 2006	Collected monthly for 1 year
Rio de Janeiro, Brazil	Atlantic Forest	170 ± 70	128	Oliveira et al., 2005	Collected monthly for 1 year
Langtjern, Norway	Boreal Forest	37 ± 10	2.7	Larsen *et al.*, 2008	6 months sampling
ELA, Ontario, Canada	Boreal Forest (Forested wetland)	38 ± 7	10.3	Graydon et al., 2008	625 cm^2 collectors sampling in 2001–2006
16 States across Eastern USA	Temperate Forest	40.6 (21.4–62.7)	11.7 (2.2–23.4)	Risch et al., 2017	Mean value of 6 years (Sept. Dec.) Litterf all sampling
Great Smoky Montains National Park, USA	Temperate Forest	37 to 63	10 to 29	Fisher & Wolfe, 2012	Collected in 3 elevations (Apr.–Nov.) in 2008–2009
Mt. Simian National Reserve, SW China	Subtropical Forest	106 ± 18	42	Ma et al., 2016	Collected monthly for 1 year, from 4 sites
Mt. Ailao, SW China	Subtropical Forest	54	71	Zhou et al., 2013	Collected monthly for 1 year
LeiGongShan, SW China	Subtropical Forest	135 ± 31	78	Wang et al., 2009	Collected monthly for 1 year

concentration in litterfall (92 ± 49 ng g^{-1}) and its annual Hg flux (83 ± 47 μg m^{-2} yr^{-1}), followed by China (46 ± 25 ng g^{-1}, 78 ± 72 μg m^{-2} yr^{-1}) and both North America and Europe (43 ± 12 ng g^{-1}, 15 ± 8 μg m^{-2} yr^{-1}). These results were higher than those observed in the present study, as shown in Table 5 for the different forest ecosystems.

The Hg values reported in litterfall in the mangrove forest (this study) were smaller than other Brazilian and Chinese studies and similar to boreal and temperate ecosystems. However, the annual Hg input seems to be greater in the present study compared with boreal and temperate regions (Table 5).

A global modeling study for terrestrial forest ecosystems suggested that the Hg deposition flux decreases spatially from the tropical and subtropical regions (70%) to the temperate and boreal zones (30%) (Wang et al., 2016). This pattern can be observed in Table 5, although comparisons must be carried out with caution due to the numerous differences between these ecosystems, as well as the methodological differences in the studies (e.g., form and time of sampling). Additionally, natural and anthropogenic sources that affect Hg concentrations in the atmosphere and the meteorological features of the region (e.g., precipitation, temperature, and winds) should be considered (Wright et al., 2016; Sprovieri et al., 2017; Travnikov et al., 2017).

Furthermore, industrial areas and large urban centers can directly influence the deposition of atmospheric Hg in vegetation, which explains the high values found in the studies by Silva-Filho et al. (2006) and Teixeira *et al.* (2012) (Table 5), which were conducted close to urban centers and industrial regions. The opposite is true for the studies by Mélières et al. (2003) and Zhou et al. (2013), which were performed in remote areas of French Guiana and China that are free from anthropogenic Hg pollution and found values similar to the values obtained from the leaves of *A. germinans*.

The results of the Hg input from leaf litter indicate *A. germinans* as the species with the highest contribution of the element to the ecosystem. This plant species is the dominant one in the estuary of the Paraíba do Sul River (53% dominance) (Bernini and Rezende, 2011) and, as mentioned before, shows a faster litterfall decomposition rate than *L. racemosa* and *R. mangle* (Matos et al., 2012). These facts, in addition to the higher concentration and input of Hg values, suggest that *A. germinans* is the species most responsible for the transport and release of the Hg that has accumulated in the litterfall of this mangrove. Furthermore, throughfall analysis in the same sampling area shows mean values of 4.8 ± 2.6 ng L^{1}, and throughfall samples associated with trees of *A. germinans* show the highest values among all other plant species (Lima et al., *personal communication*).

Previous studies have reported that the Hg delivered to the forest floor is mainly associated with litterfall (~60–80%), with a smaller contribution of Hg from precipitation (i.e., throughfall) (~20–40%) (St. Louis et al., 2001; Rea et al., 2002; Demers et al., 2013). Once deposited into the mangrove sediment, Hg can be associated with important geochemical substrates such as oxides and hydroxides (e.g., Fe and Mn) and organic matter, or precipitate as HgS (Lechler et al., 2000). Moreover, Hg can be converted to monomethylmercury (a more toxic form) (Correia and Guimarães, 2017) and be incorporated into the coastal food web through the Hg biomagnification process (Hylander et al., 2000; Di Beneditto et al., 2012). Almeida and Souza (2008) found that the sediments of the flooded areas and in the estuary of the Paraíba do Sul River exhibit the highest THg concentrations and the highest proportion of Hg^{II}, compared with the elemental form (Hg^{o}). While in the mangrove, ~80% of the Hg is associated with the fraction strongly bound to the sediment (Araújo et al., 2015), some studies have shown that the mangrove ecosystem can become an important exporter of Hg into the adjacent aquatic systems (Paraquetti et al., 2007).

On a global scale, the dynamic of Hg in the mangroves may be controlled by specific variables such as the presence of point sources of contamination, Hg concentration in the atmosphere, physiological and morphological mechanisms of each plant species, phenology (e.g., litterfall production), salinity and tide amplitude. These variables regulate the Hg distribution and its flux in the different compartments (vegetation, sediment and biota), its accumulation and/or exportation to the adjacent coastal areas and the food chain associated with the ecosystem.

5. Conclusions

The highest Hg concentrations (leaves and sediment) and its annual input through litterfall were reported for the dominant plant species in the mangrove of Paraíba do Sul River (*A. germinans*). The isotopic and elemental analyses of C and N demonstrated the sources of organic matter and its association with the levels of Hg. These results highlight the importance of the rate of litterfall in the flux of Hg and suggest that atmospheric deposition has been playing a relevant role in the Hg biogeochemical cycle of the mangroves. Although the Hg input via litterfall was lower than in other areas with closer sources of contamination, our results suggest that mangroves are an important integrator for Hg in the atmosphere, vegetation and sediment.

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