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Zinc isotopes as tracers of anthropogenic sources and biogeochemical processes in contaminated mangroves

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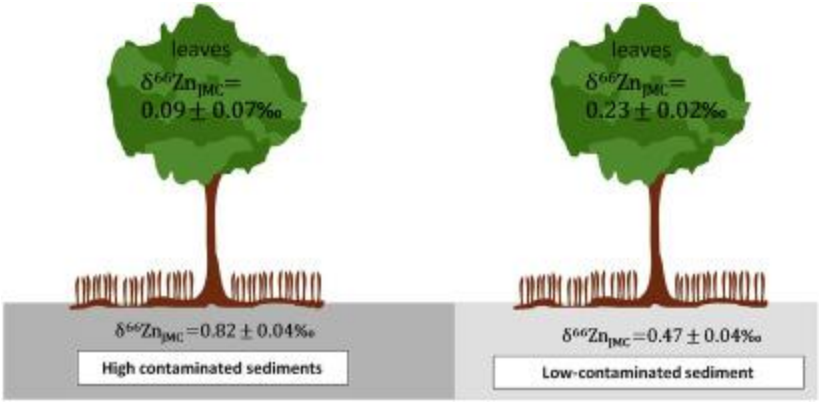
Abstract :

Recent work has shown that variations in zinc (Zn) isotope ratios enable us to identify contamination sources in the terrestrial environment and uptake processes in higher plants. Here in this study, we demonstrate that this also holds true for mangrove forests, which play an important role in the biogeochemical cycling of metals in tropical coastal ecosystems and that are seriously threatened by anthropogenic pollution. To this end, we determined zinc concentration and isotope composition (expressed using the δ66Zn notation relative to the JMC 3-0749-L standard) in sediments and tree leaves collected from a mangrove close to Rio de Janeiro in Brazil. The δ66ZnJMC values of sediments vary between +0.36 and + 0.84‰ and fall on a mixing line between detrital terrestrial sources (characterized with δ66ZnJMC = +0.28 ± 0.12‰, 2σ) and metallurgical ore sources (δ66ZnJMC = +0.86‰ ±0.15‰, 2σ). Leaves of Laguncularia racemose, in contrast, showed δ66ZnJMC values ranging between +0.08 and + 0.23‰, suggesting that processes including uptake, translocation and bioavailability in the rhizosphere control the isotope composition of zinc in the mangrove plant.

Graphical abstract



Highlights

► The $\delta^{66}Zn_{JMC}$ values of mangrove sediments suggest a mixing source processes. ► Leaves of *Laguncularia racemose* showed $\delta^{66}Zn_{JMC}$ values ranging between +0.08 and + 0.23‰. ► Zn uptake, translocation and bioavailability control the isotope composition of leaves. ► Zn isotope compositions of leaves may indicate environmental changes in mangrove systems.

Keywords : Metal transition isotopes, Metal contamination, Mass spectrometry, Coastal ecosystems, Mangrove leaves

1. Introduction

Mangrove forests are found in the inter-tidal region between sea and land in tropical and subtropical regions of the world, growing typically under harsh environmental conditions such as high salinities, elevated temperatures, extreme tides, high sedimentation rates and muddy anaerobic soils (Alongi et al., 2008; Giri et al., 2010; Bayen et al., 2012). These

unique forests are among the most productive ecosystems in the world and provide valuable food, energy sources and raw materials for the local economies (Giri et al., 2010; Agardy and Alder, 2010; Marchand et al., 2016).

Mangroves shelter many species of economic and ecological value such as mammals, birds, reptiles and insects (Nagelkerken, 2008). Epibionts (tunicates, sponges, algae, and bivalves) and in- and epi-faunal species (prawns and crabs) live in the roots-sediment mangrove system (Nagelkerken, 2008). The complex mangrove food web is supported by recycling of tree leaves, which once converted into detritus by decomposers serve as food to primary consumers as plankton, epiphytic algae and microphytobenthos (Nagelkerken, 2008; Castro and Huber, 2010).

Despite mangroves supporting a wide variety of ecosystem services and being economically valuable (up to several thousand US$ yr^{-1} ha^{-1}, Walters et al., 2008), they remain one of the world's more threatened tropical environments (Valiela, 2001). It is estimated that human activities have led to a loss of at least 35% of the world's mangrove area due the conversion to mariculture, agriculture, urbanization and to other activities (Valiela, 2001).

Environmental pollution has played an important factor in the degradation of mangroves (Lewis et al., 2011; Bayen et al., 2012; Sandilyan and Kathiresan, 2014). Urban sprawl combined with industrial expansion has led to the release of toxic metals and metalloids into the mangrove environments (Machado and Lacerda, 2004; Lewis et al., 2011; Da Souza et al., 2014; Marchand et al., 2016; Araújo et al., 2017d). Depending on bioavailability and speciation, these elements are incorporated into bio-geosphere cycles. Essential elements (e.g., Zn, Cu, Mo) play an important biological role and participate in a wide range of important cellular biochemical reactions (Reilly, 2004). At high

concentrations, however, these elements lead to reduction of photosynthesis in mangrove plants and of growth and biomass, and finally induce mortality (Adriano and Adriano, 2001; Sparks, 2005; Bayen et al., 2012 and references therein; Alongi, 2017).

Since metal contaminations of mangroves may pose major risks to biota and human health, developing tools to trace anthropogenic sources and to identify plant responses to environmental stress triggered by metal contamination is of great interest. To this end, the application of stable isotope ratios is promising for zinc (Zn). Firstly, they fractionate during industrial processes (e.g., metallurgy and combustion by high-temperature or electrolysis processes) resulting in fingerprints isotopically distinct for man-made materials and by-products from those found in nature (Kavner et al.; 2008; Sivry et al., 2008; Borrok et al.; 2010; Ochoa and Weiss, 2015; Thapalia et al., 2015; Yin et al.; 2015), which allows to use Zn isotope ratios to discriminate between natural and anthropogenic sources in marine, terrestrial and atmospheric compartments (Yin et al., 2016; Souto-Oliveira et al., 2018). Secondly, Zn isotope fractionation occurs during uptake, translocation and distribution between the internal compartments of plants (Viers et al., 2007; Moynier et al., 2009; Caldelas et al., 2011; Jouvin et al., 2012; Arnold et al., 2015). These processes seem dependent on plant uptake strategies, concentration, speciation, redox conditions, transpiration flow and height (Moynier et al., 2009; Couder et al., 2015; Caldelas and Weiss, 2017).

To date, only a few studies have explored isotope fractionations of Zn during the biogeochemical cycling in terrestrial or wetland ecosystems (Viers et al., 2007; Aucour et al., 2015; Viers et al., 2015; Aucour et al., 2017). To this end, we conducted a preliminary study of Zn isotope variations in mangrove sediment-plant systems in Sepetiba Bay, a site historically impacted by Zn-enriched wastes from an old electroplating plant (Molisani et

al., 2004). Previous studies of our group testing Zn isotopes as tools to discriminate and quantify the relative contributions of natural and anthropogenic Zn sources to Sepetiba Bay focused on mud flat sediments, suspended particulate matter and a single mangrove sediments core located close to the old electroplating plant (Araújo et al., 2017a, c). This complementary study focuses on sediments and leaves of mangrove trees (*L. racemosa*) collected from sampling locations with different extent of Zn contamination. The specific questions addressed during this study are: (i) do mangrove sediments record the isotope compositions of pollutant sources? (ii) do mangrove trees fractionate Zn isotopes during uptake and transport to aerial tissues? If so, (iii) which are the possible effects of concentration, speciation, bioavailability and physiological processes (uptake, translocation, tolerance mechanism) on the Zn isotopes composition of the mangrove leaves?

2. Study area

The study was conducted in Sepetiba Bay (southeastern Brazil), a micro tidal estuary type lagoon, located 60 km west from Rio de Janeiro city (Fig.1). Nine rivers drain an extensive watershed of approximately 2,654 km^2, which includes agricultural, industrial and urban areas. The main river (Guadu River) reach the bay through artificial channels, which among them, the São Francisco channel, with an annual flow of 6.5 x 10^9 m^3, is responsible for over 86% of the total freshwater input (Molisani et al., 2004). Mangrove forests extend along the bay shore, providing nursery and feeding areas for the bays fisheries. The dominant tree species are red mangrove (*Rhizophora mangle*), black mangrove (*Avicennia shaueriana*) and white mangrove (*Laguncularia racemosa*).

In the 1960's, an electroplating plant started to operate close the northeastern shore (Fig.1). The zinc purification process used silicate ores (calamine: $Zn_2SiO_3(OH)_2$ and willemite: SiO_4Zn_2) acquired from Vazante (Minas Gerais, Brazil), the most important Zn deposit in Brazil (Barone, 1976). The waste produced during the ore refining processes were exposed to the open air and lixiviated during rainfalls, reaching surrounding mangroves and the bay through a small tidal creek located in the Saco do Engenho mangrove, considered as the *hot spot* area (Fig.1) (Molisani et al., 2004). The amounts of zinc and cadmium remobilized from the waste were estimated to be about 24 t y^{-1} for Cd and 3,660 t y^{-1} for Zn (Molisani et al., 2004). Despite the end of zinc refining operations in 1997 and the removal of the waste in 2012, Zn-enriched sediment particles from the *hot spot* continue to be remobilized throughout the bay during tidal cycles (Araújo et al., 2017a; Araújo et al., 2017c). Computational modeling of the lagoon hydrodynamics suggests a trend of fine sediments deposition along the northeastern coastal area of the bay where the tidal flats and mangroves acts as sinks of contaminants (Montezuma, 2013).

3. Materials and Methods

3.1 Sampling and sample preparation

Surface sediments were collected at three different mangrove sites (Fig.1), during low tide in 2008. The first site is located in the Saco do Engenho (station A), the second site is located close the mouth of São Francisco channel (station B) and the third site is located in the mangrove of Enseada das Garças (station C). The latter site is located within an environmental protection area surrounded by urbanized and landfill areas. At each sampling site, three superficial (~ 0-5 cm depth) surface sediment replicates were sampled and

142 packed into polyethylene bags. The samples were dried at 40 ºC, crushed and sieved at 63
143 µm. This grain size fraction (<63 µm) was used for elemental and isotopic analyses.

144 At the three sampling sites, *L. racemosa* trees colonize the sediments. *Laguncularia*
145 *racemosa* leaves were sampled in triplicate from trees surrounding the sampled sediments.
146 The leaves were stored in plastic bags until the return to the laboratory and then washed
147 using ultrapure water. These samples were dried at 80°C during 24 h and finely ground for
148 homogenization. Surface sediment samples and certified materials (BCR-2 and BHVO-2
149 basalts from the US Geological Survey and 1646a estuarine sediment from National
150 Institute for Standards and Technology, NIST) were weighed in Savillex® Teflon beakers
151 and digested on a hot plate using a multiple-step acid procedure with HF, HNO_3, HCl. Leaf
152 samples and a plant certified reference material (1573a tomato leaves from NIST) were
153 digested using a microwave system (Speedwave 4, Berghof) and concentrated acid mixing
154 (HF, HCl and HNO_3). After total sample digestion, aliquots were taken for the subsequent
155 determination of Zn concentrations and isotopic compositions.

156 Aliquots of sediments samples were leached using 0.1 M acetate to remove weakly-
157 sorbed metal species (Quevauviller et al., 1997; Rauret et al., 1999, Gleyzes et al., 2002).
158 To this end, about 500 mg of sediment were weighted in tube flacons and 17.5 ml of 0.1 M
159 acetate were added. The sediment and acetate mixtures were shaken for 16 hours at 30±10
160 rpm. The solutions were centrifuged at 3000 g for 20 min and the supernatants were filtered
161 using a syringe and membrane filter (0.22 µm). The filtered solutions were stored at 4 ºC
162 until analysis day.

163 All acids used during the cleaning of bottles and lab ware and during the sample
164 preparation were distillated by sub-boiling in Teflon™ stills. The water used was < 18.2

MΩ (Nanop System®). The chemical procedures were performed at the clean laboratory suites at the University of São Paulo (USP) and the University of Brasília (UnB).

3.2 Elemental and isotope ratio analysis of zinc

Aluminum, Fe, Ti, Ca, Mg, P, Mn, Zn, Cu, Ni and Cr were analyzed using inductively coupled plasma optic emission spectrometry (ICP-OES, Spectro Ciros Vision, Spectro, at Campo Laboratory, Minas Gerais, Brazil). Multi-elemental standard solutions (Merck®) were used to produce external calibration curves. Certified reference materials (BHVO-2 and BCR-2 basalts from the USGS; 1646a estuarine sediment and 1573a tomato leaves from the NIST) were used to assess the accuracy of analysis. The accuracy expressed as percentage relative error was always within 10% of the certified values for all the elements studied.

Before the isotope ratio determinations, Zn was separated from other elements using an ion-exchange chromatography procedure employing a Bio-Rad PolyPrep column filled with 2 ml of the anion exchange resin AG-MP1, 100-200 mesh, (Araújo et al., 2017b). For subsequent mass bias corrections, the Cu standard NIST-976 was added to the purified fractions after the ion exchange procedure and concentration matched with the ratio 1:1 (300 µg ml^{-1} in 0.05 M HNO_3). Zinc isotopic ratios were measured using a ThermoFinnigan Neptune MC-ICP-MS at the Laboratório de Geocronologia of the University of Brasília and at the Laboratorio de Geocronologia of the University of Sao Paulo. The introduction interface consisted of quartz glass spray chamber (cyclone + standard Scott double pass) coupled with a low flow PFA nebulizer (50 µl min^{-1}). The analytical sequences ran automatically using a Cetac ASX-100 autosampler and low mass resolution collector slits.

189 The zinc isotopes ratios were measured relative to the in-house single element
190 standard MERCK Lot #9953 labeled henceforward as Zn_{UnB} standard. The standard-sample
191 bracketing technique was used, i.e., each sample was bracketed by standard solution
192 mixture (Zn_{UnB} and $Cu_{NIST\text{-}976}$) with rinses between sample and standard analyses with 3 %
193 (v/v) HNO_3. The raw ratios were corrected for instrumental mass fractionation using the
194 exponential law based and the certified ratio ($^{65}Cu/^{63}Cu = 0.4456$) for Cu of the NIST SRM
195 976 standard.

196 The $\delta^{66}Zn$ values were calculated as the deviation of the mass bias corrected isotope
197 ratio of the samples from the mean of the mass bias-corrected isotopes ratios of the
198 bracketing standards:

199

200 $$\delta^{66}Zn(‰) = \left(\frac{^{66}Zn/\ ^{64}Zn_{sample}}{^{66}Zn/\ ^{64}Zn_{standard}} - 1\right) \quad \text{eq.1}$$

201

202 Zinc isotope data reported in this study are expressed relative to the Johnson Matthey
203 Company 3-0749-L ($JMC_{3\text{-}0749\text{-}L}$) reference standard calibrated against our Zn_{UnB} standard
204 ($\Delta Zn_{JMC\text{-}UnB}$ = +0.17 ‰). For analytical quality control, the certified isotope reference
205 material Zn IRMM-3702 was measured two or three times along each session analysis
206 yielding a $\delta^{66}Zn_{JMC}$ value of -0.27 ± 0.06 ‰ (*n*=30, 2σ). This value agrees with values the
207 average value of compiled data from other laboratories (+0.30 ± 0.01, 2SE, Moynier et al.,
208 2017). The 1573a tomato leaves showed $\delta^{66}Zn_{JMC}$ values of +0.79 ± 0.09 ‰ (2σ, n=4). The
209 $\delta^{66}Zn_{JMC}$ values obtained for BHVO-2 basalt (+0.25 ± 0.10‰, 2σ, *n=5*), BCR-2 basalt
210 (+0.25 ± 0.08‰, 2σ, *n=1*), and AGV-2 andesite (+0.29 ± 007, 2σ, *n*=2) are in line with
211 those reported in the literature for silicate rocks (Chen et al., 2013; Sossi et al., 2015).

Average reproducibility for $\delta^{66}Zn_{JMC}$ values determined for the certified reference material Zn IRMM-3702 and unknown samples was ±0.06‰ (2σ). This value was taken to represent the external reproducibility of the method.

4. Results

The analytical results for the mangrove superficial sediments and leaves are shown in Table 1. Highest Zn concentrations (expressed in µg g^{-1}, 1σ, n=3) in surface sediments are found at station A (21,551 ± 2072), while intermediate values are found in station C (316 ± 112), and the lowest values in station B (164 ±17). The sediment samples of Sepetiba Bay display a wide range of $\delta^{66}Zn_{JMC}$ values (between +0.36 and +0.84‰, Table 1). Samples from Saco do Engenho mangroves (station A) exhibit the highest values, ranging between +0.80 and +0.84 ‰ (Fig. 2) with an average of +0.82 ±0.04 ‰ (*n*=3). Surface sediments collected in the mangrove close to the São Francisco Channel (station B) display $\delta^{66}Zn_{JMC}$ values between +0.44 and +0.49‰ (average of +0.47 ±0.04‰ (*n*=3), slightly heavier than values found in the mangrove of Enseada das Garças (station C) which range between +0.36 to +0.42 ± ‰ (Fig.2) with an average of +0.39 ±0.06‰ (*n*=3). Zinc concentrations (µg g^{-1}, 1σ, *n*=3) in the exchangeable fraction (0.1 M acetate leach) were 8836 ± 1788, 71 ± 19 and 173 ± 94 (*n=3)* for the mangrove stations A, B, C, respectively. This corresponds to 41, 43 and 55% of the bulk sediment Zn concentration.

Average Zn concentrations in *L. racemosa* leaves in the mangrove stations follow the same trend observed for sediments, i.e. the highest concentrations (µg g^{-1}, 1σ, *n*=3) are found in station A (47±5), followed by station C (25 ±2) and station B (15±2) (Fig.2). The leaves collected at the stations with higher Zn concentrations in sediments (stations A and C) display similar $\delta^{66}Zn$ values of +0.09 ± 0.04‰ and +0.08 ± 0.10‰ (±2σ, n=3),

236 respectively (Fig.2). These values are very different from those observed in leaves from
237 station B, which display heavier $\delta^{66}Zn$ values of +0.23 ± 0.02‰ (2σ, n=3, Fig.2).
238
239 **5. Discussion**
240 **5.1 Zinc isotope composition of end-members from Sepetiba Bay**
241 Two previous studies of our group (Araújo et al., 2017a,c) assessed the variability of the Zn
242 isotope values within a single sediment core and of suspended particulate matter collected
243 in the estuary. We found that the isotope signatures in the sediment core can be accounted
244 for by mixing of three main end-members: a terrestrial detrital source ($\delta^{66}Zn_{JMC}$ = +0.28
245 ±0.12‰, 2σ), a marine detrital source ($\delta^{66}Zn_{JMC}$ = +0.45 ±0.03‰, 2σ), and an
246 anthropogenic source associated with electroplating wastes released into the bay ($\delta^{66}Zn_{JMC}$
247 = +0.86 ±0.15‰, 2σ, Araújo et al., 2017a; Araújo et al., 2017c). Table 2 summarizes
248 relevant data compiled from Araújo et al. (2017a), including the Zn isotopic signatures of
249 top layers (~5 cm) from sediment cores of mud flat sediments collected close the stations
250 A, B and C determined in this study. The compiled dataset is used in the following sections
251 to support the interpretations of the new dataset in the mangrove systems presented in this
252 study.
253
254 **5.2 Tracing anthropogenic zinc sources in the mangrove sediments**
255 $\delta^{66}Zn_{JMC}$ values of the surface sediments at Saco do Engenho (station A) range between
256 +0.72 and +1.15‰ (Araújo et al., 2017a). They are likely controlled by the isotope
257 composition of waste derived from the electroplating plant as station A is located within the
258 hot spot contamination area (Table 1). In addition, isotope values previously reported for
259 waste and slag produced during metallurgical processes are in the same range (+0.59 to

+1.49‰, Sivry et al., 2008; Juillot et al., 2011). The large isotope fractionation between electroplating waste and ores minerals (average of +0.03 ± 0.24‰ for willemite, Araújo et al., 2017a) and concentrates ores of sphalerites from worldwide (average of +0.03 ± 0.1‰, Ochoa et al., 2016) may be associate to the electrochemical separation process used during ore refining (Kavner et al., 2008; Yin et al., 2016).

Suspended particles enriched in Zn as well as dissolved Zn are transported from the hot spot area throughout the bay and deposited in the tidal flats and mangroves along the shore (Leal Neto et al. 2006; Roncarati and Carelli, 2012). There, dissolved metal contaminants including Zn and suspended particles are immobilized within organic-rich and anoxic sediment due to the formation of insoluble metallic sulfides and complexes with organic matter (Machado et al., 2008; Andrade et al., 2012; Ribeiro et al., 2013). This metal trapping capacity likely explains the moderate to high concentrations of Zn in stations B and C, even though the latter station is located as far as 16 km from the old electroplating plant. Additional input from other anthropogenic sources (e.g., urban effluents) also could play a role.

The surface mangrove sediment from stations B and C show $\delta^{66}Zn_{JMC}$ values between the geological background of Sepetiba Bay, estimated at +0.28 ±0.12‰ (2σ), represented by granites rocks and sediment core sections from pre-industrial period (Table 2) and electroplating wastes, estimated at +0.86 ±0.12‰ (2σ) represented by waste from the old electroplating plant (Araújo et al., 2017a, Fig.2, Table 2). The mangroves of Sepetiba bay are known to act as sinks of the suspended particulate matter brought during the high tides (Lacerda et al., 1988). In Figure 3, we observe an overlap of the isotope signature between the first 5 cm layers of sediment cores of mud flat and mangrove surface sediments. This suggests that the Zn isotope compositions of suspended particle material

and dissolved Zn remain unchanged during the transport and after deposition in the mangrove system. The lack of overlap in the station C may indicate inputs from an additional, unknown source in this mangrove system. This would well be in agreement with the location of and proximity of untreated urban sewage effluents observed during the field work.

5.3 Zinc concentrations and isotope compositions of tree leaves

The zinc isotope composition of the leaves of *L. racemosa* (ranging between +0.08 and +0.23‰) are lighter than that of the bulk sediments (ranging between +0.36 to +0.84‰). The smaller variation of δ^{66}Zn found in the leaves is possibly due to an isotopically more homogenous bioavailable pool (see discussions further below). The leaves collected at the stations with higher Zn concentrations in the surface sediments (stations A and C) display similar δ^{66}Zn values (+0.09 ± 0.04‰ and +0.08 ± 0.10‰, ±2σ, *n*=3) but are significant different from those observed in leaves of trees collected at station B (+0.23 ± 0.02‰, 2σ, *n*=3, Fig.2). As will be discussed later, this difference between mangrove sites can be associated to physiological responses and tolerance mechanisms of mangrove trees.

5.3.1 Suggested control of mineral phases and rhizosphere processes

The changes in Zn concentrations in *L. racemosa* leaves reflect changes in Zn concentrations in surface sediments (Fig.2) though the magnitudes of increase or decrease is different. For example, we observe between the stations A and B a 100-fold increase in Zn concentrations in the sediments but only a 3-fold increase in the leaves. It is conceivable that the bioavailability of excess anthropogenic Zn is strongly reduced at station A. The

capability of mangroves to reduce metal bioavailability is attributed to the formation of stable metal sulfides, metal–organic matter complexes and sorption on clays minerals (Machado et al., 2005; Marchand et al., 2006; MacFarlane et al., 2007; Marchand et al., 2011; Lewis et al., 2011). The lower Zn concentrations in the leaves may also reflect tolerance mechanisms including root iron plaque formation, excretion through leaves or roots and compartmentation in root cells (Macfarlane and Burchett, 1999; MacFarlane and Buchett, 2000; MacFarlane and Burchett, 2002; Machado et al., 2005; MacFarlane et al., 2007; Naido et al., 2014). The large contribution of Zn in the exchangeable fraction, i.e., from 41 to 55% (Table 1), suggests a weak role of the sediment on the retention of Zn and a prevailing of tolerance mechanisms on the reduction of Zn bioavailability.

Iron plaques formation is a critical process to control metal uptake via root. They are formed during oxidation of Fe^{2+} in anoxic, waterlogged conditions at the root surface by O_2 diffusing through the aerenchym (Machado et al., 2005; Aucour et al., 2017; Garnier et al., 2017). In Sepetiba Bay, a previous study of seedlings of *L. racemosa* showed that almost 90% of Zn in the roots are associated with iron plaque and only a minor fraction is stored in the root tissues (Machado et al, 2005). It is therefore likely that Zn adsorption on iron plaques is an important process with respect to isotope fractionation. Several laboratory studies have demonstrated significant Zn isotope fractionation during sorption processes on Fe-bearing phases with preferential enrichment of heavy isotope in the solid phase (Pokrovsky et al., 2005; Balistrieri et al., 2008; Juillot et al., 2008, Dekov 2010, 2014). This would lead a preferential immobilization of heavy Zn isotopes on iron plaques, resulting in a Zn phyto-available pool isotopically lighter.

A second important reservoir of Zn in mangrove sediments are sulfide compounds formed during anoxic conditions by microbial activity. Previous studies demonstrated that

Zn sulfides are isotopically lighter compared to other mineral phases (John et al., 2008; Kelley et al., 2009; Veeramani et al., 2015; Jamieson-Hanes et al., 2017) and Aucour and co-workers (2016) found enrichment of light Zn isotopes in roots compared to the soil in a wetland system in France, due to the dissolution of ZnS enriched in light isotopes.

Mangroves are subjected to daily redox changes triggered by tidal cycles and bioturbation processes. This leads to re-precipitation and re-dissolution of mineral phases. In anoxic conditions (e.g., during high tides), Fe-oxyhydroxides are partially reduced and dissolved releasing metals into solution, while sulfides produced from the microbial activity immobilize metals. During oxic conditions, sulfides may be oxidized releasing metals to pore- or column water (Huerta-Diaz and Morse, 1992; Marchand et al., 2011; Andrade et al., 2012; Machado et al., 2014). Previous mineralogical analyses (XRD) of the mangrove sediments in Sepetiba bay showed presence of ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$) and pyrite, evidencing an intense redox cycling of Fe and Mn during diagenetic processes involving carbon-iron-sulfur interactions and microbial metabolism (Araújo et al., 2017d).

The changes in sedimentary mineralogy induced by diagenetic processes, tidal cycles and bioturbation affects the Zn mobility in the sediment/water interface and its isotope compositions (Veeramani et al., 2015; Jamieson-Hanes et al., 2017, Deckov et al., 2010, 2014). A flow-through cell experiment designed for the study of Zn speciation *in situ* in natural sediments demonstrated an enrichment of the heavier Zn isotope in the aqueous phase due to the continuous Zn removal via microbially-mediated ZnS precipitation in reducing conditions (Jamieson-Hanes et al., 2017). Leaching experiments of metallurgical slags showed different directions and extent of Zn isotope fractionation depending on the formation or dissolution of secondary phases such as carbonates, hydroxides, or oxides during weathering (Yin et al., 2018). To predict accurately the overall magnitude or

direction of Zn isotope fractionation resulting from these various processes in mangrove sediments, however, remains difficult due to the wide variety of Zn bearing mineral phases.

Nevertheless, it is important to note that despite the wide range of Zn concentrations found in the sampled sediments, the Zn isotope compositions of the leaves displays a rather narrow range of $\delta^{66}Zn_{JMC}$ values, varying between +0.08 and +0.23‰. This small range of $\delta^{66}Zn_{JMC}$ values suggests that the isotopic composition of the Zn pool available for uptake is similar at the different sites. This is supported by the isotope analysis of the exchangeable phase (data unpublished).

5.3.2 Zinc uptake and translocation to aerial parts of mangrove plants

The enrichment of light isotopes in leave tissues may be associated to the combined effects of biological isotope fractionation during Zn uptake and translocation to aerial parts of mangrove plants. The direction and magnitude of the Zn isotope fractionation during Zn uptake is depending of Zn speciation and uptake mechanisms (Jouvin et al., 2012). The enrichment of the light isotope in the leaves of *L. racemosa* found in this study is in line with uptake of free Zn^{2+} via diffusion. The transport of Zn from root to shot and leaves in higher plants occurs via the xylem sap, which seems, in general, to lead an enrichment of light isotopes in the leaves of high plants (Caldelas and Weiss, 2016) possibly due to ion exchange processes (Moynier et al., 2009).

It is also evident that sampling sites with medium (station C) and high (station A) degrees of Zn contaminations show lighter isotope compositions than the mangrove station with the lowest contamination degree (station B) (Fig.2). To explain this observation, we suggest physiological responses and tolerance mechanisms of mangrove trees as controlling process. Mangroves plants exclude metals or regulate uptake of metals at the root level and

limit translocation to the shoot to maintain the concentration of metals within physiological limits. This involves the use metallothioneins, phytochelatins and Cys-rich membrane proteins for metal transport, chelation, compartmentalization, exclusion and sequestration processes (Zhou and Goldsbrough, 1995; Cobbett, 2000; Hasan et al., 2017; Weng et al., 2012). Thus, Zn isotope compositions of leaves will reflect the various mechanisms that control uptake, accumulation, trafficking and detoxification of metals (MacFarlane et al., 2007; Da Souza et al., 2014; Arrivabene et al., 2016). Zinc complexation with organic ligands containing O and N donor atoms favor the heavy isotopes and the magnitude of Zn isotope fractionation during complexation seems proportional to the affinity constant (Markovic et al., 2017). Hence, complexation to organic ligands with O and N donor atoms could lead to the immobilization of heavy isotopes in cell roots and stems with a subsequent preferential translocation of light isotopes to aerial parts of plants. Sulphur containing molecules (cys-rich proteins, phyto-chelatins, metallo-thioneins) are likely also involved in membrane transport, chelation, compartmentalization, exclusion and sequestration processes of metals (Zhou and Goldsbrough, 1995; Cobbett, 2000; Weng et al., 2012, Fuji et al., 2014, Hasan et al., 2017), further imparting significant isotope fractionation.

Different Zn isotope signature patterns in plants as response to high or low Zn supplies have been reported in the literature. Caldelas et al. (2011) pioneered experiments with wetland plants (*Phragmites australis*) in substrates with toxic levels of Zn and observed heavier isotopic compositions in roots than in leaves. Similar observations were made studying plants grown in soils contaminated by metallurgic waste (Couder et al., 2016). Both groups suggested that under conditions of high Zn supplies, Zn is immobilized

by organic ligands and stored in cell organelles (e.g., vacuoles) leading to preferential accumulation of the heavy isotope of Zn excess in the roots.

Mangrove trees across genera and families tend to accumulate higher amounts in roots than leaves (MacFarlane et al., 2007) as detoxification mechanism. This would increase the enrichment of the light isotope in the Zn pool translocated to aerial plant compartments. Thus, metal stress should lead to different isotope patterns of mangrove leaves than those observed under normal conditions.

6. Conclusions

Mangrove ecosystems play an important role in the dynamics of metal contaminants in coastal areas. This work demonstrates that Zn isotopes is useful to trace anthropogenic sources in superficial mangrove sediments, especially, those associated to metallurgical pollution. We demonstrate that post-depositional biogeochemical processes do not significantly fractionate zinc isotopes in surface sediments.

Zinc isotopes in mangrove tree leaves show significant fractionation compared to the sediments, likely as result of Zn uptake and translocation to aerial parts. The subtle isotopic signatures among mangrove stations may be associated to tolerance mechanisms employed by mangroves under high Zn exposure to exclude metals or regulate uptake of metals to maintain Zn levels within physiological limits. Therefore, Zn isotope compositions of leaves are not indicative of sources. However, changes in Zn isotope compositions of leaves may be potential indicators for responses of mangrove plants to environmental changes and changes in physiological status.

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Table 1. Analytical data set for mangrove surface sediments and *L. racemosa* leaf samples

Samples	$\delta^{66}Zn_{JMC}$	Zn (EF)	Zn ($\mu g\ g^{-1}$)	Ca (%)	Ti (%)	Fe (%)	Si (%)	Al (%)	K (%)	Mn ($\mu g\ g^{-1}$)	P ($\mu g\ g^{-1}$)
Mangrove station A (Saco do Engenho)											
Sediment A1	+0.80	364	21,387	0.5	0.6	10.3	20.2	12.1	1.1	255.1	877
Sediment A2	+0.82	362	19,566	0.4	0.6	10.2	18.7	11.1	1.1	308.0	887
Sediment A3	+0.84	395	23,700	0.5	0.6	10.6	20.3	12.3	1.2	543.8	1111
Leaves A*	+0.09 ± 0.04		47 ± 5								
Zn-exchangeable¥			8836 ± 1788 (41%)								
Mangrove station B (São Francisco Channel)											
Sediment B1	+0.49	3.0	151	1.0	1.1	3.8	32.1	10.5	3.2	364.3	759
Sediment B2	+0.44	3.5	183	1.1	1.5	4.7	29.2	10.7	2.9	440.5	350
Sediment B3	+0.47	3.3	158	1.3	1.1	3.7	30.2	9.7	2.9	359.5	789
Leaves B*	+0.08 ± 0.10		15 ± 2								
Zn-exchangeable¥			71 ± 19 (43%)								
Mangrove station C (Enseada das Garças)											
Sediment C1	+0.42	8.0	251	0.5	0.6	3.1	30.5	6.4	0.4	349.8	1022
Sediment C2	+0.40	8.5	445	0.7	0.6	4.7	21.8	10.7	1.0	341.2	1351
Sediment C3	+0.36	5.0	252	0.9	0.6	4.5	19.7	10.3	0.9	204.7	962
Leaves C*	+0.02 ± 0.02		25 ± 2								
Zn-exchangeable¥			173 ± 94 (55%)								

*Average concentration and standard deviation (σ) obtained from three different replicates. Each replicate is composed by leaves sampled from different trees.

¥Average concentration and standard deviation (σ) obtained from 0.1 M acetate leaching from the three sediments collected in each mangrove station. Values in brackets correspond the percentage value relative to total Zn concentration.

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Table 2. Zinc isotope composition (expressed using $\delta^{66}Zn_{JMC}$) of the end-members and the mud flat sediments from Sepetiba Bay Data compiled from Araújo et al.(2017a).

End-members	$\delta^{66}Zn_{JMC}$ (2σ)
Electroplating wastes	+0.86 ±0.15‰
Terrestrial detrital material	+0.28 ±0.12‰
Marine detrital material	+0.45 ±0.03‰
Mud flat sediments (top layers of mud flat cores)	
Station A	+0.83 ±0.06‰
Station B	+0.67 ±0.06‰
Station C	+0.46 ±0.06‰

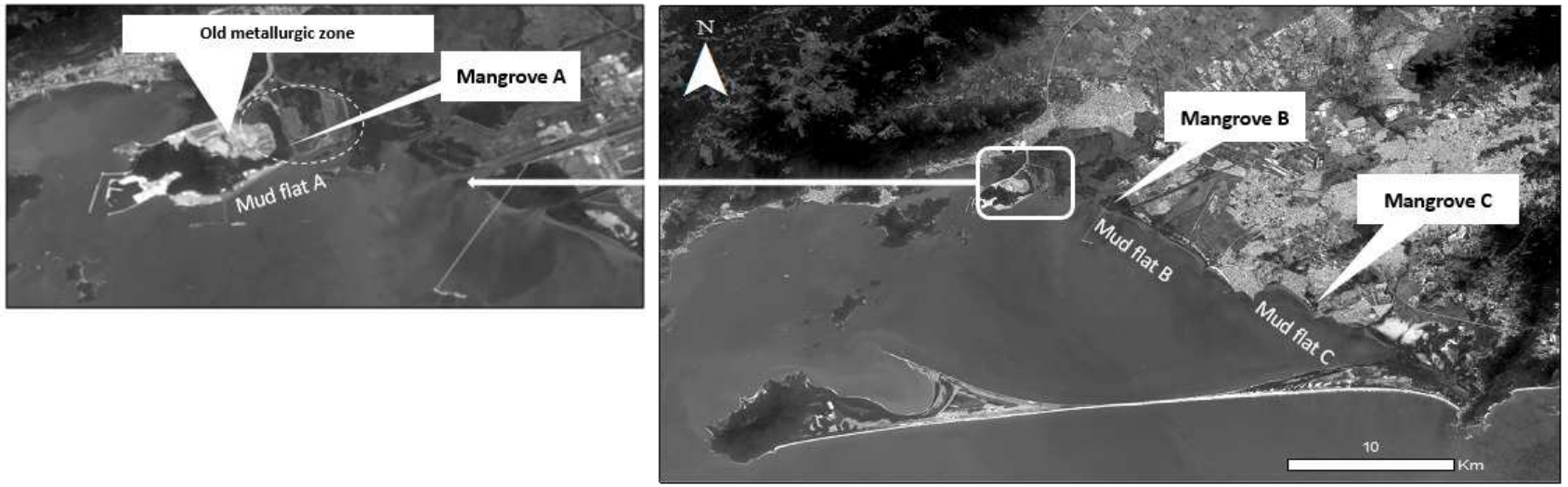

Fig.1. Map showing the sampling stations at the Sepetiba Bay. Station A: Saco do Engenho; station B: São Francisco Channel; station C: Enseada das Garças. Zinc isotope compositions of mud flat sediments are taken from Araújo et al. (2017) (Table 1). The insert at left shows the old metallurgic zone, where the electroplating activity operated from 1960's to end of 1990's. The dashed circle line highlight the Saco do Engenho mangrove, one site heavily impacted by the wastes lixiviated from the old wastes produced by the electroplating processes.

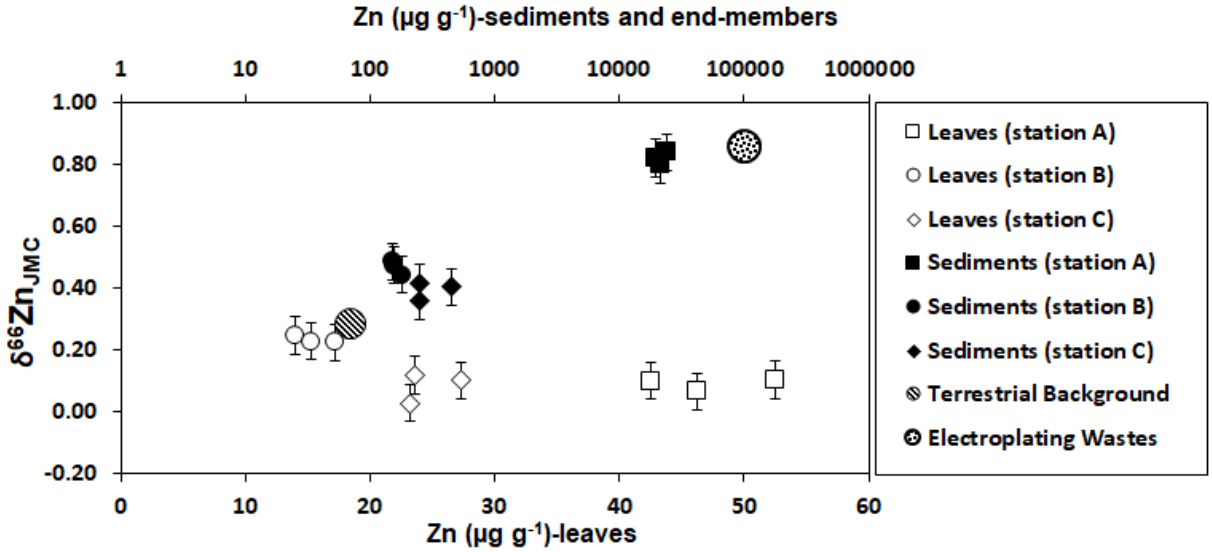

Fig.2. Zinc isotope composition (expressed using $\delta^{66}Zn_{JMC}$) and concentration of sediment and of leaves samples. The end-members (terrestrial detrital material and electroplating wastes) identified in a previous study perfomerd by Araújo et al. (2017a) are included.

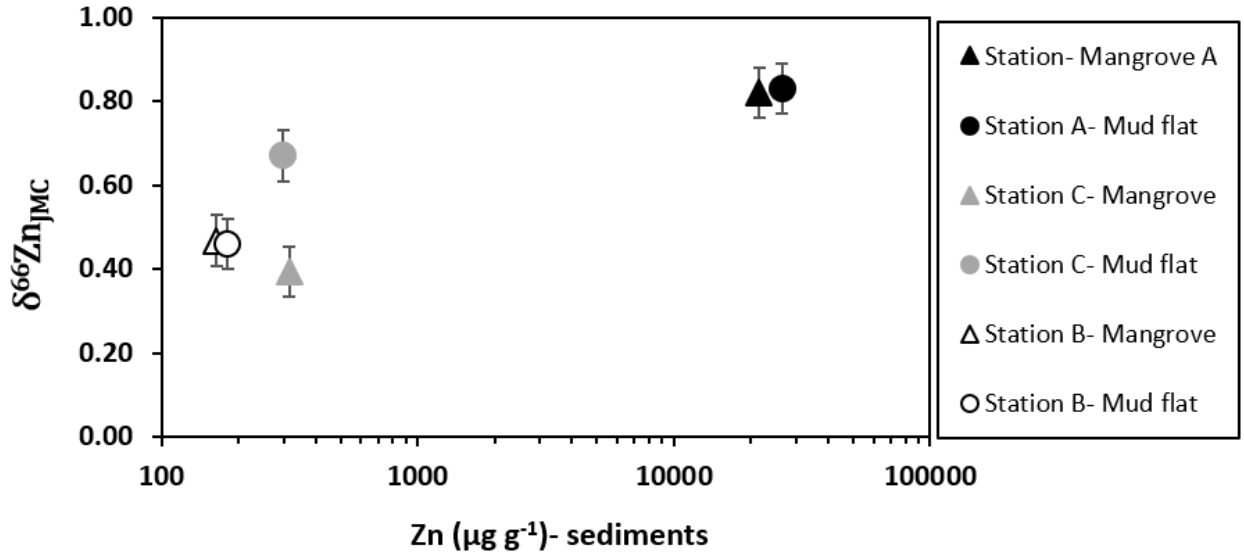

Fig. 3. Zinc isotope composition (expressed using $\delta^{66}Zn_{JMC}$) of mangrove (this study) and mud flat (Araújo et al., 2017a) surface sediments (0-5 cm depth**)**