

Bioavailability and sequential extraction of mercury in soils and organisms of a mangrove contaminated by a chlor-alkali plant

Paula Renata Muniz Araújo, Caroline Miranda Biondi*, Clístenes Williams Araújo do Nascimento, Fernando Bruno Vieira da Silva, Alfredo Montero Alvarez

Department of Agronomy, Federal Rural University of Pernambuco, Dom Manuel de Medeiros Street, S/n - Dois Irmãos, 52171-900, Recife, PE, Brazil

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ABSTRACT

Botafogo river estuary poses the highest Hg concentration reported for mangrove soils in Brazil. Such high contamination took place owing to the improper waste disposal for 24 years from a chlor-alkali plant nearby the estuary. Here we determined Hg concentrations in soils, mangrove plants (*Rhizophora mangle* and *Laguncularia racemosa*), and an aquatic organism (the oyster species *Crassostrea rhizophorae*) to assess Hg bioavailability. Besides, a sequential extraction procedure was used to separate soil Hg into five fractions: water-soluble; 'human stomach acid' soluble; organically bound; elemental Hg; mercuric sulfide. Results showed that environmentally available concentration of Hg in the mangrove soils were up to 150-fold higher than a pristine mangrove under the same geological context used as a reference. Additionally, Hg concentration in soils was also above sediment quality guidelines and Hg adverse effects towards sensitive estuarine organisms are likely. Mercury concentrations in oysters were the highest reported in Brazil, but within safety standards according to the country food security agency. It seems that Hg stocks in the studied soils are governed by organic matter and redox conditions, but changing on environmental conditions and land use can alter this balance and convert these mangrove areas from sink to source of Hg to the environment.

1. Introduction

Mercury (Hg) is one of the most concerning global pollutants owing to its high toxicity, environmental persistence, and bio-accumulation. Production of chlorine and caustic soda is a significant source of Hg contamination as the metal is widely used as a catalyst in chlor-alkali plants and discharged in effluents or emitted in the gaseous elemental form (Hg^0) (Hisler and Probst, 2006; Song et al., 2018). Thus, chlor-alkali plants can potentially contaminate surrounding soils and water bodies through effluent disposal and atmospheric deposition (Esbrí et al., 2015; Gordeeva et al., 2017).

A mercury-cell chlor-alkali plant that eliminated residues for 24 years in the vicinity of the Botafogo River (northeastern Brazil) caused a widespread Hg contamination. The amount of Hg emitted from this plant into the Botafogo estuary is estimated between 22 and 35 tonnes (CETESB, 1984; Meyer, 1996). Mercury concentration in mangrove sediments of Botafogo estuary is one of highest reported for the country, being 15-fold higher than the average value ($0.185 \pm 0.3 \text{ mg kg}^{-1}$) found in the Brazilian coast (Marins et al., 2004). In this scenario, the

understanding of the chemical and biological processes occurring at the solid-solution interface of these soils and sediments is essential to predict Hg solubility and bioavailability in the estuary.

Soils play a fundamental role in the mangrove Hg cycle, acting both as a sink and source of Hg to biota and adjacent waters (Reis et al., 2016; Zhu et al., 2018). Mercury retention in soils can occur on adsorption sites of both organic matter (SOM) and mineral surfaces (Fe, Mn, or Al oxides and silicate minerals), with the Hg availability to plants and organisms being determined by Hg^{+2} and Hg complexes (Jing et al., 2007; Reis et al., 2016; Zhu et al., 2018). It is also well known that the distribution of a metal in the solid phase of soils or sediments is crucial to determine its environmental mobility and bioavailability (Bloom et al., 2003; Oliveri et al., 2016; Ramasamy et al., 2012). Data on the distribution of Hg in mangrove soils are scarce in Brazil (Araujo et al., 2015) and nonexistent so far to Botafogo estuary. Such studies are essential not only to assess the environmental impacts due to the transfer of Hg to organisms but also to support human health risk assessments.

Mangroves are regarded as hotspots for methylmercury (MeHg)

* Corresponding author. Tel.: +55 81 3320 6222; fax: +55 81 3320 6220.

E-mail addresses: paula.cienciasolo@gmail.com (P.R.M. Araújo), caroline.biondi@ufrpe.br (C.M. Biondi), cwanascimento@hotmail.com (C.W.A. do Nascimento), ferbruno01@yahoo.com.br (F.B.V. da Silva), amlopez3000@hotmail.com (A.M. Alvarez).

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production (Bravo et al., 2017; He et al., 2019). Indeed, some features of the mangrove environment such as anoxia, high temperature, high S contents, and abundant SOM to < grant-highlight > support < / grant-highlight > reducing bacteria are ideal for promoting Hg methylation. In the suboxic and anoxic environment ($E_h < 300 \text{ mV}$) of mangrove soils, the SOM decomposition rate is slow, which results in organic matter accumulation (Chakraborty et al., 2015). In such an environment, iron-reducing bacteria (IRB) and sulfate-reducing bacteria (SRB) are capable to methylating Hg^{+2} and originates MeHg species (Janssen et al., 2016; Si et al., 2015), which can ultimately accumulate in fishery products and pose a risk to human health.

The work aimed at determining Hg concentrations in mangrove soils and plants (*Rhizophora mangle* and *Laguncularia racemosa*) of the Botafogo river estuary. A soil sequential extraction was used to assess the Hg distribution into soil fractions and their relationship with soil chemical characteristics and Hg biota availability. Taking into account that the estuary is regularly used by oystercatchers who either consume the product or sell it on local markets, we also collected samples of an oyster species (*Crassostrea rhizophorae*) in order to assess Hg bioaccumulation and human health risks. We also calculate soil Hg stocks in order to estimate the potential release of Hg into the environment in case soil conditions are disturbed by climate or land use change.

2. Materials and methods

2.1. Study area and sampling of soil and biota

The study area lies in the estuary of the Botafogo River, north-eastern Brazil ($34^{\circ}50' - 34^{\circ}54' \text{ W}$, $7^{\circ}42' - 7^{\circ}44' \text{ S}$) (Fig. 1). Botafogo River is the largest tributary of the Botafogo-Aratuca basin, which supplies water to Recife, one of the largest cities in the country. It is also used for traditional fishing and mollusks gathering by local communities.

Samples of six soil profiles (0–50 cm) were collected between January and February 2017 during the dry season at low tides. Sites were selected based on soil Hg concentration and vegetation cover (*R. mangle* or *L. racemosa*) as follows: 1R ($1.50 \text{ mg kg}^{-1} \text{ Hg}$), 2R

($4.00 \text{ mg kg}^{-1} \text{ Hg}$) and 3R ($6.50 \text{ mg kg}^{-1} \text{ Hg}$) under *R. mangle*; and 1L ($2.80 \text{ mg kg}^{-1} \text{ Hg}$), 2L ($4.50 \text{ mg kg}^{-1} \text{ Hg}$) and 3L ($8.00 \text{ mg kg}^{-1} \text{ Hg}$) under *L. racemosa* (Fig. 1). As expected, the most contaminated sites (3R and 3L) were found nearly 8 km from the chlor-alkali plant while sites presenting the lowest contaminations (1R and 1L) lied 16 km away from the plant.

At each sampling site, four undisturbed soil samples were collected using PVC pipes (5 cm inside diameter x 50 cm length) coupled to a flooded soil sampler. Soil samples were kept in icebox up to chemical analyses. Approximately 50–60 leaves of the third branch of three adult *R. mangle* and *L. racemosa* plants were collected at each site. Three composite samples of oysters containing 20 individuals with a standard size of 4–5 cm were collected per sampling site; no oysters were found in the 3L site. In order to estimate the oysters' moisture content, three samples composed of 10 individuals were collected at each sampling site and transported to the lab under refrigeration.

2.2. Samples processing to analyses

The four soil cores from each sampling site were divided into eight sections (0–4 cm, 4–8 cm, 8–12 cm, 12–16 cm, 16–20 cm, 20–30 cm, 30–40 cm, and 40–50 cm) and each section was homogenized into a composite sample that was stored at 4° C prior to analyses. Oysters were opened with the aid of a spatula, and the soft, edible tissue was removed and stored at -20° C ; the material was then lyophilized for 48 h, homogenized and macerated in agate mortar before analysis. Leaves were washed with tap water and then three times with ultrapure water; afterward, leaf samples were oven-dried at 35° C and ground in a Wiley knife mill.

2.3. Soil chemical and physical characteristics

Redox potential (E_h) and pH were measured *in situ* with a portable potentiometer. The E_h readings were corrected with the addition of $+244 \text{ mV}$ potential, referring to a calomel reference electrode. Soil organic matter (SOM) was estimated by loss on ignition (Davies, 1974) while soil texture was obtained by the densimeter method (Camargo

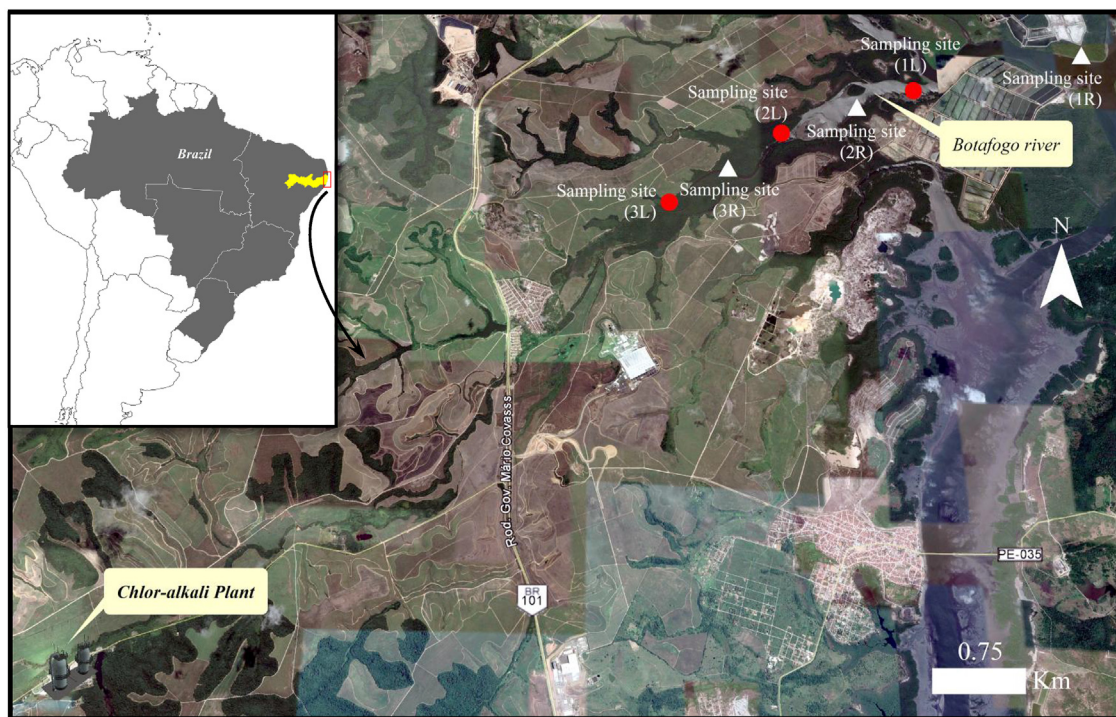


Fig. 1. Study area ($34^{\circ}50' - 34^{\circ}54' \text{ W}$, $7^{\circ}42' - 7^{\circ}44' \text{ S}$) and sampling sites under *R. mangle* (1R, 2R, and 3R) and *L. racemosa* (1L, 2L, and 3L).

et al., 2009). Soil cores of each section were oven-dried to constant weight to estimate soil bulk density (Ds) and to calculate the soil Hg stocks.

2.4. Soil Hg stocks

Soil stocks are used to estimate the ability of a certain soil for sequestering an element and acting as a drain or a source of this element to other adjacent ecosystems. Soil Hg stock was calculated per m² as a sum of Hg contents in the eight soil sections (0–50 cm) described above, based on Hg concentration and soil bulk density for each section.

2.5. Environmentally available concentration of Hg in soil

A sample of 0.200 g of soil previously dried at 35 °C, powdered in an agate mortar and sieved in a 0.15 stainless steel mesh was acid digested in a microwave oven according to EPA method 3051A, the so-called ‘environmentally available fraction’ (U.S.EPA, 2007). Environmentally available refers to the portion of total Hg in soil or sediment that is available for physical, chemical, and biological modifying influences. The digestion extracts were filtered and diluted with ultrapure water (18.2 mΩ cm) into 25 mL volumetric flasks.

2.6. Sequential extraction of Hg in the soils

The sequential extraction was based in Bloom et al. (2003) and separated Hg compounds into five operationally-defined fractions (water-soluble; ‘human stomach acid’ soluble; organically bound; elemental Hg; and mercuric sulfide) which are detailed below.

F1 (water-soluble Hg): Hg was extracted with 25 mL of ultrapure water under continuous stirring for 18 h. Following that, centrifuge tubes were centrifuged and the supernatant filtered. The soil in the tube was shaken with 20 mL of ultrapure water for 15 min, centrifuged, and the rinse was added to the initial extract, being the combined sample diluted to 50 mL with ultrapure water. Afterward, 0.5 mL of a 0.2 mol L⁻¹ bromine chloride solution was added to the extract in order to prevent Hg reduction. This solution was added to all extracts from this sequential extraction.

F2 (‘human stomach acid’ soluble Hg): 25 mL of a HCl 0.01 mol L⁻¹ + CH₃COOH at 0.1 mol L⁻¹ pH 2.0 solution was added into the tube from the previous step and sample was agitated for 18 h. Washing and centrifugation procedures were the same as those performed in F1.

F3 (organically bound Hg): 25 mL of a 1 mol L⁻¹ KOH solution was added into the tube and stirred for 18 h. Centrifugation and filtration steps as F1 were used.

F4 (elemental Hg): 25 mL of HNO₃ 12 mol L⁻¹ was added to the remaining soil sample and the same procedure as F1 was followed.

F5 (mercuric sulfide): Hg bound to sulfides was extracted with 13 mL of aqua regia (HCl and HNO₃ at a 3:1 ratio), which was allowed in contact with the soil for 12 h at room temperature. After that, the tube was centrifuged and the supernatant was filtered and made up to 50 mL with ultrapure water.

2.7. Hg in plants and oysters

Ground samples (0.500 g) of plants (*R. mangle* and *L. racemosa*) and oysters (*C. rhizophorae*) were predigested with nitric acid (8 mL) and hydrogen peroxide (2 mL), and then digested in a microwave oven for 10 min at 180 °C. The extracts were filtered and diluted to 25 mL with ultrapure water. To obtain the wet mass Hg concentration in oysters, the results were divided by a factor (f) of 5.88, which was obtained according to equation (1):

$$f = M(w)/M(d) \quad (1)$$

where M (w) refers to the wet mass of the edible part of the oyster (g),

and M (d) is the dry mass used in the analysis (0.500 g). The value of M (w) was estimated taking in account the mean water content of 83% obtained by the difference between the wet mass and the dry mass at 60 °C. Oyster Hg concentrations were compared to the maximum allowable limits of Hg in edible tissues of bivalves according to the Brazilian Health Regulatory Agency (ANVISA, 2013).

2.8. Biota-sediment accumulation factors

Biota-sediment accumulation factor (BSAF) was used as a parameter to describe bioaccumulation of sediment-associated Hg into tissues of ecological receptors (Burkhard, 2009). Here we calculated BSAF for the bivalve *C. rhizophorae*, which is commonly used for biomonitoring contaminated coastal environments (Olivares-Rieumont et al., 2012; Rios et al., 2016) and for two mangrove plants (*R. mangle* and *L. racemosa*). The BSAF was obtained from the ratio between Hg concentration in the ecological receptor and the respective paired Hg concentration in the first 4 cm (*C. rhizophorae*) or 30 cm (plants) of soil.

2.9. Hg determination and quality control analyses

Mercury concentrations in soil, oyster and plant extracts were determined by cold vapor atomic absorption spectrometry (CVAAS - AAAnalyst 800 PerkinElmer) using a flow injection mercury system (FIMS). Quality control of Hg analysis was ensured by analyzing certified materials from the National Institute of Standards and Technology (SRM, 1944 New York/New Jersey Waterway Sediment and SRM 1570a Spinach leaves), which presented average recoveries of 96% and 99%, respectively.

3. Results and discussion

3.1. Soil chemical and physical characteristics

Soil pH values varied from acidic (5.8) to slightly alkaline (7.3) (Fig. 2). Values close to neutrality are common in soils flooded for long periods owing to production of basic ions (HCO³⁻) and proton (H⁺) consumption by reduction of oxidizing agents (O₂, NO⁻³, Mn⁺⁴, Fe⁺³, SO₄⁻²) during microbial respiration (Otero et al., 2017).

Soils in Botafogo estuary were classified as suboxic (100 < Eh < 300 mV) and anoxic (Eh < 100 mV) and a general trend towards lower Eh values with depth were observed (Fig. 2). The lowering of soil redox potential leads to SOM accumulation and reduction of iron, manganese, and sulfate (Adame and Fry, 2016; Balk et al., 2016). It is known that Hg⁺² is strongly adsorbed on iron oxides and interacts with dissolved organic matter (Chakraborty et al., 2015; Petrus et al., 2015; Zhu et al., 2018), hence such reducing soil conditions can influence Hg bioavailability by destabilization of Fe oxides and increased metal solubility.

Organic matter contents were higher in soil superficial layers (Fig. 2) probably as a result of the continuous contribution of both the organic loads brought by river and sea and the mulch deposition on the soil surface by plants (Chakraborty et al., 2015; Machado et al., 2016), but even below 30 cm, SOM values were > 120 g kg⁻¹ due to the reducing, sedimentary environment. Lower SOM levels were associated with soil layers presenting lower clay contents. Clay minerals interaction with organic colloids protects SOM from microbial degradation (Banerjee et al., 2018). Clay contents ranged from 83 to 831 g kg⁻¹, with the clay loam to clay textures predominating in all sampling sites, except for the 30–40 cm layer of soil profiles 1R and 2R and 40–50 cm layer of 1R, 2R and 2L. The higher sand content in these layers may indicate past sedimentation cycles, with the contribution of coarser material or more intense hydrodynamic regimes.

Mangrove plants have been shown to alter soil characteristics and Hg methylation (Oliveira et al., 2015), but no influence of the vegetation cover on the soil chemical and physical characteristics was

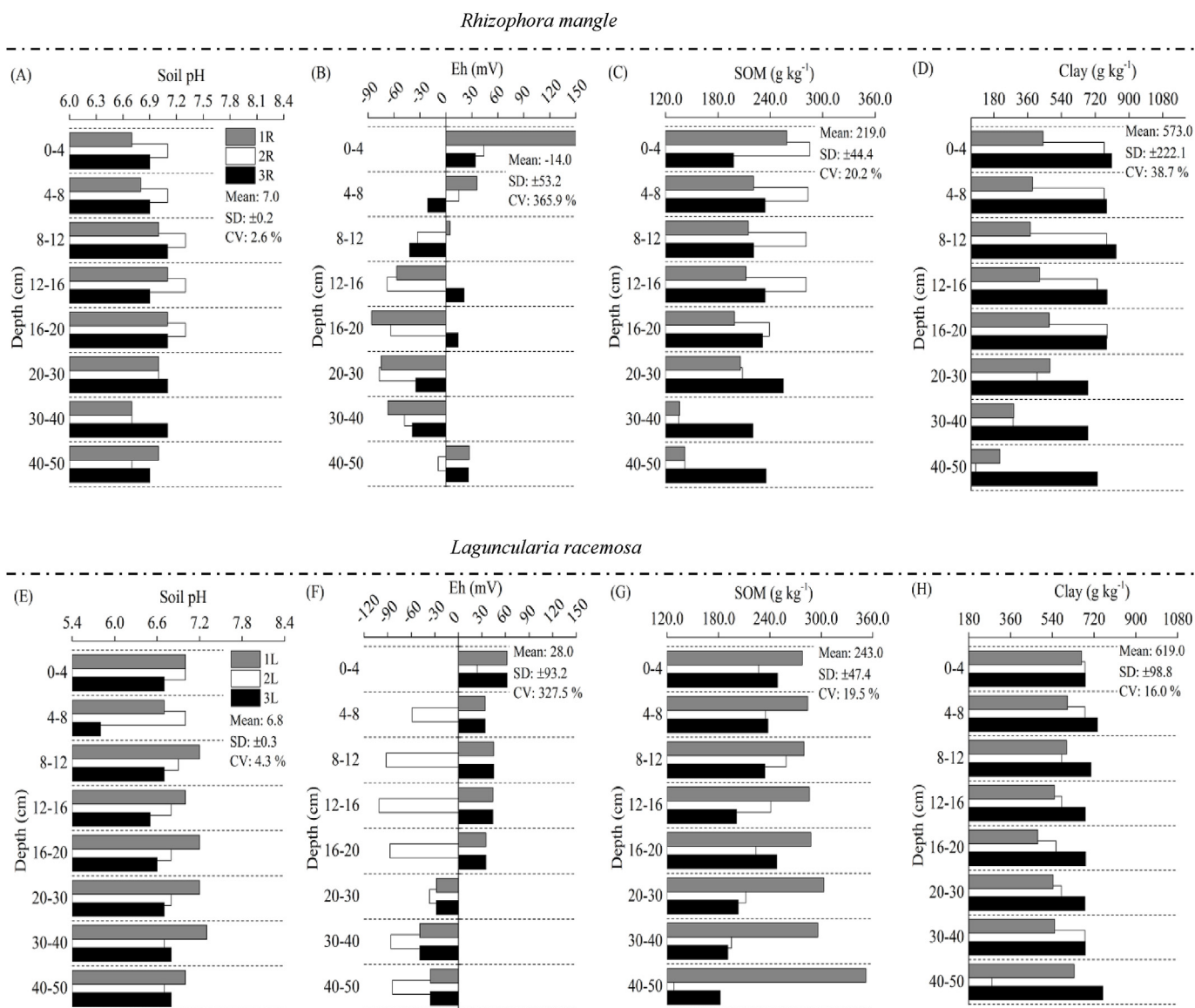


Fig. 2. Mean values of chemical and physical characteristics of soil profiles under *Rhizophora mangle* (A–D) and *Laguncularia racemosa* forests (E–H). SOM soil organic matter, SD standard deviation and CV coefficient of variation.

observed in our work. Variations in sampling sites data seem to be related to the position to river mouth only, which interferes with sedimentation processes and hydrodynamic regimes.

3.2. Hg concentration in soil profiles

The environmentally available concentration of Hg ranged from 0.13 to 10.44 mg kg⁻¹ (Fig. 3). The Hg concentrations in uncontaminated sediments usually range from 0.01 to 0.5 mg kg⁻¹ (Gworek et al., 2016; Ullrich et al., 2001). The Hg values in the Botafogo estuary are much higher than the mean Hg concentration (0.07 mg kg⁻¹) we measured for a reference area (Jaguaribe river mangrove) under the same geological context and with no anthropic interference. On the other hand, our results are within Hg concentration ranges reported in soils and sediments of other areas impacted by chlor-alkali plants: China (0.35–74.6 mg kg⁻¹), Cuba (0.16–97 mg kg⁻¹), Nicaragua (1–123 mg kg⁻¹), Canada (0.04–4.8 mg kg⁻¹), Spain (0.044–12.9 mg kg⁻¹) and France (3.5–4.5 mg kg⁻¹) (Bolaños-Álvarez et al., 2016; Esbrí et al., 2015; Fernández-Martínez et al., 2016; Hunt, 2016; Maillard et al., 2016; Song et al., 2018).

Compared with the interim sediment quality guidelines – ISQG

(ANZECC/ARMCANZ, 2000), Hg concentrations in soils of the Botafogo estuary were over both the ISQG-low value (0.15 mg kg⁻¹ Hg) and the ISQG-high value (1 mg kg⁻¹ Hg). ISQG values represent the lower 10th percentile and 50th percentile, respectively, of Hg concentrations associated with adverse biological effects.

The vertical soil distribution of the Hg concentrations showed distinct contamination patterns (Fig. 3). With exception of sampling sites 1R and 2L, Hg concentrations are higher in the first 30 cm. This accumulation pattern is in line with the soil texture as peaks of Hg accumulation were related to higher clay contents. Mercury translocation processes mediated by the soluble organic matter are likely responsible for increased Hg concentration below 30 cm (Figs. 3, 1R and 2L). In agreement with our results, Biester et al. (2002) found that leaching of Hg as soluble organic complexes such as fulvic acid-bound Hg took place in soils contaminated by emissions from chlor-alkali plants while Hg leachability was inhibited in soils with a high clay content.

It is worth pointing out, however, that most of the Hg in soil can be fixed in the bulk organic matter, which significantly limits the metal mobility. For instance, S-containing functional groups, especially thiol, sulfide and disulfide groups and, to a lesser extent, groups containing N (amine group) or O (carboxylic and phenolic groups) in the bulk SOM

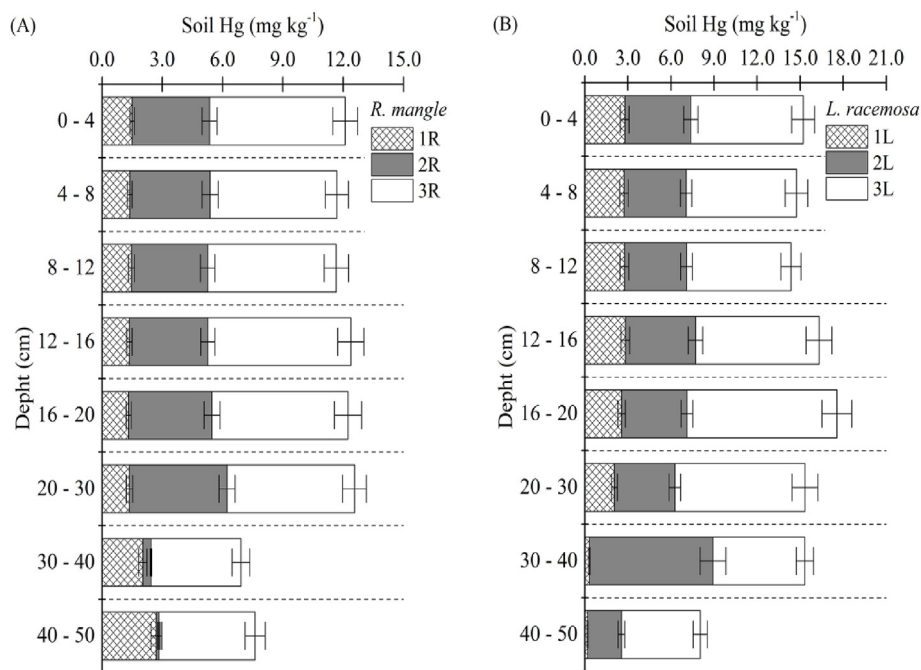


Fig. 3. Average contents (\pm standard deviation) of Hg (mg kg^{-1}) in soil profiles 1R, 2R e 3R under *Rhizophora mangle* (A) and 1L, 2L e 3L under *Laguncularia racemosa* (B).

have high affinity for Hg (Ding et al., 2017; Khan et al., 2016). Besides, not only the content of SOM but also both its type and origin exert a significant effect on Hg retention (Chakraborty et al., 2015; Machado et al., 2016). For example, Hg concentration along a sediment profile varied accordingly to the sources of organic material; soil surface layers rich in organic matter derived from algae were positively correlated with Hg accumulation whereas a negative correlation was found between Hg and SOM from the local mangrove vegetation (Machado et al., 2016).

Although many works reported the ability of sedimentary organic matter to bind Hg (Abessa et al., 2002; Hung and Chmura, 2006; Kim et al., 2014; Pant and Allen, 2007), we found a negative correlation between SOM and Hg concentrations ($r = -0.39$; $p < 0.01$; $n = 48$). Our result is in line with other reports that did not confirm a correlation between Hg and SOM (Dreher and Follmer, 2004; Ivanov and Kashin, 2010; Tack et al., 2005). Indeed, Machado et al. (2016) have proposed that accumulation of refractory organic matter in sediments may affect the role of sediments in trapping Hg. Likewise, Schartup et al. (2015) suggested that dissolved organic matter composition is a critical driver of Hg reactivity and bioavailability in offshore marine waters. Therefore, more studies on the role the type of SOM plays on Hg retention in mangrove soils are needed.

3.3. Sequential extraction of Hg in soils

Determining the environmentally available concentration of Hg is essential to assess the degree of Hg contamination in soils and sediments. However, only a sequential extraction procedure can provide information on the Hg distribution into the different soil fractions that govern the toxicity, environmental mobility and bioavailability of Hg in the ecosystem.

Elemental Hg (Hg[e]) was the dominant fraction on all samples (Fig. 4) and represented between 33% and roughly 100% of the Hg environmentally available concentrations. These results confirm the preferential accumulation of elemental Hg in soils and sediments contaminated by chlor-alkali plants (Oliveri et al., 2016; Ramasamy et al., 2012). Although Hg[e] is regarded to be in elemental form, Bloom et al. (2003) found that the use of HNO_3 12 mol L⁻¹ could access Hg bound

to the amalgams of Hg and silver, organosulfur compounds and the crystalline phases of iron and manganese. We did not observe silver-colored Hg bubbles typical from highly contaminated areas (Bloom et al., 2003) in our sampling sites. Thus, likely, a significant fraction of Hg[e] is not indeed in the elemental metallic form.

The presence of Hg[e] in soils and sediments in the vicinity of chlor-alkali plants is common due to atmospheric emission of elemental Hg and disposal of solid wastes containing metallic Hg (Biester and Scholz, 1996). Owing to its high reactivity, part of the elemental Hg initially dumped in the area was probably oxidized and incorporated into the structure of low stability iron-sulfides minerals (Alshehri et al., 2016), complexed by SOM (Machado et al., 2016) or methylated by microorganisms (Du et al., 2017; Lu et al., 2017).

Organic matter is believed to have significant impacts on the storage, distribution, and methylation of Hg in mangrove sediments (Bravo et al., 2017; He et al., 2019). The organically bound Hg fraction (Hg[ob]) retained up to 47% of the metal in our samples. This fraction comprises the organo-complexed Hg and the Hg bound to the organic structures of living and dead biota (Bloom et al., 2003). The Hg[ob] fraction poses moderate mobility as it enables the burial of Hg in sediments or its transport to adjacent waters. Additionally, organic matter plays a role on the formation of MeHg species in estuarine and marine sediments (Du et al., 2017; Lu et al., 2017; Ramasamy et al., 2012). Thus, sampling sites with higher Hg[ob] (1R, 2R and 1L; Fig. 4) have potentially the highest methylation potentials, but variables such as redox potential, predominant bacteria and type of SOM also influence the MeHg production (Bigham et al., 2016; Bravo et al., 2017; He et al., 2019). However, SOM can affect MeHg formation in mangroves in different ways. Some studies have shown that organic matter can provide substrate for sulfate, iron and methanogenic reducing bacteria and hence increase Hg methylation (Bravo et al., 2018; Gilmour et al., 2018; Janssen et al., 2016; Zeng et al., 2016); others reported a decrease in MeHg production through stable complexation of Hg by organic compounds with reduction of the metal available to methylation (Schartup et al., 2015). Further studies on the relationship between organically bound Hg and microbial methylation potential in the Botafogo estuary are warranted.

The fraction extracted by aqua regia (Hg[ms]) corresponds mainly

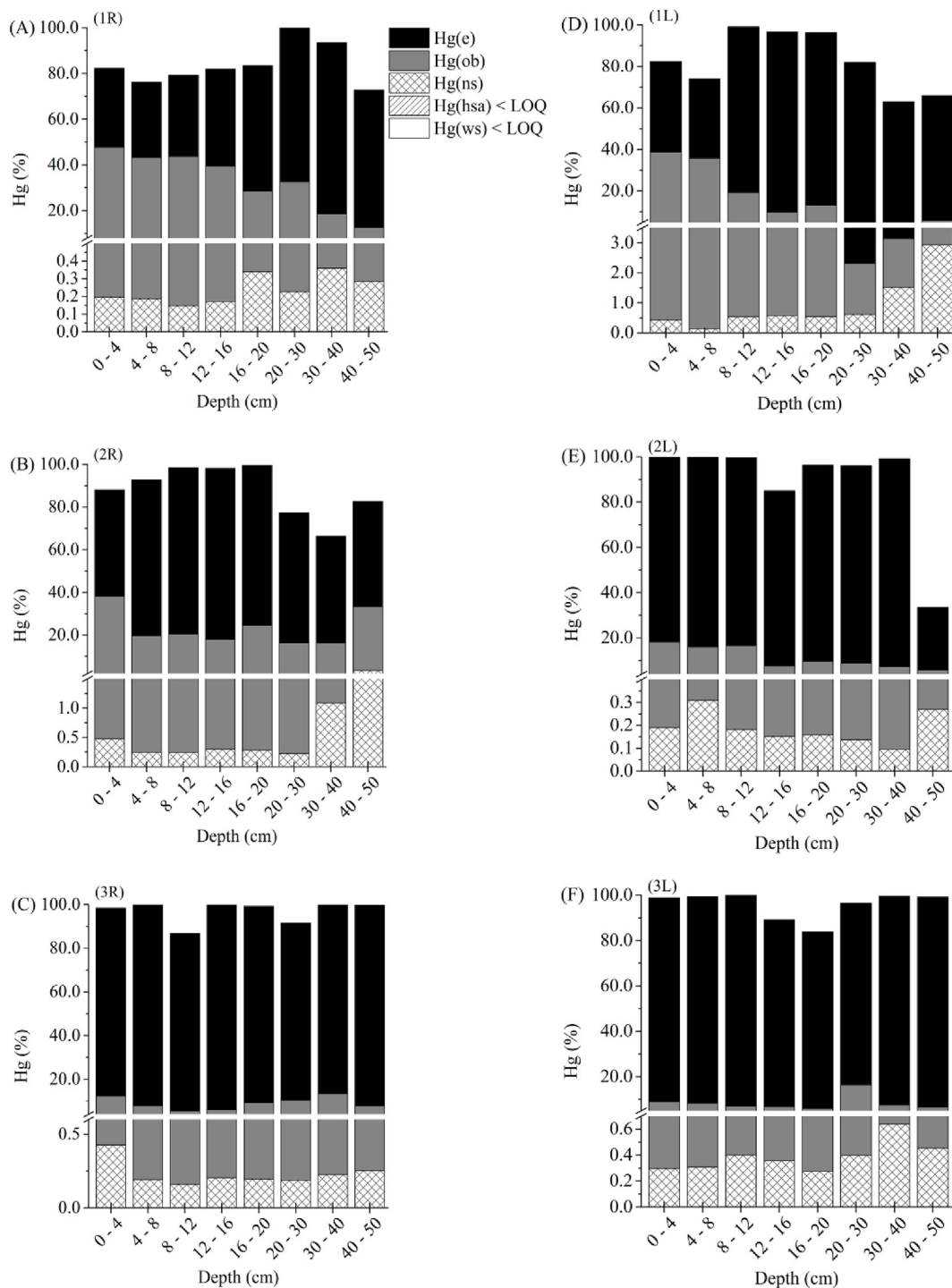


Fig. 4. Percentage of total Hg extracted in each mineral and organic fraction of soils under *R. mangle* and *L. racemosa* in low (A and D), medium (B and E) and high (C and F) contamination scenarios. Hg[ws] water-soluble Hg, Hg[hsa] human stomach acid soluble Hg, Hg[ob] organically bound Hg, Hg[e] elemental Hg and Hg[ms] mercuric sulfide. LOQ limit of quantification ($0.0005 \text{ mg kg}^{-1}$).

to sulfide bound Hg (cinnabar and metacinnabar, HgS) but also accesses Fe sulfides, such as mackinawite and pyrite (Alshehri et al., 2016). The Hg[ms] fraction in our samples was low, ranging from 0.09% to 2.93% of the environmentally available Hg (Fig. 4). Low accumulation of Hg [ms] is likely in organic matter-rich soils as an association of Hg with humic organic matter may limit the formation of Hg sulfides (Bloom et al., 2003). On the other, Hg in mining sites is mostly bound to sulfides owing to the low SOM level (Yin et al., 2016).

The water-soluble Hg (Hg[ws]) and ‘human stomach acid’ (Hg[hsa]) fractions in the mangrove soils of the Botafogo estuary were below the

quantification limit (Fig. 4). These pools are regarded as the most labile fractions of Hg and therefore, the most susceptible to microbial methylation and trophic chain entry (Ramasamy et al., 2012). This result was expected owing to the high values of SOM and pH (Fig. 2) as Hg is known to be effectively bound to soil humic substances and formation of inorganic soluble Hg compounds such as HgCl_2 and Hg(OH)_2 can immobilize Hg in soils. However, when the three most labile fractions (Hg[ws], Hg[hsa], and Hg[ob]) are summed up, Hg concentration in topsoil varies from 0.71 to 1.45 mg kg^{-1} . These values exceeded the probable effect level (PEL) for Hg (0.7 mg kg^{-1}), i.e., the level above

Table 1
Concentrations and stocks of Hg at the sampling sites (0–50 cm) of Botafogo river estuary.

Sampling site	Hg concentration (mg kg ⁻¹)	Hg stock (mg m ⁻²)
1R	1.64	524
2R	3.14	590
3R	6.12	1125
1L	2.02	237
2L	4.73	1154
3L	7.85	1764

which Hg adverse effects to the most sensitive organisms in estuarine sediments are expected to occur frequently (CCME, 1999).

3.4. Hg stock in the soils

Mercury stocks varied greatly between sampling sites (Table 1). The largest Hg concentrations and hence, Hg stocks were found in the sampling sites 3R (1764 mg m⁻²) and 3L (1154 mg m⁻²). These Hg stocks are approximately 70-fold higher than the Hg stock in the pristine mangrove area (25 mg m⁻²) we used as a reference. Despite the lower soil bulk density of the surface soil layers, Hg sequestered in the first 30 cm accounted for roughly 70% of the Hg stocked in the 50 cm soil layer. In the same way, mean Hg concentrations in European soils are about twice lower in subsoil (0.02 mg kg⁻¹) than in topsoil (0.04 mg kg⁻¹) (Salminen et al., 2005).

3.5. Accumulation of Hg by oysters and mangrove plants

Ease of sampling, small size and high consumption by most socioeconomic groups in coastal areas make oysters ideal to assessing Hg bioavailability and human health risks (Briant et al., 2017; Costa et al., 2012). For the present evaluation, we selected the most locally consumed oyster species (*C. rhizophorae*). The Hg concentrations found in the Botafogo estuary oysters exceed 7- to 14-fold those measured in oysters collected in our nearby reference area and are the highest reported for the Brazilian coast (Table 2).

According to the guidelines of the Brazilian Health Regulatory Agency (ANVISA), however, Hg concentrations in the *C. rhizophorae* wet weight samples from Botafogo estuary are within safety standards (Fig. 5A). It is worth mentioning, however, that Hg concentration in bivalves set by local health authorities is not necessarily based on the World Health Organization recommendations (Costa et al., 2012). For instance, Hg speciation is not taken into consideration by ANVISA or other countries' food security agencies. Some works have shown that

Table 2
Hg levels reported in *Crassostrea rhizophorae* soft tissue.

Local	Hg (mg kg ⁻¹ dry weight)	Reference
Rio Botafogo estuary	0.804–1.644	Present study
Reference area	0.101–0.114	Present study
Rio Botafogo estuary (Brazil)	< 0.300–2.000	Meyer et al., 1998
Rio Jaguaribe estuary (Brazil)	0.090–0.234	Vaisman et al., 2005
Rio Ceará estuary (Brazil)	0.040–0.076	Vaisman et al., 2005
Fortaleza estuaries (Brazil)	0.040–0.121	Reis et al., 2016
Santos estuary (Brazil)	0.320–0.370	Torres et al., 2012
Paranáguá estuary (Brazil)	0.140–0.350	Torres et al., 2012
Sepetiba Bay (Brazil)	0.015–0.023	Kehrig et al., 2006
Caribbean Coast (Nicaragua)	0.080–0.180	Aguirre-Rubí et al., 2018
Caribbean Coast (Colombia)	0.030–0.130	Aguirre-Rubí et al., 2018
Villa Clara Coast (Cuba)	0.032–1.810	Olivares-Rieumont et al., 2012

the highly toxic MeHg can vary from 13% to 64% of total Hg concentration in bivalves (Briant et al., 2017; Kehrig et al., 2006), with different impacts on human or animal toxicology that need to be better understood. Additionally, as MeHg can biomagnify in the aquatic web food, Hg accumulation in bivalves can pose a widespread concern for the estuary ecosystem.

We found a positive correlation between Hg in soils and oysters ($r = 0.68$, $p < 0.05$), which confirms the Hg biomonitoring ability of *C. rhizophorae*. However, the SBAF was always below unity (Fig. 5B). As bivalves are filtering organisms that feed upon dissolved organic matter and debris in the water, likely, the relatively low percentage of Hg in labile soil fractions (Fig. 4) is responsible for this result.

Mercury concentrations in leaves ranged from 0,019 to 0,040 mg kg⁻¹ for *R. mangle* and from 0,033 to 0,081 mg kg⁻¹ *L. racemosa* (Fig. 5C). The Hg concentration in *R. mangle* leaves did not follow the Hg concentration difference found throughout the sampling points. For example, sampling site 2R displayed an intermediate Hg contamination but the highest Hg concentration in leaves. On the other hand, Hg concentrations in *L. racemosa* leaves were directly correlated with Hg soil concentration, which suggests that *L. racemosa* is better as a biological indicator of Hg contamination than *R. mangle*.

SBAF values for plants were below 1.00 for sampling sites (Fig. 5D), showing that Hg transfer from soil to plants species is limited. This result may be associated with either a natural Hg exclusion mechanism from uptake or an avoidance of Hg translocation to shoots. Some studies reported mangrove plants can alter anatomical characteristics of the root system, such as epidermal thickness in response to Hg contamination (Souza et al., 2014a and b). Additionally, the results of our sequential extraction (Fig. 4) showed that most of the Hg in the Botafogo estuary soils is retained in non-labile fractions, i.e., not available for plant uptake.

The assessment of Hg concentrations in soils and biological matrices aids to elucidate the biogeochemical processes involved in the Hg cycle in the estuarine environment contaminated by chlor-alkali plants. Such results allow for estimating the potential of Hg diffusion to the biosphere and hydrosphere.

4. Conclusions

The assessment of Hg concentrations in mangrove soils, soil fractions, and biological matrices of the Botafogo river shed some light on the biogeochemical cycling of Hg in tropical estuarine environments contaminated by chlor-alkali plants. The environmentally available concentration of Hg in the mangrove soils were 2–100 times higher than the global Hg concentration for uncontaminated sediments; when compared to a pristine reference mangrove under the same geological context, soil Hg concentration in Botafogo estuary was up to 150 times higher. Additionally, Hg concentration in soils was also above international quality guidelines for sediments, and hence adverse biological effects are expected to occur frequently. Although the soil sequential extraction method showed that Hg was mostly allocated into less mobile fractions (Hg[e] and Hg[ms]), the sum of the three most labile pools (Hg[ws], Hg[hsa], and Hg[ob]) exceeded the probable effect level, which means that Hg adverse effects towards sensitive estuarine organisms are likely.

Mercury concentrations in oysters from Botafogo estuary are the highest reported in Brazil, but within safety standards according to the country food security agency. The positive correlation between Hg in soils and oysters confirmed the ability of *C. rhizophorae* for Hg biomonitoring. The SBAF < 1 to oysters and plants indicates a limited soil to biota Hg transfer; which is probably due to low availability in soil and retention of Hg in plant roots. We suggest that the stability of Hg stocks in the mangrove soils is guaranteed by reducing conditions and maintenance of a high SOM level. However, changing on environmental conditions and land use, such as the mangrove conversion into shrimp farming or soil drainage to agricultural use, can alter this balance and

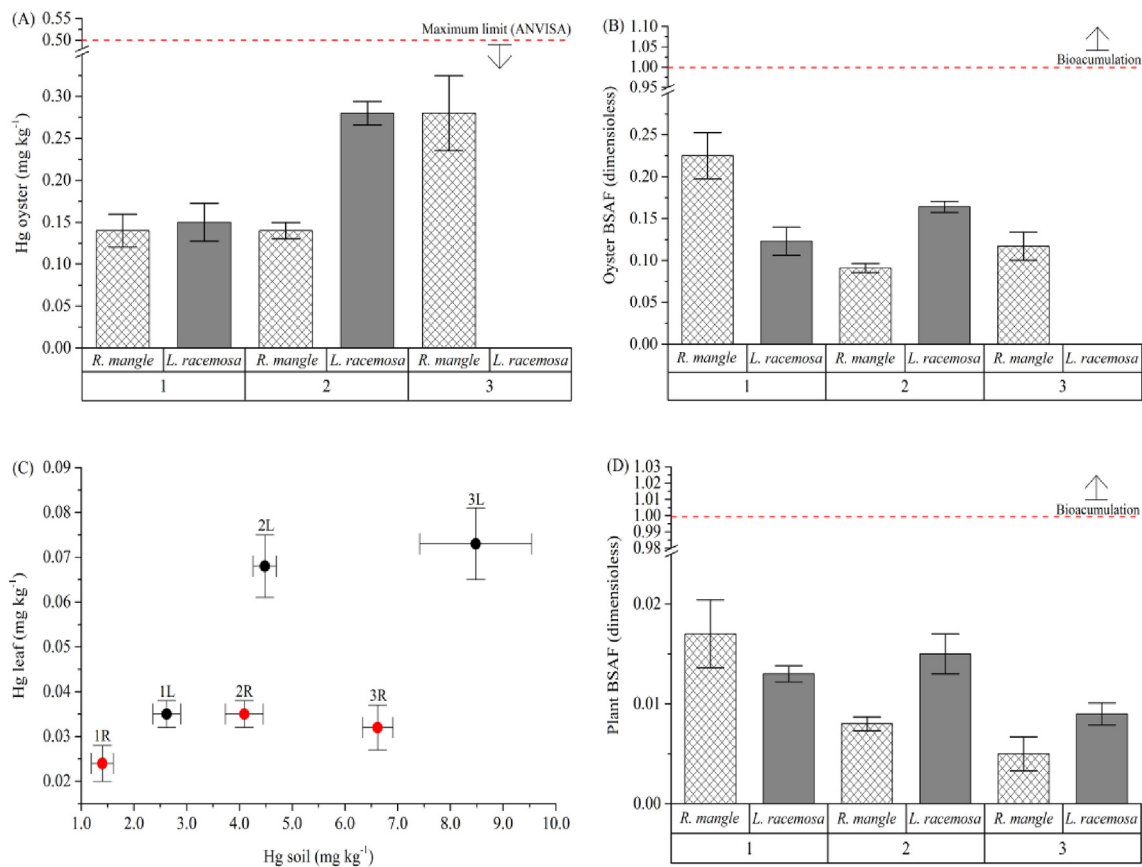


Fig. 5. Hg contents (\pm standard deviation) based on wet weight, in soft tissue of *Crassostrea rhizophorae* in sampling sites under *R. mangle* and *L. racemosa* (A); biota-sediment accumulation factor for oyster (B); relation between Hg contents in the soils and leaves of *R. mangle* and *L. racemosa* (C); biota-sediment accumulation factor for plants (D). Dashed line in Fig. 5A indicates the maximum limit of Hg (mg kg⁻¹) recommended for bivalves (ANVISA, 2013). No oysters were found in the 3L site.

convert these mangrove areas from sink to source of Hg to the environment.

Declarations of interest

None.

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