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Bruno Cunha[1,2,3]
Daniel Ferreira Araújo[4*]
Jeremie Garnier[3,5]
Elton Dantas[3]
Marly Babinski[2]
Izabel Ruiz[2]
Carlos E. Souto Oliveira[6]
Mauro Geraldes[7]
Davi Rocha[8]
Wilson Machado[1]

[1] Universidade Federal Fluminense
Programa de Pós-Graduação em Geoquímica
Niterói RJ Brazil
CEP 24020-141

[2] Universidade de São Paulo
Instituto de Geociências,
Cidade Universitária,
São Paulo SP Brazil
CEP 05508-080

[3] Universidade de Brasília
Instituto de Geociências
Campus Darcy Ribeiro,
Brasília DF Brazil
CEP 70910-900

[4] Laboratoire de Biogéochimie des Contaminants Métalliques
IFREMER, Centre Atlantique
F44311 Nantes Cedex 3 France

[5] Laboratoire Mixte International
Observatoire des Changements Environnementaux – LMI-OCE
Institut de Recherche pour le Développement (IRD)
Universidade de Brasília
Campus Darcy Ribeiro,
Brasília DF Brazil
CEP 70910-900

[6] Universidade de São Paulo
Instituto de Astronomia, Geofísica e Ciências Atmosféricas
Cidade Universitária,
São Paulo SP Brazil
CEP 05508-080

[7] Universidade do Estado do Rio de Janeiro
Faculdade de Geologia
Maracanã
Rio de Janeiro RJ Brazil
CEP 20550-900

[8] Serviço Geológico do Estado do Rio de Janeiro
Niterói RJ Brazil
CEP 24030-060

*Corresponding author:
brcunha@usp.br

RESUMO

Os processos sedimentares em ambientes costeiros desempenham um papel fundamental na dispersão espacial de contaminantes metálicos, incluindo o Zn. A combinação de assinaturas de isótopos estáveis de Zn (δ^{66}Zn) com proxies tradicionais para fontes sedimentares, processos de dispersão e pós-deposição é uma abordagem promissora para entender a dinâmica antropogênica de Zn em sistemas costeiros que ainda não foram testados. Para tanto, acoplamos ferramentas geoquímicas e isotópicas para inferir contribuições sedimentares no destino e comportamento do Zn em sedimentos superficiais da baía de Sepetiba, estado do Rio de Janeiro, cronicamente contaminada por uma antiga pilha de rejeitos de galvanoplastia enriquecidos com Zn. Os resultados mostram uma alta variabilidade nos valores de δ^{66}Zn (0,43‰ a 0,89‰) e fatores de enriquecimento de Zn (1 a 23 vezes), evidenciando um gradiente na mistura de fontes sedimentares. O biplot δ^{66}Zn *versus* 1/[Zn] destaca que a variabilidade isotópica de Zn da maioria das amostras é explicada por um processo de mistura entre uma fonte de Zn natural (+0,29‰, 67 mg kg^{-1}) e antropogênico (+0,89‰, 3.440 mg kg^{-1}), sendo este último atribuído à histórica contaminação metalúrgica de Zn da baía de Sepetiba. Com base no modelo de mistura de isótopos e proxies geoquímicos (por exemplo, razão elementar Ti/Al), foi possível calcular a contribuição antropogênica de Zn na Baía de Sepetiba (42% a 98%). A distribuição do enriquecimento de Zn ao longo da baía confirmou a dispersão antrópica de Zn a partir do Saco de Engenho, controlada principalmente pela corrente superficial principal, no sentido horário. A composição mineralógica dos sedimentos e as correlações entre as razões isotópicas e concentrações de Al indicam que o alto teor de Zn antropogênico está associado, principalmente à frações sedimentares de siltosas e argilosas, com partículas compostas por gibbsita, e minerais argilosos como caulinita e matéria orgânica. Estes resultados demonstram que a combinação de razões isotópicas de Zn com outros proxies geoquímicos podem ajudar na identificação de fontes e no rastreio de sua dispersão no contínuo continente-mar. Neste caso, esta abordagem fornece informações mais precisas sobre a dispersão da contaminação de Zn na Baía de Sepetiba, evitando possíveis interpretações erradas sobre as origens do Zn antropogênico em baixos níveis de concentração de Zn.

Palavras-chave: Isótopos de metais; proxies geoquímicos; avaliação de fontes; poluição costeira; Baía de Sepetiba.

ABSTRACT

Sedimentary processes in coastal environments play a key role in the spatial dispersion of metal contaminants, including Zn. Combining Zn stable isotope signatures (δ^{66}Zn) with traditional proxies of sedimentary sources and dispersal and post-depositional processes is a promising approach to understanding Zn anthropogenic dynamics in coastal systems that remains untested. To this end, we coupled geochemical and isotope tools to infer sedimentary contributions on Zn fate and behavior in surface sediments of Sepetiba bay, a tropical lagoon in Rio de Janeiro state chronically contaminated by an old stake of electroplating wastes Znenrich. Our results show high variability in δ^{66}Zn values (0.43‰ to 0.89‰) and Zn enrichment factors (1 to 23-fold), evidencing a gradient in mixing sedimentary sources. The biplot δ^{66}Zn versus 1/[Zn] highlights that the Zn isotope variability of most samples fell within a mixing source trend involving natural Zn (+0.29‰, 67 mg.kg^{-1}) and anthropogenic Zn (+0.89‰, 3,440 mg.kg^{-1}), the latter attributed to the Sepetiba bay's historical Zn metallurgical contamination. Based on the isotope mixing model and geochemical proxies (e.g., Ti/Al ratio), we calculated that Zn excess in the Sepetiba Bay varies from 42% to 98%. The Zn enrichment distribution across the bay confirmed anthropogenic Zn dispersal from the Saco de Engenho, mainly controlled by the clock direction water current. Sediments mineralogical composition and correlations between Zn isotope and Al concentrations indicate that the high content of anthropogenic Zn is associated with silt and clay sediment particles composed of gibbsite and clay minerals such as kaolinite and organic matter. Our findings demonstrate that combining Zn isotope ratios with other geochemical proxies may help pinpoint Zn anthropogenic origins and behavior as well as track its dispersion in the land-sea continuum. In this case, this approach provides more accurate results on Zn contamination dispersion in the Sepetiba Bay and avoids possible misleading interpretations concerning anthropogenic Zn origins at low Zn concentration levels.

Keywords: metal isotopes; geochemical proxy; source assessment; coastal pollution; Sepetiba Bay.

1. INTRODUCTION

Zn isotopes have been successfully applied over the past two decades as anthropogenic Zn tracers in diverse environmental contexts, including rivers (SIVRY *et al.,* 2008; CHEN *et al.,* 2008, 2009; PALUMBO-ROE *et al*., 2010; GUINOISEAU *et al.,* 2018; XIA *et al*., 2020; ZIMMERMANN *et al*., 2020; TONHÁ *et al*., 2021), atmospheric particulates (CLOQUET *et al.,* 2006; GIOIA *et al*., 2008; BORROK *et al*., 2010; SOUTO-OLIVEIRA *et al*., 2018), soils (BIGALKE *et al*., 2010; FEKIACOVA *et al*., 2015; AUCOUR *et al*., 2017; LIU *et al*., 2020; WANG *et al*., 2021), and coastal environments (PETIT *et al*., 2008, 2015; SHIEL *et al*., 2012, 2013; ARAÚJO *et al*., 2017a,b,c, 2019, ARAÚJO *et al*., 2021). More recently, a widespread influence of anthropogenic sources on Zn isotopic signatures in the marine environment has been hypothesized, as indicated for surface waters from the North Atlantic (LEMAITRE *et al*., 2020).

Zinc isotopes are fractionated during ore refining processes in the metallurgical and electroplating sectors (KAVNER *et al.,* 2008; SIVRY *et al.,* 2008; BORROK *et al.,* 2010; YIN *et al*., 2016), resulting in distinct isotope compositions between the final metallic products (ZnO; Zn) and solid and effluent byproducts. Zn fingerprints in materials produced in the anthroposphere can differ from those observed in geogenic materials, enabling the tracking and quantification of anthropogenic Zn sources in natural compartments (WIEDERHOLD, 2015). However, identifying mixing source processes requires deconvolving the isotope fractionation between biogeochemical processes and sources.

In coastal systems, multiple natural (*e.g.,* different lithological origins, weathered material, and authigenic minerals) and anthropogenic (*e.g.,* urban, agricultural, port activity, and industrial refuse) sources are mixed along with estuarine plume dispersion, driven by hydrodynamics features (BIANCHI, 2006). These intricate dispersal and post-depositional biogeochemical processes can occur concurrently in sediments and potentially overprint Zn isotope source records (PEEL *et al*., 2009; ARAÚJO *et al*., 2017b). Notably, intense primary biological productivity can influence elemental and isotopic partitioning in the water column and settling particles (LITTLE *et al*., 2016). Thus, a critical assessment of sources and biogeochemical processes is essential for the successful application of Zn isotopes as a geochemical tracer in coastal systems. Previous studies have successfully applied Zn isotopes as anthropogenic Zn tracers associated with electroplating industry wastes in Sepetiba Bay, an industrialized lagoon located in southeastern Brazil (Fig. 1) (ARAÚJO *et al.,* 2017b, c; TONHÁ *et al*., 2020). In agreement with other studies performed at Zn smelter-polluted sites (SIVRY *et al.,* 2008; PALUMBO-ROE *et al.,* 2010; JUILLOT *et al.,* 2011; DESAULTY *et al.,* 2020), anthropogenic metallurgical Zn is characterized by a heavy isotope signature, allowing for origin identification through sediment, suspended particulate matter (SPM) and bivalve mollusk sample analyses (ARAÚJO *et al*., 2017b, c; TONHÁ *et al*., 2020). Recent studies on sediments and biota from Sepetiba bay have characterized the Zn speciation in surficial sediment and biota contamination (TONHÁ *et al.,* 2020; KUTTER *et al*., 2021). These previous studies focus on Zn contamination and behavior in sediment, considering a period later than the waste encapsulation. However, the anthropogenic Zn liberation from waste, its remobilization from contaminated sediments, and distribution along the bay before this period remain less characterized.

This study analyzes Zn isotopes and geochemical compositions of a new grid-sampling of surface sediments samples distributed across Sepetiba bay which were collected in 2008, therefore, before tailing encapsulation. Thus, this sampling provides a screenshot of Zn contamination baseline previous to local actions intended to reduce wastes releasing into the bay. This study seeks to improve spatial Zn contamination dispersion constraints by combining Zn isotope ratios with mineralogy and chemical proxies of geochemical sediment sources. The findings will provide a more accurate assessment of anthropogenic Zn dispersion in a coastal system. Indeed, tracking metallic contaminants using metal stable isotope compositions without considering mineralogy, hydrodynamic and sediment variation along the transport can lead to misleading interpretations.

2. METHODS

2.1 STUDY AREA

The Sepetiba Bay is a 520 km2 semi-enclosed estuary in the Rio de Janeiro State (southeastern Brazil, Fig. 1). The geology of the Sepetiba watershed is composed of Quaternary sediments and igneous granite-gneisses rocks (RONCARATI; CARELLI, 2012). The sediments in the bay are governed by fluvial (terrigenous), marine, and biogenic sources (BARCELLOS *et al*., 1997). The clock-wise direction of the surficial current in the bay led to the dispersion of fine clay and/or organic-rich terrigenous sediments in the eastern part of the bay, and the coarsest in the western part opened to the Atlantic Ocean (RONCARATI; CARELLI, 2012). Accordingly, the geochemical composition of sediments from the Sepetiba bay varies according to the different bay zones, presenting sandy particles in the bay entrance and navigational channel (west region) and clayed organic-rich material in the shallow sheltered zones.

The watershed hosts a large population (estimated to contain 1.4 million inhabitants) in the Metropolitan Rio de Janeiro area, a huge industrial park, and voluminous harbor activity (ore shipping, metallurgy, rubbery, and food, among others). It also included the largest steel industry complex in Brazil. A Zn electroplating plant (Mercantile Company Inga) operated close to the northeastern shore of Sepetiba Bay (Fig. 1, old electroplating facility). From the 1960s to the end of the 1990s, 600,000 tons of byproducts generated by this electroplating plant were stored in the open-air, covering an area of 40,000 m^2 (BARCELLOS *et al.,* 1991).

To avoid frequent waste leaching episodes, a dam was built in 1984. Nevertheless, several events of dam collapses (in 1996, 2003, and 2006), with effluents and mud leakage into the surrounding mangroves of *Saco do Engenho* and Sepetiba Bay, have been registered. Finally, the byproduct tailing was encapsulated *in situ* in 2012 to prevent material leaching and further contamination.

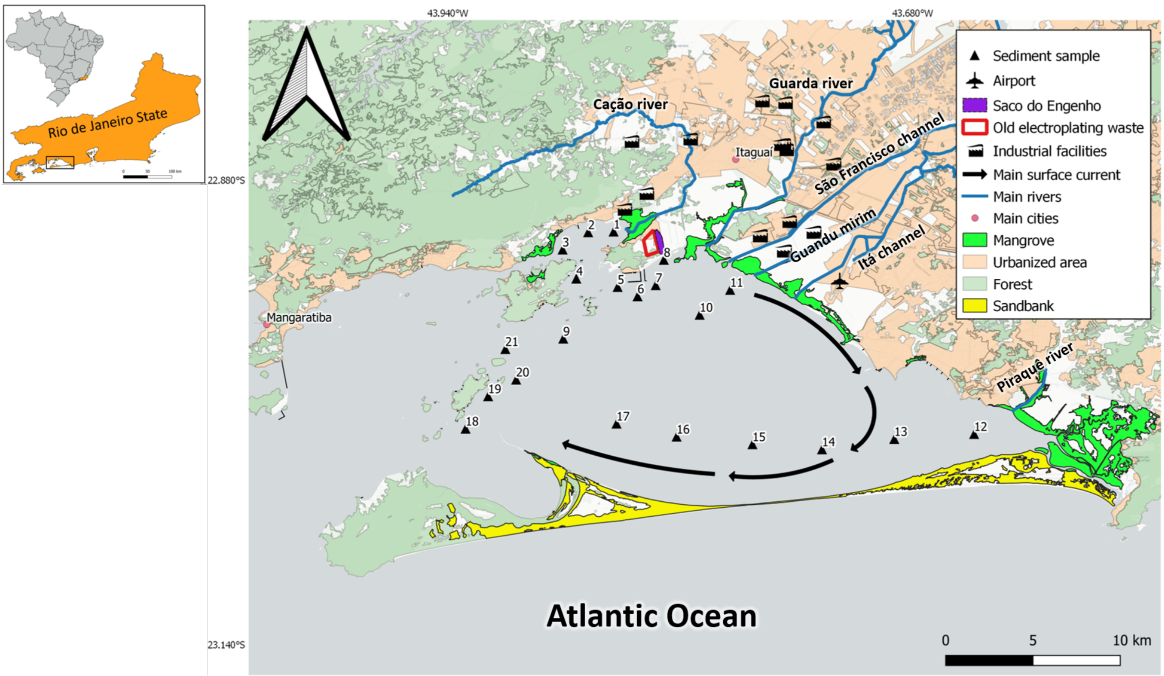

Figure 1

Sepetiba bay and the sediment sampling site locations investigated herein.

2.2 SAMPLING, ELEMENTAL AND MINERALOGICAL ANALYSES

Sepetiba Bay surface sediments (~ 0-10 cm depth) were sampled from 21 stations using a Van Veen grab in 2008 before metallurgical waste encapsulation (Fig. 1). Sample preparation for major elements and total zinc concentration analyses were performed at the Geological Sample Preparation Laboratory at the Rio de Janeiro State University (LGPA-UERJ). Sediments samples were (i) sieved (<200 mesh, i.e., 74 µm), (ii) dried, (iii) weighed (0.25 g) before (iv) total acid digestion ($HF+HCl+HNO_3$) using a Teflon vial in a hot plate. The determination of total zinc concentrations and other selected elements (Al, Ca, Fe, Ti, and Mn) (HR-ICP-MS) was performed at ActLabs Canada (ISO 17025). The Zn concentrations for the vessel blanks, reagent blank, and procedural blanks were lower than the analysis limit of detection (LD) (LD = 0.025 µg L^{-1}). The mineralogical composition of sediments was determined, at the XRD laboratory of the University of Brasilia, by x-ray diffraction (XRD) (Rigaku®, Ultima IV diffractometer, JPN) using Ni-filtered Cu-Kα radiation and a graphite monochromator. The XRD patterns were recorded from 2θ values of 2° to 80° with a scanning speed of 2°/min. The XRD patterns interpretation was performed using the software Jade®.

2.3. ZINC ISOTOPE ANALYSES

Zn isotope analyses were performed in 2016 at the Geodynamics and Environmental Studies Laboratory at Brasilia University (UnB). Further details concerning analytical procedures and sample preparation can be found elsewhere (ARAÚJO *et al.,* 2017a). Briefly, 100 mg of sieved sediment samples were digested in Savillex® beakers applying multiple-step acid digestion using HCl, HF, and HNO_3 on a hot plate (TONHÁ *et al.,* 2020). The sample batch also included certified material (BHVO-2) and blanks. The elution protocol followed an adaptation of the steps described by Maréchal *et al.* (1999). Prior to the isotope analysis, 2 µg aliquots of Zn were purified through an ion-exchange chromatographic column packed with AG-MP1 resin and eluted with HNO_3. Zinc isotope ratios were determined using a Thermo Finnigan Neptune plus Multicollector Inductively Coupled Plasma Mass Spectrometry at the Center for Research in Geochronology and Isotopic Geochemistry of the University of São Paulo (CPGeo, USP). Samples were doped with Cu NIST SRM 976 at a 1:1 Cu/Zn ratio and introduced into the spectrometer through a 0.05 M HNO_3 medium using an SIS spray chamber. Raw ratios were corrected for instrumental fractionation (mass bias), combining the standard bracketing technique and external normalization with the Cu-dopant applying the exponential law (ARAÚJO *et al.*, 2017a). Samples and certified materials used for analytical control were analyzed in a single analytical session comprising two successive runs. The final Zn isotope data reported in this study are expressed relative to the Johnson Matthey Company 3-0749-L (JMC3-0749-L) as follows:

$$\delta^{66}Zn_{JMC}(‰) = \left(\frac{(^{66}Zn/^{64}Zn)_{\ sample}}{(^{66}Zn/^{64}Zn)_{\ JMC-Lyon}} - 1\right)X1000 \qquad \text{(Eq. 1)}$$

Two different BHVO-2 reference material aliquots were run in every batch sample through digestion and chromatographic steps, yielding a $\delta^{66}Zn_{JMC}$ average of +0.29 ± 0.05‰ (2s, n=2). The $\delta^{66}Zn_{JMC}$ average for the certified isotope material IRMM (Institute for Reference Materials and Measurements) corresponded to +0.32 ± 0.01‰ (2s, n=2). Both certified materials agree with the long-term concentrations obtained by our method by MC-ICP-MS from different laboratories compiled by Moynier *et al.* (2017) (+0.30 ± 0.01‰, 2s, for IRMM and +0.28 ± 0.07‰, 2s, n=4 for BHVO-2). The external reproducibility of our method based on a long-term sample and certified material measurements corresponds to 0.04‰ (2s, n = 42). Considering previous measurements performed in the same laboratories over the last five years according to the identical analytical sequences (ARAÚJO *et al.*, 2017a, b, c; SOUTO-OLIVEIRA *et al.*, 2019; TONHÁ *et al.*, 2020), the present $\delta^{66}Zn_{JMC}$ concentrations are indistinguishable.

2.4. GEOCHEMICAL PROXIES AND ENRICHMENT FACTORS

Manganese and Fe distributions are also associated with diagenetic redox cycling involved in microbial metabolism and carbon-iron-sulfur interactions (ARAÚJO *et al.*, 2017d; GUEIROS *et al.*, 2003). The participation of these elements in redox processes is supported by the frequent occurrence of ankerite and pyrite in Sepetiba Bay sediments (ARAÚJO *et al.*, 2017d). Furthermore, in this case, Al is mainly associated with aluminosilicate materials from terrestrial sources, while Ca is mainly related to carbonates from biogenic or/and authigenic marine sources (BARCELLOS *et al.*, 1997; ARAÚJO *et al.*, 2017d). Based on previous studies carried out at Sepetiba Bay, Mn and Fe were adopted as proxies for redox processes, whereas Al and Ca were used to evaluate terrigenous and marine provenances, respectively.

The trace element enrichment factor (EF) was used to compute anthropogenic influences, adopting the combined physical (sieving) and geochemical (ratio for a conservative reference element) normalization approach (Kersten and Smedes, 2002). The Enrichment Factor was calculated as follows:

$$EF = \left(\frac{(M/Ti)_{Sample}}{(M/Ti)_{terrigenous\ background}}\right) \qquad \text{(Eq. 2)}$$

Where (M) is the concentration of the metal of interest and (Ti) comprises titanium concentrations, a conservative reference element with no significant anthropogenic source. The Upper Continental Crust (UCC) composition and local sediment background $\delta^{66}Zn_{JMC}$ signatures reported for Sepetiba bay by Araújo *et al.* (2017b) were used for these calculations (67 mg kg^{-1} and $\delta^{66}Zn_{JMC}$ =0.29‰ for Zn and 8.1 wt.%, 0.38 wt.% for Al and Ti respectively). A Principal Component Analysis (PCA) was performed to identify possible associations between $\delta^{66}Zn_{JMC}$, Zn, Cd, Mn, Fe, Al, and Ti. Statistical treatments were performed using Statsoft software (Statistica, release 8.0).

3. RESULTS AND DISCUSSION

Sediments were grey, with grain size ranging from clay to fine sand, composed of quartz, gibbsite, clay minerals (kaolinite and traces of illite), and a small proportion of pyrite and/or ankerite. It has also been observed calcite in sediments from the west part of the bay (Fig. 2). Halite was also observed and interpreted as crystalized mineral during sediment drying. In a previous study, framboidal pyrite was determined by scanning electron microscopy (SEM) (TONHÁ *et al.,* 2020). The Al concentration in sediment ranged from 3.60 to 8.92 % wt., Ca from 0.27 to 7.72 % wt., and Ti from 0.32 to 0.84 % wt (Table 1). The organic matter concentration of Sepetiba Bay sediments has been quantified in a previous study and ranges from 3 to 18.6% (ARAÚJO *et al*., 2017d). The PCA of the sediment dataset yields two principal components accounting for 72% of the variability (Fig. 3A e 3B). The PCA analysis separated three main clusters, interpreted to be related to the origin of sediments, with marine sediment (Ca and Mn cluster) and terrigenous one (Al, Fe, and Ti cluster), and anthropogenic contamination (Zn, Cd, and $\delta^{66}\text{Zn}_{\text{J}}$ cluster).

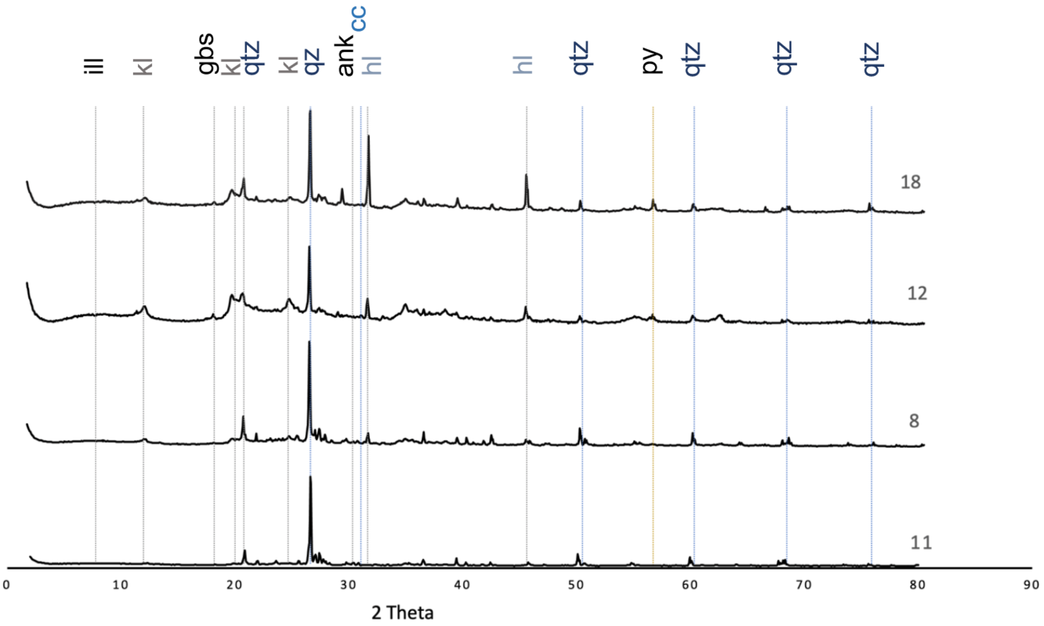

Figure 2
XRD diffractograms of sediments samples 11, 8, 12 and 18, showing characteristics peaks (qtz: quartz, kl: kaolinite, gbs; gibbsite, ill: illite, cc: calcite, ank: ankerite, py: pyrite and hl: halite crystallized during drying).

3.1 SPATIAL Zn CONCENTRATION AND ISOTOPIC SIGNATURE TRENDS

The Zn concentrations, isotopic compositions, and Zn enrichment factors are presented in Table 1. In contrast to major elements, Zn concentrations of the Sepetiba Bay sediments are much greater than the natural background. Zn concentrations ranged from 145 (sample 20) to 3,440 mg kg^{-1} (sample 8) from the southwest part of the bay to the Saco of Engenho mangrove, located in the north bay area and indicated by previous studies as the source of Zn-contaminated sediments (BARCELLOS *et al*., 1991; BARCELLOS; LACERDA 1994; ARAÚJO *et al.,* 2017b). Previous studies show that the high Zn EF of Sepetiba Bay sediments, ranging from 2 to 23, highlights non-natural Zn origin in these samples.

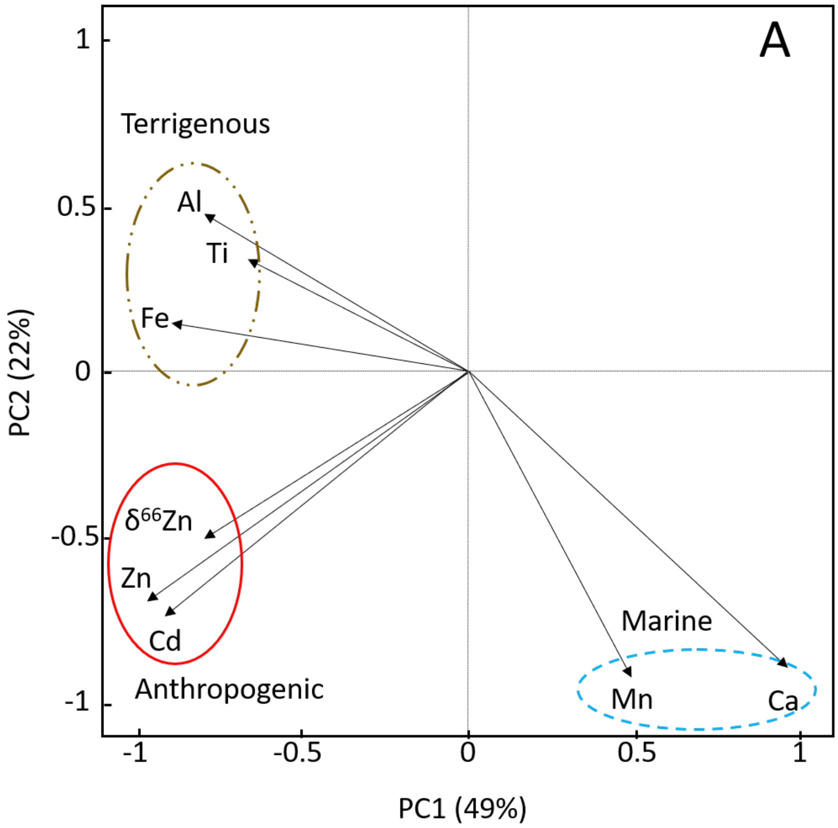

Figure 3
PCA analysis of variables in sediments from Sepetiba bay

Table 1- Major element and Zn concentration (Fe, Ca, Al and Ti in %; Mn, Cd, and Zn in mg kg^{-1}), Calculated Zinc anthropogenetic (Ant. Zn in %) based on normalized-Zn concentration binary mixing model proposed and Zinc isotopic composition ($\delta^{66}Zn_{JMC}$ in ‰).

Sample Id.	Fe	Al	Ca	Ti	Mn	Cd	Zn	Ant. Zn	$\delta^{66}Zn_{JMC}$
	%				mg kg^{-1}			%	‰
1	4.61	8.00	1.99	0.61	616	1.8	436	77	0.64
2	4.61	8.23	0.61	0.64	531	3.4	946	90	0.70
3	3.64	3.97	6.01	0.28	1,230	0.7	240	81	0.57
4	4.66	7.62	0.64	0.68	483	2.6	750	86	0.72
5	4.02	7.35	0.52	0.57	386	2.5	724	88	0.66
6	4.23	7.69	0.68	0.54	401	2.1	574	85	0.54
7	4.82	8.01	0.75	0.65	494	3.3	715	85	0.54
8	6.45	6.62	1.99	0.84	693	23.0	3,440	98	0.89
9	3.77	3.98	2.86	0.60	468	1.1	179	42	0.48
10	5.28	8.25	0.57	0.58	397	4.0	783	88	0.65
11	5.27	8.92	0.35	0.64	461	2.1	676	85	0.64
12	3.68	6.78	0.56	0.49	841	2.0	574	86	0.65
13	3.67	6.52	0.41	0.49	498	2.6	823	91	0.71
14	3.51	5.81	0.27	0.44	398	3.5	1,100	95	0.83
15	4.20	7.16	0.27	0.50	430	1.5	574	86	0.69
16	3.77	6.28	0.31	0.50	486	2.8	721	89	0.70
17	3.86	6.48	0.66	0.54	502	1.9	405	78	0.55
18	2.26	3.60	10.6	0.32	891	0.6	153	64	0.56
19	4.45	5.45	2.18	0.64	587	0.7	222	50	0.55
20	3.51	3.69	2.34	0.40	508	0.6	145	52	0.43
21	3.62	4.33	7.72	0.49	440	0.5	156	45	0.51

The $\delta^{66}Zn_{JMC}$ values determined on sediments (+0.43 to +0.89‰; Table 1) are within the range reported in previous studies concerning Sepetiba Bay sediments (+0.20 to +1.15‰; ARAÚJO *et al*., 2017b; TONHÁ *et al*., 2020). These studies showed that Zn-enriched sediment particles coming from the hot spot zone display high positive $\delta^{66}Zn_{JMC}$ values. Moreover, these $\delta^{66}Zn_{JMC}$ values agree with previously analyzed anthropogenic materials, such as Zn smelter tailings (+0.18 to +1.49‰; SIVRY *et al.* 2008), smelter effluents (+0.41 to +0.51‰; SHIEL *et al.,* 2010), and sediment´s contaminated by metallurgical activities from France (+0.75 to +1.36‰; SIVRY *et al.,* 2008), China (+0.40 to +0.67‰; ZHANG *et al*., 2018) and Sepetiba Bay (+0.20 to +1.03‰; ARAÚJO *et al*., 2017b; TONHÁ *et al*., 2020). All studies pointed out heavy $\delta^{66}Zn_{JMC}$ values indicating input of solid metallurgical byproducts.

A further study conducted in the Saco do Engenho surrounding mangrove shows that part of the anthropogenic metallurgical Zn was redistributed from the exchangeable/carbonate fraction in the waste to the mangrove sediment. Then, this contaminated sediment with heavy $\delta^{66/64}Zn$ values was exported and dispersed into the Sepetiba Bay (TONHÁ *et al*., 2020). Accordingly, the higher Zn EF evidenced the region near the former electroplating plant as the most enriched in anthropogenic Zn (with a Zn-EF larger than 23 for sample 8). In contrast, the lowest concentrations, varying from 3.7 to 4.6 for samples 9, 18, 19, 20, and 2, were observed in the west area of the bay. Nonetheless, medium Zn-EF values were observed close to Saco de Engenho, and oppositely high Zn-EF values were observed far away from this source point.

A $\delta^{66}Zn_{JMC}$ versus 1/[Zn] plot (Fig. 4) supports a general mixing trend between two main end-members: a geogenic, encompassing weathered detrital products (e.g., clays); and an anthropogenic source, representing the Zn released from the legacy electroplating waste (ARAÚJO *et al.,* 2017b; TONHÁ *et al.,* 2020). Exceptionally, a group of few samples (3, 9, 18, 19, 20, and 21) exhibited moderate-heavy $\delta^{66}Zn$ values (+0.54‰ to +0.57‰) and relatively lower Zn concentrations (from 179 to 240 mg kg^{-1}). These findings argue for a third unknown source and/or biogeochemical processes affecting Zn concentrations and/or Zn isotope compositions during the dispersion of contaminated sediment. According to the higher concentration of Ca (ranging from 2,18 to 10,6 % wt.) and the presence of calcite in this zone, we cannot exclude a small contribution of Zn-carbonate with heavier Zn isotopic concentration as reported by Pichat *et al.* (2003).

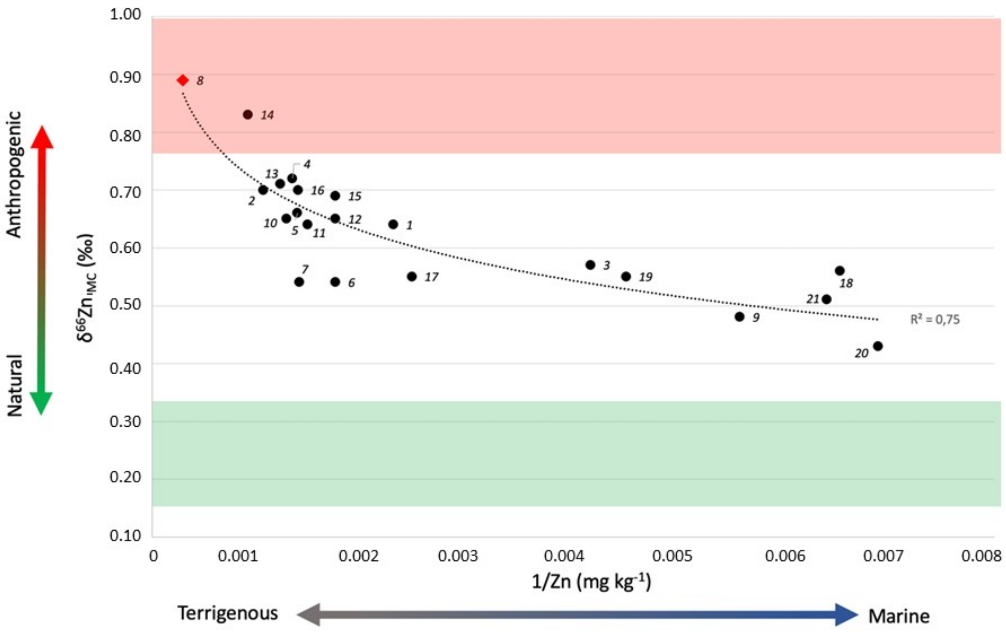

Figure 4

Plot presenting the $\delta^{66}Zn_{JMC}$ versus 1/[Zn] concentrations from this study. Based on previous studies (ARAÚJO *et al.,* 2017b, and TONHÁ *et al.,* 2020), the green and red areas represent the natural geogenic isotope range (y-axis) and local anthropogenic emissions, respectively. The double arrow along axe X represents the expected Zn concentrations for sediment sources with terrigenous and marine origins, respectively.

3.2 MODELING SPATIAL DISPERSION OF THE ZN CONTAMINATION

The distribution of geochemical proxies for redox processes (Mn, Fe) and sediment source mixing (Al, Ca) is presented in Table 1 and Figure 4. Higher calcium concentrations, up to 2 wt.%, were observed in samples located in the southwestern portion of the bay (samples 9, 18, 19, 20, and 21), closer to the main ocean connection, and in one sample in the northern portion of the bay (sample 3). Manganese is higher in samples 12 and 18, with a peak concentration of 1,230 mg kg^{-1} in sample 3. Pyrite and ankerite, a Ca-Fe-Mn carbonate, have been observed in Sepetiba bay sediments by XRD analysis (Fig. 2). The presence of framboidal pyrite and Mn (II) carbonate mineral in Sepetiba surficial sediments highlights reducing conditions associated with early diagenesis processes. Moreover, it suggests that the redox cycling induces remobilization and redistribution of Mn and Fe from anoxic to oxygenated sediments, where Mn oxide accumulation in the uppermost layers is favored, as reported previously (LACERDA *et al.,* 1999; GUEIROS *et al.,* 2003).

However, the Zn concentrations were not correlated with Mn and Fe ($R^2 < 0.26$), showing that Mn-Fe oxyhydroxides were not the main Zn-host phases. A moderate positive correlation between Al (a proxy for terrigenous sediment source) and Zn (R2 = 0.67) suggests Zn associations with clay minerals previously reported for this bay (TONHÁ *et al.*, 2020). This moderate correlation agrees with the composition of clay sediment contaminated by Zn liberated from the legacy smelter waste, i.e., the end-member used in the mixing model. In addition, a stronger negative correlation (R^2 = 0.59) between Zn and Ca, coupled with a positive one between Zn and Al, suggests the dispersion effect of Zn-contaminated sediment in the Sepetiba Bay with a larger oceanic contribution in the western part (richer in carbonate) and oppositely terrigenous sediment in the eastern part (rich in clay). These correlations disregarded sample 8, corresponding to the electroplating source signature. This sediment with a very large Zn concentration represents an outlier considering general sediment correlation trends observed throughout the bay.

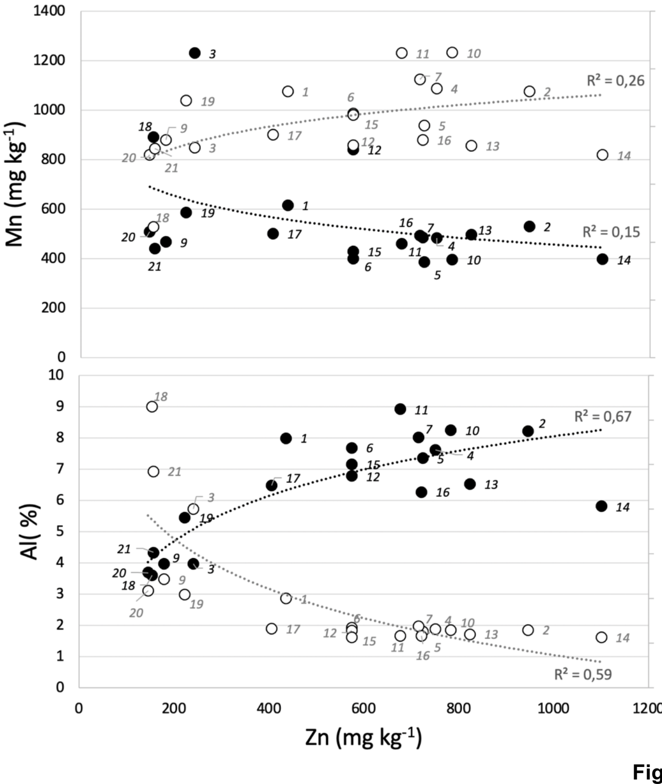

Figure 5
Plot presenting the Zn versus Mn (black circle), Fe (white circle), Al (black circle), and Ca (white circle) concentrations from this study (except sample 8).

Sedimentary environments in land-ocean transition typically involve mixing terrigenous, biogenic, and authigenic marine carbonates (BARCELLOS *et al.,* 1997). In Sepetiba Bay, the mixing of sediment material from several origins is likely to affect trace metal concentrations and behavior, as evidenced by the cited studies and observed Zn correlations with Ca and Al. In order to deconvolve potential biogeochemical processes during the dispersion of terrestrial clay sediments contaminated by Zn liberated from the legacy smelter waste, a normalized-Zn concentration binary mixing model analogous to that developed by Chen *et al.* (2009) was applied.

Although Chen *et al.* (2009) initially used more than one element normalized to Zn (such as Al, Cr, Ni, Ba, and Th), generating convergent results, most of these normalized trace elements used in this study (Cr, Ni, and Ba) can have concentration affected by pollution in the Sepetiba Bay area. Titanium was, therefore, chosen to represent natural conservative elements in this coastal system, as indicated in the discussions above. Ti/Zn ratios derived from Table 1 data were applied in anthropogenic source contribution calculations, adopting the following binary mixing equations (CHEN *et al.,* 2009):

$$\delta^{66}Zn_{sample} = \delta^{66}Zn_{nat}{*}x_{nat} + \delta^{66}Zn_{anth}{*}x_{anth}$$

$$\frac{Ti}{Zn}_{sample} = (\frac{Ti}{Zn})nat{*}x_{nat} + (\frac{Ti}{Zn})anth{*}x_{anth} \qquad \text{(Eq. 3)}$$

Satisfying that $1 = x_{nat} + x_{anth.}$

The Zn amounts from the natural and anthropogenic sources are represented by x_{nat} and x_{anth}, respectively. Sample 8 was chosen to represent the anthropogenic end-member, as it was located in the old electroplating plant region and presented similar Zn concentration and δ^{66}Zn values previously reported for this region (3,440 mg kg^{-1} of Zn and $\delta^{66}Zn_{JMC}$ = 0.89‰) (ARAÚJO *et a*l., 2017b; TONHÁ *et al.*, 2020). Oppositely, UCC sediment with 67 mg kg^{-1} of Zn (RUDNICK; GAO, 2014) and a $\delta^{66}Zn_{JMC}$ value of 0.29‰ from watershed background sediment (ARAÚJO *et al.*, 2017b) has been considered as pristine Zn sample in the region.

The relative contribution from the major anthropogenic source ranged from 42% to 98% outside the electroplating plant hot spot area (Figs. 6 and 7). Excluding sample 8, the correlation between Zn anthropogenic proportion and Al-EF and Zn-EF values are notable ($R^2 = 0.83$ and 0.86, respectively) (Fig. 5). As already shown in Zn contaminated area, Zn-phyllosilicate or Zn-layered double hydroxide (Zn-LDH) may be quantitatively relevant in slightly acidic to neutral soils contaminated by mining and smelting emissions (MANCEAU *et al.*, 2000; TRIVEDI; AXE 2000; JUILLOT *et al.,* 2003; VOEGELIN *et al.*, 2005; GOU *et al.*, 2018).

3.3. DISPERSION OF ZN-CONTAMINATED SEDIMENT IN THE SEPETIBA BAY

The Zn anthropogenic proportion value has been plotted on granulometric and sediments Carbon concentration map (RIBEIRO *et al.,* 2013) (Fig. 7A and 7B). As expected, the higher Zn anthropogenic concentrations were observed in areas rich in clayed and organic-rich sediment. For example, the contribution from the electroplating byproduct legacy was high, reaching 95%, even far from the point source (samples 12 to 17; Fig. 5 and 6a and 6b), showing the Zn contamination dispersion along the bay. This feature can be partly explained by the bay's hydrodynamics, resulting in anthropogenic Zn predominantly transported by a clockwise circulation. Sediments encountered in this area were fine clayed organic-rich sediment (RONCARATI; CARELLI, 2012).

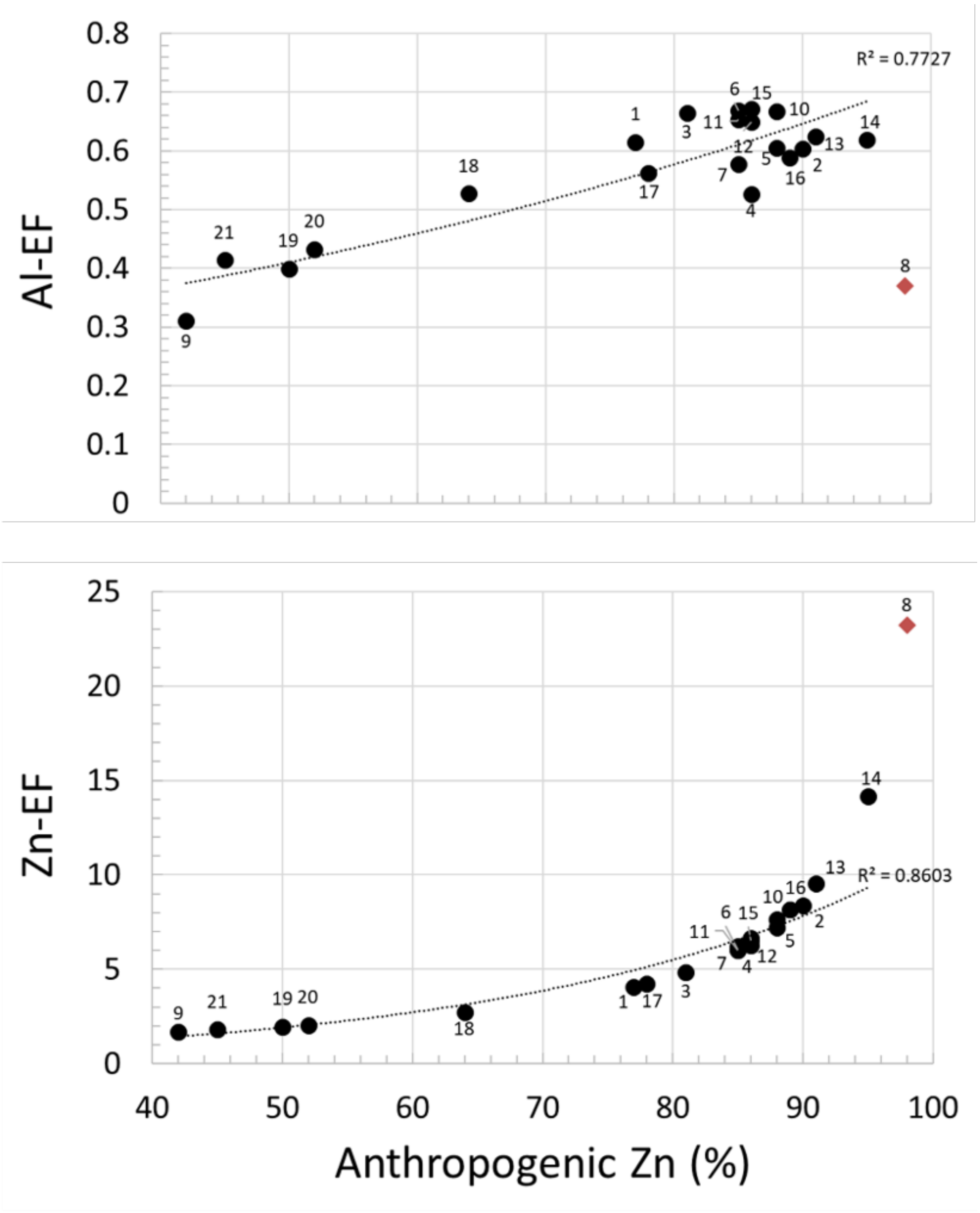

Figure 6
Plot presenting the Al-EF and Zn-EF versus calculated relative contributions from the anthropogenic Zn from the study area, correlation calculated on all samples except sample 8 considered as anthropogenic end-member in this study (red diamond).

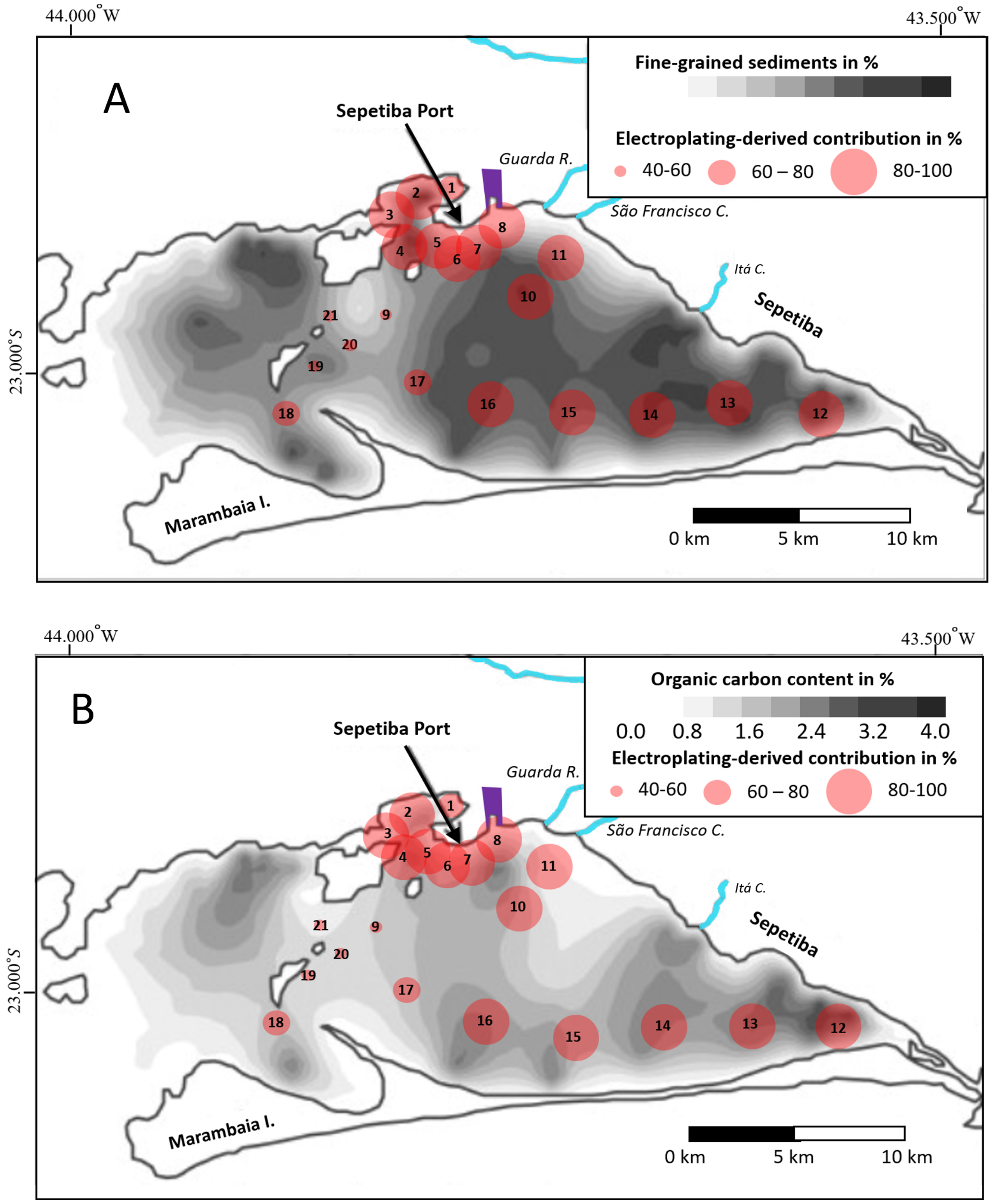

Figure 7
Calculated relative contributions from the anthropogenic Zn plotted in fine-grained sediments (A) and Organic carbon distribution maps (B) (modified from Ribeiro *et al.* 2013). The purple polygon rerpesents Saco do Engenho.

Following the main clockwise direction of coastal circulation, the anthropogenic Zn-enriched particles released from the SE mangrove are mixed with a large terrigenous sediment load delivered by the main local river, the São Francisco channel (SF), located in the northern bay area (Figs. 1 and 7A). During this mixing, terrigenous material rich in clay-mineral and (Mn-Fe-Al) oxides may also contribute with metals to the bay, including Zn derived from diffuse source emissions along the land-sea continuum (TONHÁ *et al.*, 2021). This river exhibits an annual discharge of 6.5 x 10^9 m^3 (MOLISANI *et al.*, 2004), with a δ^{66}Zn signature of +0.30 ‰ and Zn concentration of about 85 mg kg^{-1} in suspended particulate matter (TONHÁ *et al.,* 2021). Additionally, channels such as Cabuçu-Piraquê and Globo Rivers, draining urban areas, are possible sources of metal contaminants associated with untreated sewage effluents discharged directly in the watershed (ALVES-NETO *et al*., 2014). The SE mangrove and SF and canals sediments are free of carbonates and dominated by organic matter, Al oxides (gibbsite), and clay minerals (kaolinite and traces of illite) (TONHÁ *et al.,* 2020 and 2021).

Consequently, sources of natural (i.e., geogenic) and anthropogenic Zn (i.e., electroplating wastes) contribute to the isotope compositions and elemental Zn contents of SPM transported into the bay. Our results suggest that the anthropogenic Zn initially present in particles from SE mangrove (hot spot zone) is re-allocated in different mineralogical phases after mixing with the terrigenous sediment plume. The sediment mixture and Zn re-allocation drive to Zn enrichment of terrigenous sediments from SF and other canals, rich in kaolinite, gibbsite, and organic matter. Concurrently, as sediments are transported toward the open sea, they are mixed with marine sediments enriched in calcium and manganese.

Considering that sediment dredging activities occurred periodically in the eastern part without regulation in the past (WASSERMAN *et al.,* 2013), anthropogenic Zn spatial variability in the eastern part may also be affected by irregular dumping and dispersion of contaminated dredged sediments. Besides possible natural sediment resuspension events (BARCELLOS *et al*., 1997), metal-contaminated sediment remobilization due to dredging operations, causing contamination plume dispersion, has also been evidenced for Sepetiba Bay (WASSERMAN *et al.,* 2016). However, the present Zn contaminated sediment dispersion model agrees with such dredging activities, through large Zn concentration observed associated with fine sediments and sometimes far away from the main sources, the *Saco do Engenho* mangrove.

4. CONCLUSIONS

Our findings indicate that applying Zn isotopes combined with geochemical and mineralogical characterizations is helpful to better constrain the sedimentary controls on the dispersion of anthropogenic Zn in coastal sediments. Combining Zn isotope tools with traditional proxies allowed tracing the anthropogenic Zn behavior and its spatial dispersion composed in the land-sea continuum. As demonstrated here, clay-rich marine sediment particles are the main carriers of anthropogenic Zn from the Saco of Engenho, i.e., the mangrove surrounding the legacy electroplating wastes, to the inner bay. Following the major circulation pattern of the bay in the clockwise direction, the Zn-enriched clay particles emitted from this hotspot are mixed with Zn-depleted sediments of terrigenous sources brought by rivers. As mixing proceeds following the circulation pattern toward the eastern part of the bay, major marine sediment contributions result in further Zn concentration dilutions, but without effect on Zn isotope compositions because of very low Zn concentration in carbonate. The present work confirms the conservative isotopic behavior of Zn in the mixing processes throughout a coastal system, i.e., transport, deposition, and post-depositional processes. The relative geographical contributions of the different continental and marine sediments resulting from the sedimentary mixing dynamics reflect a conservative mixing isotope process involving natural and anthropogenic Zn end-members. These findings reaffirm that considering sedimentary dynamics, geo-chemical proxies, and normalizing- concentration approaches improve isotope tracking and help may prevent misleading interpretations concerning metal sources contributions and related attenuation processes.

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6. DECLARATIONS

The authors and technicians declare that they have no competing interests. No human participants and/or animals were involved in this study.

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