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Copper and lead isotope records from an electroplating activity in sediments and biota from Sepetiba Bay (southeastern Brazil)

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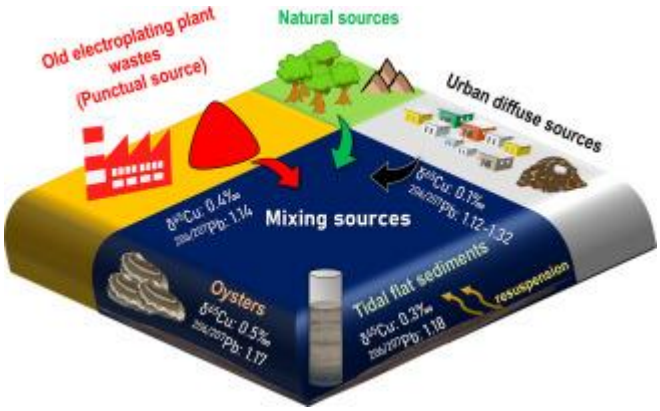
Abstract :

An old electroplating plant in Sepetiba Bay discharged metal-enriched wastes into the surrounding mangroves for 30 years (from the 1960s to 1990s), resulting in a hotspot zone of legacy sediments highly concentrated in toxic trace metals. This study applies Cu and Pb isotope systems to investigate the contributions of past punctual sources relative to emerging modern diffuse sources. The electroplating activity imprinted particular isotopic signatures (average δ65CuSRM-976: 0.4 ‰ and 206Pb/207Pb: 1.14) distinct from the natural baseline and urban fluvial sediments. The isotopic compositions of tidal flat sediments show intermediate isotope compositions reflecting the mixing of Cu and Pb from the hotspot zone and terrigenous materials carried by rivers. Oyster isotope fingerprints match legacy sediments, attesting that anthropogenic Cu and Pb are bioavailable to the biota. These findings confirm the interest in combining two or more metal isotope systems to discriminate between modern and past metal source emissions in coastal environments.

Graphical abstract



Highlights

► Electroplating wastes imprint particular metal isotope ratios in legacy sediments. ► Isotope analysis reveals the anthropogenic Cu and Pb dispersion across the bay. ► Tidal flat isotope ratios reflect mixing of legacy and fluvial sediment particles. ► Isotope fingerprints of Cu and Pb in oysters match legacy contaminated sediments.

Keywords : Environmental forensics, Heavy metal contamination, Metal stable isotopes, Isotope tracers, Isotope source tracing, Isotope fingerprint

Pollution source identification and environmental policy enforcement are difficult or even unfeasible in anthropized coastal environments exposed to anthropogenic trace metals coming from multiple sources (Araújo et al., 2022; Barletta et al., 2019; de Souza Machado et al., 2016). These tasks are particularly challenging in coastal sites impacted by past pollutant activities, where legacy-contaminated sediments can act as non-negligible sources of anthropogenic metal for marine biota and indirectly for humans via diet (Araújo et al., 2018; Couture et al., 2010; Dang et al., 2015; Meng et al., 2020). Discriminating past and present-day anthropogenic contamination is a crucial step when developing emission control, remediation, and policy strategies (Nitzsche et al., 2021; Souto-Oliveira et al., 2019; Weiss et al., 2008). However, traditional approaches using elemental data tend to be limited to this end (Shiel et al., 2013). Such outcomes make the development of new environmental forensic techniques mandatory (Brčeski and Vaseashta, 2021).

Over the last decade, the combination of traditional radiogenic and non-radiogenic stable isotopes of metals has opened new perspectives in environmental forensics (Aggarwal et al., 2008; Pontér et al., 2021). Radiogenic isotope ratios (*e.g.* Pb, Nd) reflect the geological ages of original rock and ore deposits and are not altered in biogeochemical processes (Deng et al., 2021; Dickin, 2018; Ilina et al., 2013). For Pb, in general, anthropogenic sources tend to present less radiogenic isotope compositions, *i.e.* low $^{206}Pb/^{207}Pb$ ratios. Isotope ratios of non-radiogenic systems (*e.g.* Cu, Zn, Cd), in turn, may change due to isotope effects (isotope fractionation) occurring throughout biogeochemical processes that control the distribution of these elements in natural compartments (*e.g.* weathering, Liu et al., 2022; Vance et al., 2016) and in anthropic materials (*e.g.* metallurgy and electroplating, Bigalke et al., 2010; Kavner et al., 2008; Klein and Rose, 2020; Kříbek et al., 2018; Mihaljevič et al., 2019; Šillerová et al., 2017). Since anthropogenic sources typically display specific isotope fingerprints, isotope compositions can help to discriminate anthropogenic from natural origins. In successful cases, isotopes further quantify the relative contributions of different pollutant sources acting in spatial and temporal dimensions (Araújo et al., 2017b; Chen et al., 2009; Thapalia et al., 2015; Xia et al., 2020). Isotope ratios are also advantageous because they enable cross-checking abiotic or biotic samples, allowing the study of contaminant cycling in ecosystems (Araújo et al., 2021c, 2021a). However, obtaining source information with non-radiogenic stable isotopes in biological tissues requires caution due to possible isotope fractionation in biological uptake and homeostatic processes (Araújo et al., 2021b; Caldelas et al., 2011; Jaouen et al., 2016; Mieiro et al., 2011).

Sepetiba Bay is a densely urbanized coastal Brazilian lagoon bordering Rio de Janeiro's metropolitan region (Castelo et al., 2021; de Carvalho Gomes et al., 2009; Molisani et al., 2004; Pinto et al., 2019). It hosts a prominent national industrial park and strategic commercial ports in its watershed, often requiring dredging to permit navigation (Kütter et al., 2021; Trevisan et al., 2020). Metal-enriched wastes from an old Zn electroplating plant disposed directly into local mangroves from the 1960s to the 1990s resulted in contaminated sediments legacies (Barcellos et al., 1997; de Freitas Rebelo et al., 2003; Fonseca et al., 2013; Gonçalves et al., 2020). Although anthropogenic Zn levels have decreased over time, it occurs weakly bound to particles favoring its transfer to local biota such as bivalve mollusks and mangrove trees (Araújo et al., 2017a; Araújo et al., 2018; Monte et al., 2015; Nascimento et al., 2016; Tonhá et al., 2020). Conversely, the mechanisms of remobilization and transfer of Cu and Pb from contaminated sediment legacies to tidal flats and the local biosphere are unclear. Their concentrations are almost homogenous across the bay and the relative influence of external sources *versus* internal sources is not evident (Araújo et al., 2017c). Local mangrove forests naturally attenuate metal contaminant exports into the bay (Lacerda et al., 1988). However, their ongoing fast mangrove suppression processes in Sepetiba Bay over the last thirty years, *c.a.* 1% per year, risks compromising this service and yet, remobilizing these elements from sediment polluted legacies under bioavailable forms (Araújo et al., 2017c).

Sepetiba provides a unique scenario where natural geochemical processes and human-induced disturbances occur antagonistically in the biogeochemical cycling of these two trace metal contaminants. It constitutes, therefore, a natural laboratory to test new forensics isotope techniques. Thus, this study isotope records in sediment and oyster samples to legacy contaminated sediments have been a significant source of Cu and Pb contamination in the past and present for the Sepetiba Bay system.

Sepetiba Bay is a lagoon-estuary of about 519 km^2 with a mean surface area of 427 km^2, and a mean depth of 6 m (Fig. 1, Rodrigues et al., 2012). Granite, gneiss and migmatite Pre-Cambrian rocks compose the local geology and serve as the basement for the Quaternary alluvial sediments (Rodrigues et al., 2012). Seawater moving clockwise through the bay promotes preferential deposition of finer sediment particles in the tidal flat and in mangrove vegetation at the northeastern and southeastern areas of the bay (Fig. 1a, Rodrigues et al., 2012).

The Guandu River catchment is the main fresh water source of Sepetiba Bay and it represents almost 90% of the total freshwater runoff input (Fig. 1a). Since the 1950s, waters from the neighboring Paraíba do Sul watershed (PSW) have been diverted to the Guandu River to supply drinking water for about 10 million inhabitants of the metropolitan region of Rio de

Janeiro and to furnish raw water to industries (Molisani et al., 2006). The PSW hosts several industries, metallurgical activities, and two gas-fired power plants. Previous studies attributed an anthropogenic influence on Pb, Cu, Hg and Zn concentrations in the dissolved, particulate and sediment phases (Azcue et al., 1987; Lacerda et al., 1993; Tonhá et al., 2021)

In the 1960s, a large industrial park began to be implanted, inducing unstructured sprawling urbanization, drastic landscape alterations, sewage release into the environment, and metal contamination by metallurgical activities (Molisani et al., 2004). Between 1960 and 1990, an electroplating plant operated there, accumulating approximately a tailing pile about 600,000 tons directly exposed to the open air (Fig. 1, de Freitas Rebelo et al., 2003). Without suitable management and with continuous rainfall, waste materials and effluents were transported and deposited in the surrounding mangroves and, finally, remobilized into the bay through a small marine channel (Lacerda and Molisani, 2006; Tonhá et al., 2020). The plant was Brazil's third leading Zn producer when it stopped activities in 1998 due to a bankruptcy triggered by environmental lawsuits. In 2012, remediation actions concluded the removal of the pile wastes and effluents from the electroplating plant area.

A total of five sediment cores and thirteen surface sediments were collected to represent the distinct zones of Sepetiba bay (Table 1). The description of sediment sampling and respective stations can be found in the supplementary information. Cação surface sediment was taken to represent the local natural background. It displays Cu and Pb concentrations close to 14 and 24 µg/g (Table 1), which are very close to the geochemical baseline for these elements in Sepetiba bay, estimated in a previous study (Pinto et al., 2019).

All sediment cores were collected using acrylic tubes (6 cm in diameter and 60 cm in length) and sectioned in the field between 1 and 5 cm intervals. Each sub-sample was stored in a polyethylene bag and kept frozen in thermal boxes with ice packs. The “T6” and “G” cores were collected during two campaigns in 2016 and 2017, respectively, while all others were collected in 2014. For this study, the sedimentary layers of T1, T3 and T4 were pooled to obtain a continuous isotope profile (Table 1). For the “T6” and “G” cores, target layers were analyzed yielding a discrete isotope profile (Table 1).

Oyster samples (*Crassostrea brasiliana*) were obtained in 2014 through an transect between the hotspot zone and the western side of Sepetiba bay (Fig. 1b). Oysters were removed from their rocky subtract and kept under 48 h in local water for depuration. Soft tissues were then extracted, rinsed with distillated water, frozen and then lyophilized. Each sample is a composite of about twenty individuals.

Dried and sieved (<63 µm) aliquots of sediments weighting around 200 mg were digested in Teflon® vessels on a coated graphite block using multiple-step acid procedure with 6 ml HF ml, 1ml HCl and 0.5 ml HNO_3 0.5 ml. Aliquots of freeze-dried bivalve tissues (~200 mg) were digested with acid nitric solution (3 ml HNO_3 + 3 ml H_2O) in closed vessels under microwave energy. All reagents and labware acid-cleaning and dilution solutions for elemental and isotope analyses were prepared with 18.2 MΩ cm H_2O (Nanop System) and ultrapure acids (MerckSuprapur® and NORMATOM®).

Elemental concentrations and Pb isotopes were determined in the final extract solutions by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS, iCAP Qc, Thermo Fisher Scientific). Pb isotope ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) were determined using a standard bracketing method with the NIST SRM-981 isotope standard reference material. Another aliquot from the same solution containing 500 ng of Cu was purified through a chromatographic purification and determined for Cu isotopes by multicollector ICP-MS (Neptune, Thermo Scientific) at the Pôle Spectrométrie Océan (PSO) laboratory (Ifremer, France).

Reference materials (RMs) of sediments (MESS-3 and MESS-4 - NRC-CNRC®) and animal tissues (oyster SRM 1566b-NIST®, dogfish liver DOLT 5) and procedural blanks were included in each sample batch for analytical control. The extraction yields for RMs were always within ±10% of certificated values. The Pb precision analysis for unknown samples and RMs corresponded to 0.2% and 0.5% for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$, respectively. Our $^{206}Pb/^{207}Pb$ ratio reproducibility for RM MESS-4 aliquots were of 1.226±0.005 (1s, n=4), which agree with the reported value analyzed with a high-resolution multi-collector mass spectrometer (1.2263±0.0005, 1s, n=4; Jeong et al., 2021, using Neptune, Thermo Scientific). For two aliquots of RM DOLT-5, the obtained $^{206}Pb/^{207}Pb$ Pb isotope ratio average was 1.185±0.004 (1s, n=2). Blanks were lower than 1% of Pb analyte and therefore effects on Pb isotope ratios were negligible.

The precision (2s) mean for Cu isotope analysis was ±0.4‰. The corresponding long-term $\delta^{65}Cu_{SRM\text{-}976}$ average value for MESS-3 was of +0.03±0.10‰ (2s, *n*=9) agreeing with available published data for this RM (−0.12±0.10‰, 2s, n=3, Yang et al., 2020). The $\delta^{65}Cu_{SRM\text{-}976}$ values obtained for the SRM1566b replicates prepared from separate aliquots and treated along the entire procedure (digestion, chromatography, and isotope analysis) is +0.23±0.06‰ (2s, n=13, Araújo et al., 2021b). This value is close to the value of +0.30±0.01‰ (2s, n=4) reported by other laboratory (Jeong et al., 2021).

The contamination factor (Cf) is an index used to determine the contamination status of a given element in sediment (Hakanson, 1980). It is defined as the ratio between the measured content in the sample (C_{sample}) and the background concentration for a given element ($C_{background}$), following the formula (Williams and Antoine, 2020; Zhai et al., 2021):

$$Cf = \frac{C_{sample}}{C_{background}} \quad (eq.1)$$

Low contamination has a CF value ≤ 1, while moderate and considerable contamination ranges from 1 < CF < 3 and 3 < CF < 6 respectively. High contamination is considered with a CF > 6. The Cu (14 µg/g) and Pb (24 µg/g) natural background values of Sepetiba Bay was estimated by (Pinto et al., 2019). The pristine Cação sample (Table 1) have background values and was used to represent it in our study.

The dataset is available in Table 1 and associated data plots are expressed in Fig. 2. The metal contamination hotspot in Sepetiba Bay has high Pb and Cu contamination levels in sediments, far more elevated than other sediments from in the inner bay, and fluvial systems (Fig. 2a). Indeed, legacy contaminated sediments also display the lowest $^{206}Pb/^{207}Pb$ ratios, averaging around 1.14, overlapping with ores from the Pb-Zn Vazante deposit (Fig. 2b). The Vazante silicate Zn ores were the main Zn source used for refining in the electroplating plant of Sepetiba Bay (Araújo et al., 2018; Barone, 1973; Cunha et al., 2009). The corresponding $\delta^{65}Cu_{SRM\text{-}976}$ center around 0.4±0.2‰ (Fig. 2c) and is within the range of metallurgic slags reported elsewhere (Bigalke et al., 2010; Kříbek et al., 2018) (Fig. 3). Two outliers with negative values appear in the "G" core profile (−0.04 and −0.02‰, Table 1). The electroplating byproducts are chemically heterogenous and very different Zn isotope compositions were found in their refractory and labile phases, with the former being enriched in light isotopes (Tonhá et al., 2020). The two outliers correspond to reddish layers found in the profile, probably indicating the dominance of the refractory phases. Overall, the binary isotope plot (Fig. 2d) demonstrates that electroplating activity stamped particular isotope signatures in associated sediment legacies, making them distinguishable from all other zones and useful for Cu source tracking.

The Guandu River surface sediments have relatively low Cu and Pb contamination degrees and contrast with legacies sediments displaying lighter Cu isotope compositions (~0.1‰) and a more extensive Pb isotope range (Fig. 2). The $^{206}Pb/^{206}Pb$ *vs.* $^{208}Pb/^{206}Pb$ plot suggest that Guandu river is predominantly composed of lithogenic sources and clearly distinguish from common Pb anthropogenic sources, such as Pb ingot foundry, road dust, and urban aerosols (Fig. 4). This river covers a large surface, crossing different geological settings and potentially receiving anthropogenic metals from punctual and diffuse sources.

Nevertheless, a previous characterization of the geochemical partition (BCR protocol) of Cu and Pb in the studied samples revealed their prevalence in solid crystal lattices structures, suggesting a dominantly lithogenic origin (Tonhá et al., 2021). Thus, weathering processes and the release of Pb from rocks of different ages are likely to explain the Pb isotope variability (Komárek et al., 2008). At the same time, Cu homogenous isotope compositions result from common isotope fractionation mechanisms involving an uneven partition of heavy and light Cu isotopes between dissolved ligands and binding functional groups on solid surfaces (Little et al., 2018), including clay minerals and amorphous oxyhydroxides of particulate phases (Komárek et al., 2021). The present isotope dataset does not allow a precise explanation for the punctual outlier with negative isotope composition (GD2 sample, Fig. 2c), but it seems unrelated to an anthropogenic influence.

In the urban channel, the Pb isotope compositions of sediments gradually increase toward Sepetiba bay. The two upstream samples display anthropogenic Pb signatures ($^{206}Pb/^{207}Pb$: ~1.13; Fig. 2a, b), despite their low Pb concentrations. The third sample downstream fell in the range of the tidal flat, evidencing a mixing process between continental and marine Pb during tidal cycles. Analogous mixing for Zn has been noticed with Zn isotopes (Araújo et al., 2017b). The upstream samples have an anthropogenic component related to the disposal of untreated domestic wastewater. The voluminous organic matter inputs associated with these releases probably dilute Cu and Pb contents and could explain the observed low concentrations for these elements. The isotope analysis of the Guandu River and one of the urban channels of Sepetiba demonstrate that fluvial inputs of sedimentary materials contribute with a particulate Cu material relatively light, close to the isotope baseline of other marine coastal systems, between 0–0.2‰.

Metal-enriched particles remobilized from the hotspot to the inner bay affect less significantly the northern bay (Silva-Filho et al., 2011), close to Coroa Grande (Fig. 1d) Then, sediments located there should be geochemically closer to the natural baseline. Coherently, the sediment profile collected there (T6) displays mostly low Cu and Pb contamination factors (Table 1), while Pb isotope signatures are homogenous, around 1.9, being the most radiogenic (and probably natural) among sediments collected in the inner bay. The T6 sediments show more positive $^{208}Pb/^{206}Pb$ ratios differing from the Guandu river and falling close to sediments from the western marine sector of Sepetiba Bay (Fig. 1b). The enrichment in the ^{208}Pb isotope in these areas is possibly associated with local pre-Cambrian granite relatively enriched in Th, which can decay forming ^{208}Pb. These isotope patterns suggest, therefore, influences of a natural Pb.

Differently, tidal sediments bordering the northeastern shore are more susceptible to the deposition of particles carrying metal contaminants from the hotspot zone, and also from fluvial discharges (Araújo et al., 2017b; Pellegatti et al., 2001; Wasserman et al., 2001). The Pb isotope signals of the tidal flat stamped at the midpoint of urban rivers, legacy sediments (hotspot), and Guandu river prove that they are affected by mixing processes between natural and anthropogenic sources (Fig. 2b). Furthermore, the $^{206}Pb/^{207}Pb$ signature of the northern bay and tidal flat samples are also comparable to signatures from Guanabara Bay (1.15 to 1.17; Geraldes et al., 2006), a region highly contaminated by multiple anthropogenic sources, including metallurgy and sewage.

Clockwise hydrodynamic current patterns spread legacy sediment particles and fluvial sediments along tidal flats, mixing sedimentary materials from different origins, and with varying metal contamination levels, and geochemical compositions. This mixing process explains the moderate contamination levels and a very homogenous isotope range intermediate between the hotspot and northeastern bay. As noted in Fig. 2d, Pb and Cu isotope compositions for tidal flat sediments are uniforms, around 1.18 and 0.3‰, respectively. A qualitative analysis of isotope tendencies indicates undoubtedly that legacy sediments from electroplating activity contribute to Cu and Pb inputs in the tidal flat of Sepetiba Bay.

An outlier observed in the dispersion plot (Fig. 2a, gray square) corresponds to the basal layer of the T3 core profile. It displays Pb concentrations tenfold higher than upper profile data and contrasting Pb and Cu isotope ratios of 1.14 and 0.13‰ (Table 1), which suggests a different metal pollution origin. This profile depth would correspond to the 50's, therefore before the begin of the electroplating activity. Previous studies observed similar Pb isotope markers for this period and associated them with channel and dam building and the beginning of industrial activities.

Oyster Pb concentrations decrease with the distance of the hotspot zone, accompanied by slight increases on $^{206}Pb/^{207}Pb$ ratios (Table 2). Dissimilar Pb uptake efficiencies from various sources by organisms can lead to different Pb isotopic compositions (Ip et al., 2005). Pb isotopes are relatively robust in regard of metallurgical processes because they do not fractionate at high temperatures, and are physically and geologically coherent (Albarede et al., 2020). Pb showed analogous isotopic ratios despite the difference in concentration, which is consistent with previous findings (Shiel et al., 2012). Pb isotopic signal can demonstrate the large contribution from anthropogenic origins in spite of their low concentration, and their Pb isotopic composition in bivalves accounted for the mixing of modern anthropogenic Pb emissions with natural endmembers (Shiel et al., 2012). In this study, Pb isotopes in oysters

overlap partially with tidal flat sediments (Fig. 2d), suggesting that these organisms accumulate a mixing of Pb from different natural and anthropic sources from the bay.

The respective $\delta^{65}Cu_{SRM\text{-}976}$ values do not correlate with Cu concentrations or trends with geographical distance to the hotspot zone, and unexpectedly, the lowest Cu concentrations, about 17 µg/g, occur in those presumed to be more exposed to legacy sediment particles ("S1" sampling station, Table 1). The positive Cu isotope compositions of oysters match well with the legacy sediments (Fig. 2d), indicating them as the primary Cu source for bioaccumulation, at least for the two more internal sampling stations, "S1" and "M1", respectively. In general, anthropogenic metals weakly bound to particles ingested by bivalves can be desorbed by enzymes and non-enzymatic ligands in the gastrointestinal tract (Birch and Hogg, 2011; Griscom and Fisher, 2004; Snape et al., 2004). Thus, isotope systematic in oysters seems results from the preferential bioaccumulation of anthropogenic Cu related to prompt desorption during digestion. Free Cu^{2+} ion is the most bioavailable species and identifying their isotopic fractionation processes is important to understand the uptake mechanisms by organisms using Cu isotopes (Ryan et al., 2014). Isotope compositions of Cu and Zn recorded in oysters' soft tissues seem conservative, not being altered by isotope fractionation during homeostasis processes. Therefore, biomonitoring anthropogenic Cu tendencies in Sepetiba using this isotope information in these organisms is feasible and desirable to further environmental management.

This work showed that isotope records of Cu and Pb in sediments help identify the dispersion of anthropogenic Cu and Pb from electroplating wastes across Sepetiba Bay. The Cu and Pb isotopic signatures of legacy sediments allow distinguishing particle issues from natural marine and terrigenous materials. While concentrations can be homogenous between different zones of coastal environments, isotope ratios vary geographically and consistently with source balance between natural and anthropogenic sources. Indeed, isotopic compositions of oysters indicate that legacy sediments continue to contribute as vectors to transfer metals into biota. The application of non-traditional isotope systems, like Cu, to track Cu sources in marine environments is promising but still in its infancy. Subsequent studies are expected to improve anthropogenic source traceability and understand internal isotopic fractionation via organotropism and its relation with toxic effects in marine organisms.

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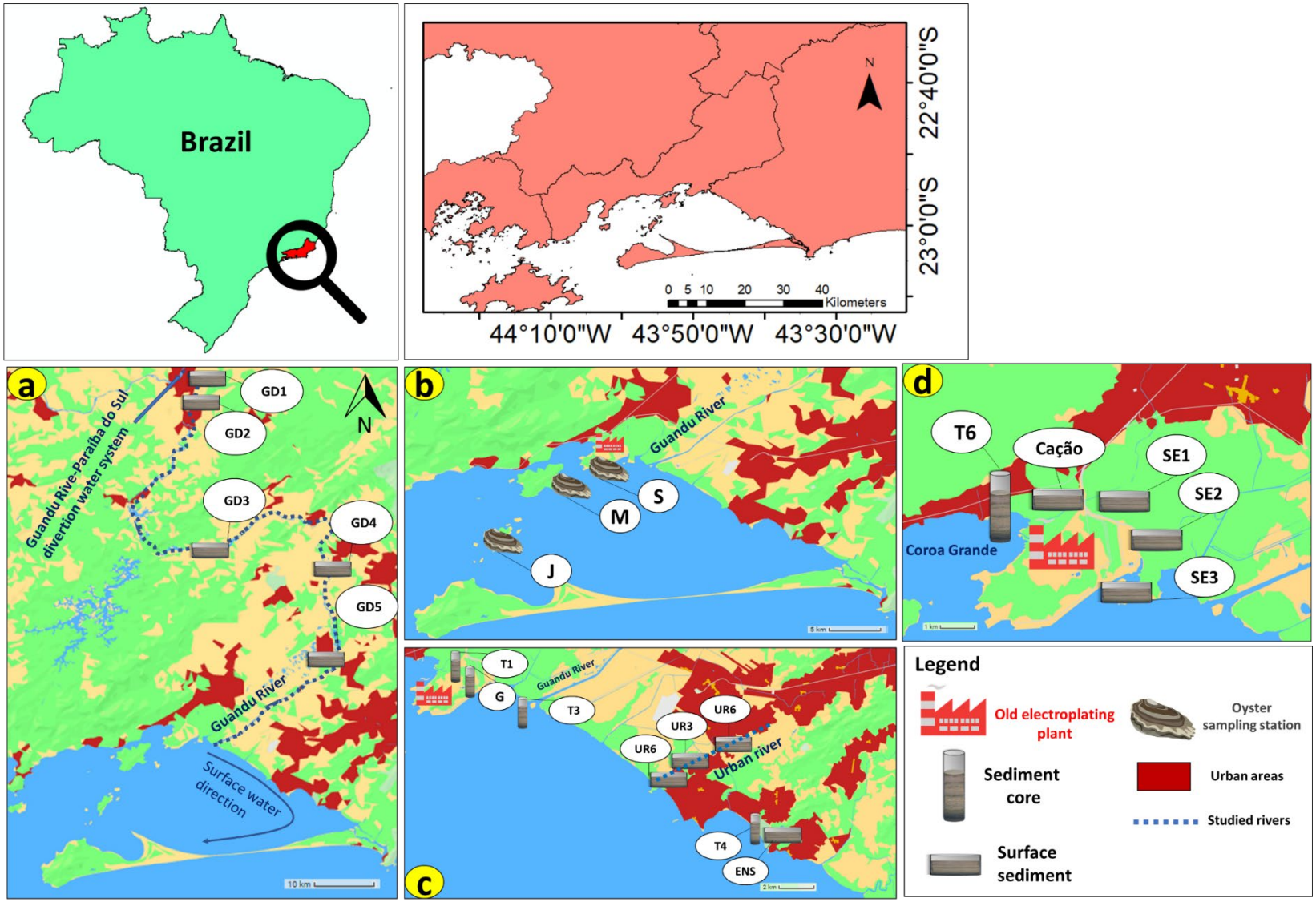

Fig. 1. Site location and Sediment and oyster sampling in the Sepetiba Bay. Surface sediments were collected in: GD (Guandu river-a), UR (urban channel-c) and SE (Saco do Engenho-d) stations. Sediment cores ("T" and "G") were sampled in the tidal flat (c), except T1, collected also in the hot spot zone (SE-Saco do Engenho, d). Sampling stations descriptions are available in the supplementary material.

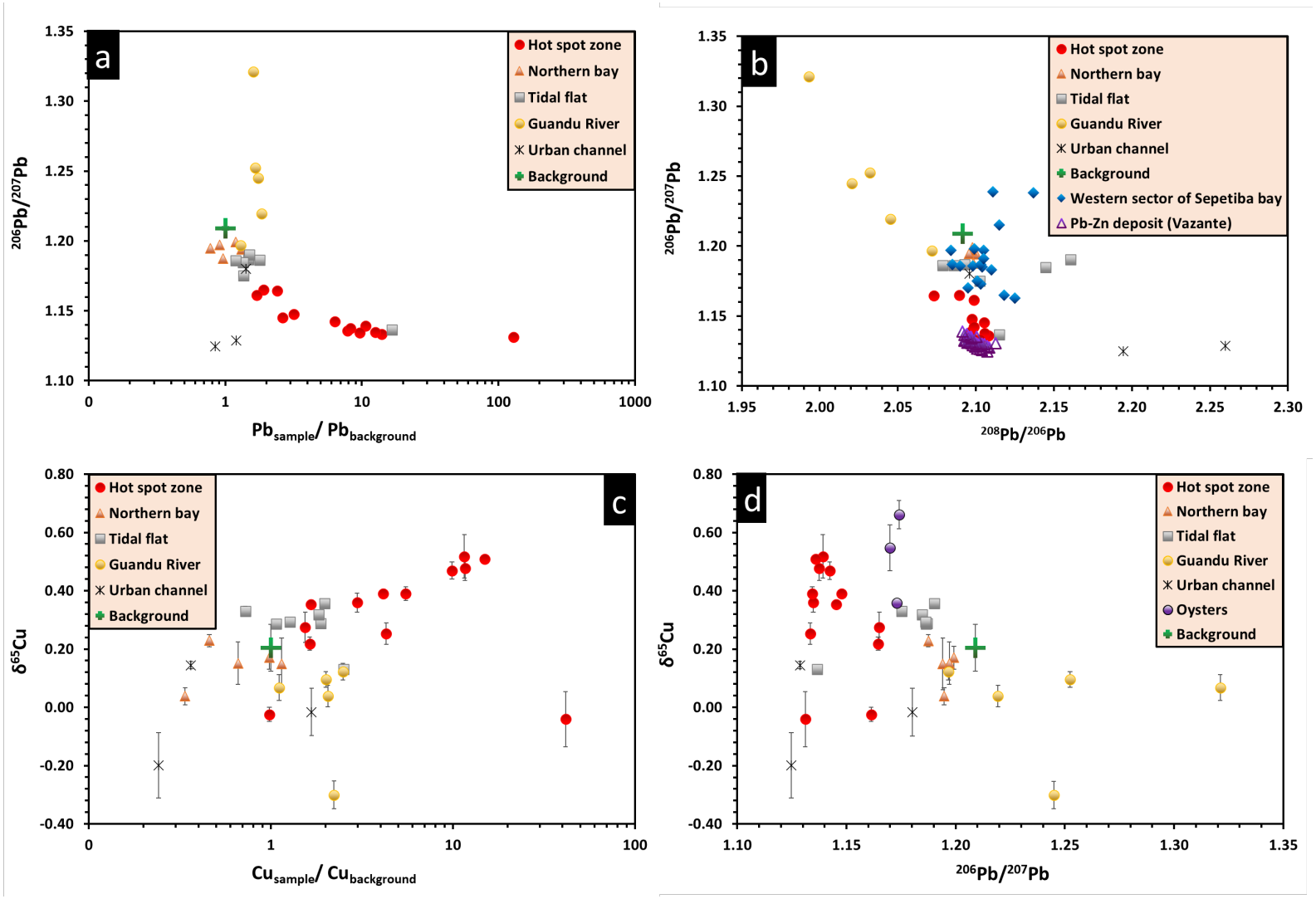

Fig. 2. Plots of elemental and isotope data of sediments. Error bars for Pb isotope ratios are smaller than plot dots. Background refers to the local natural background represented by the sample "Cação" (Table 1). In 2b quadrant: Pb-Zn Vazante deposit from Cunha et al., 2007; Western sector of Sepetiba Bay from Morales et al., 2019.

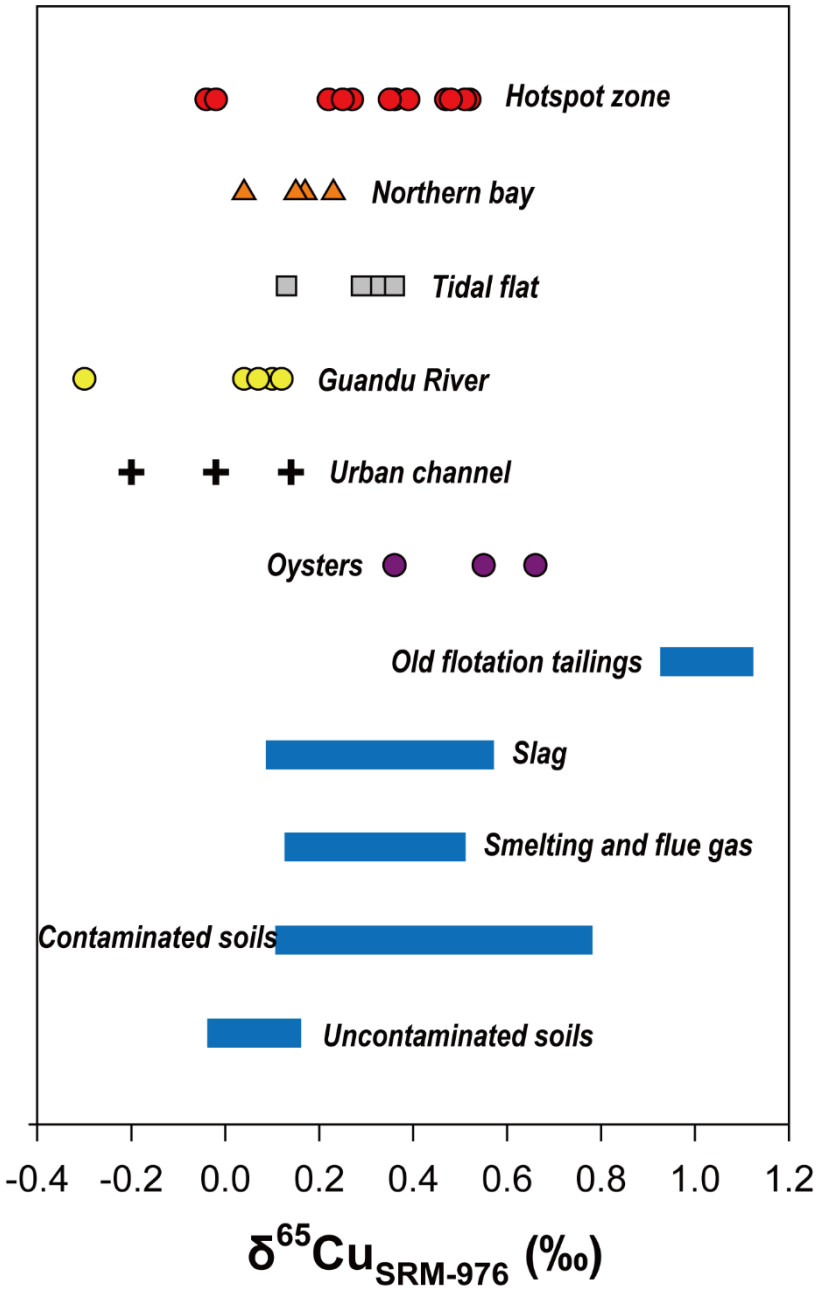

Fig. 3. The $\delta^{65}Cu_{SRM-976}$ values in sediments (hotspot zone, Northern bay, tidal flat, Guandu River, urban channel) and oyster samples of this study and in various environmental samples (old flotation tailings, slag, particles from smelting and fuel gas cleaning processes, contaminated and uncontaminated soils) from Kříbek et al., 2018.

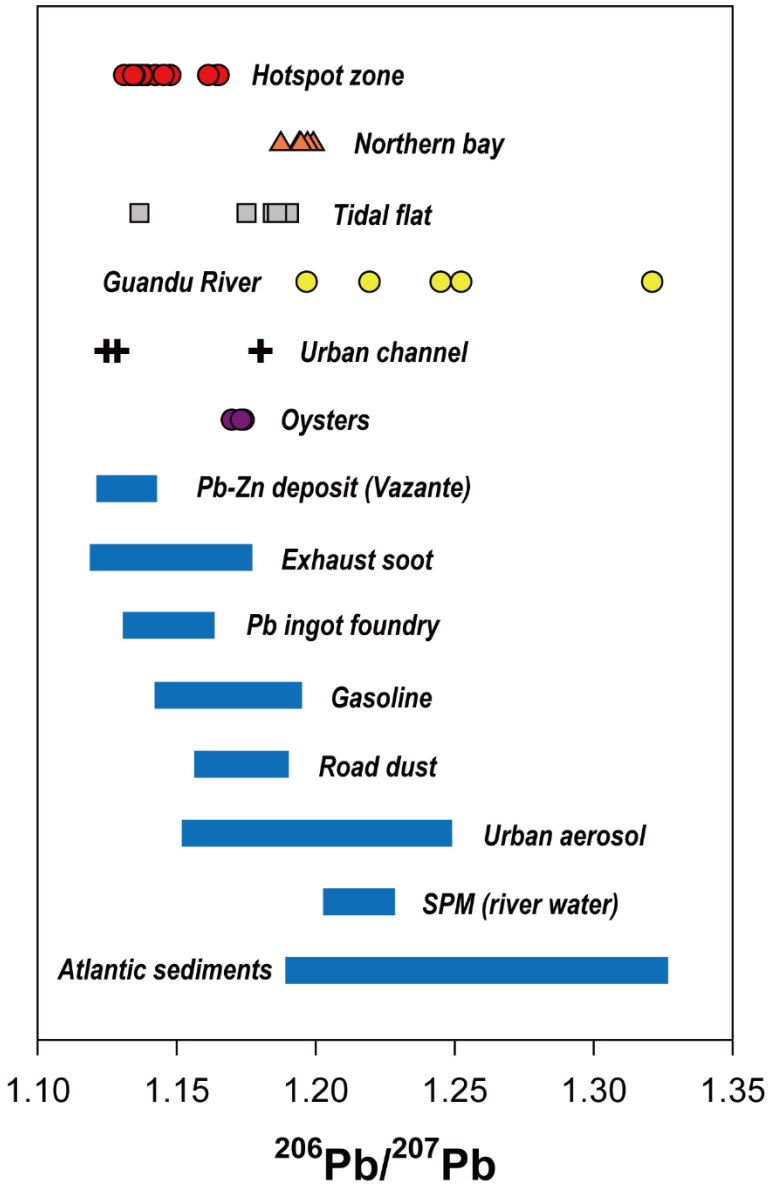

Fig. 4. The $^{206}Pb/^{207}Pb$ values in sediments (hotspot zone, Northern bay, tidal flat, Guandu River, urban channel) and oyster samples of this study and in various environmental samples (Pb-Zn deposit from Cunha et al., 2007; exhaust soot from Aily, 2001; Pb ingot foundry from Aily, 2001; gasoline from Aily, 2001; road dust from Souto-Oliveira et al., 2018; urban aerosol from Souto-Oliveira et al., 2018; particulate matter (PM) of river water from Mulholland et al., 2022; Atlantic sediment from Sun et al., 1980).

Table 1. Pb and Cu isotope composition, concentration (μg/g) and contamination factor (Cf) of sediments. Sediment cores labelled as "T", "G" and "ENS" have sample depth profile indicated.

	Sample	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	$\delta^{65}Cu$ (‰)	2s	Pb	Cf(Pb)	Cu	Cf(Cu)
Natural background	Cação	1.209	2.092	0.20	0.08	24	1	14	1
Hotspot zone	SE1	1.139	2.097	0.52	0.07	257	11	167	12
	SE2	1.165	2.073	0.22	0.02	58	2.4	24	1.6
	SE3	1.165	2.089	0.27	0.05	46	1.9	22	1.5
	T1 0_20 cm	1.148	2.097	0.39	0.01	77	3.2	60	4.1
	T1 20_40 cm	1.142	2.099	0.47	0.03	153	6	142	10
	T1 40_65 cm	1.136	2.108	0.51	0.01	190	8	215	15
	T1 65_85 cm	1.138	2.106	0.48	0.04	200	8	168	12
	G 4_6 cm	1.133	2.103	0.25	0.04	337	14	62	4.3
	G 29_31 cm	1.131	2.098	−0.04	0.09	3113	129	599	42
	G 34_36 cm	1.135	2.095	0.36	0.03	304	13	43	3.0
	G 69_71 cm	1.134	2.098	0.39	0.02	234	10	79	5.5
	G 104_106 cm	1.145	2.105	0.35	0.01	64	2.6	24	1.7
	G 114_116 cm	1.161	2.099	−0.02	0.02	41	1.7	14	1.0
Northern bay	T6 0_7 cm	1.194	2.100	0.15	0.09	32	1.3	16	1.1
	T6 7_13 cm	1.199	2.098	0.17	0.04	29	1.2	14	1.0
	T6 13_19 cm	1.197	2.098	0.15	0.07	22	0.9	10	0.7
	T6 19_31 cm	1.187	2.099	0.23	0.02	23	1.0	7	0.5
	T6 31_33 cm	1.195	2.096	0.04	0.03	19	0.8	5	0.3
Tidal flat	T3 0_15 cm	1.186	2.079	0.29	0.00	43	1.8	15	1.1
	T3 15_35 cm	1.175	2.103	0.33	0.02	33	1.4	10	0.7
	T3 35_45 cm	1.137	2.115	0.13	0.01	403	17	36	2.5
	ENS 0_15 cm	1.187	2.093	0.29	0.02	36	1.5	27	1.9
	ENS 15_25 cm	1.190	2.161	0.36	0.01	36	1.5	28	2.0
	ENS 25_35 cm	1.185	2.145	0.32	0.01	33	1.4	26	1.8
	ENS surface	1.186	2.086	0.29	0.00	29	1.2	18	1.3
Guandu River	GD1	1.252	2.032	0.10	0.03	40	1.7	29	2.0
	GD2	1.245	2.021	−0.30	0.05	42	1.7	32	2.2
	GD3	1.197	2.072	0.12	0.03	31	1.3	36	2.5
	GD4	1.219	2.045	0.04	0.04	45	1.8	30	2.1
	GD5	1.321	1.993	0.07	0.04	39	1.6	16	1.1
Urban channel	UR1	1.129	2.260	0.14	0.01	29	1.2	5	0.4
	UR3	1.125	2.194	−0.20	0.11	20	0.8	3	0.2
	UR6	1.180	2.096	−0.02	0.08	34	1.4	24	1.7

Table 2. Isotope compositions and concentrations (µg/g) of Cu and Pb in oysters (*Crassostrea brasiliana*).

Sampling station	Species	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	$\delta^{65}Cu$ (‰)	2s	Pb	Cu	References
S	*Crassostrea brasiliana*	1.1699	2.0748	0.55	0.08	0.71	16.6	This study
M	*Crassostrea brasiliana*	1.1741	2.0894	0.66	0.05	0.39	32.3	This study
J	*Crassostrea brasiliana*	1.1731	2.0976	0.36	0.00	0.32	20.9	This study
France (Atlantic Ocean)	*Crassostrea gigas*			0.38	0.10		132	Araújo et al., 2021b
Canada (North Pacific Ocean)	*Crassostrea gigas*	1.1616	2.0929			0.12		Shiel et al., 2012
USA (Atlantic Ocean)	*Crassostrea virginica*	1.1995	2.0551			0.48		Shiel et al., 2012
France (English channel)	*Crassostrea gigas*	1.1753	2.0866			0.90		Shiel et al., 2013
France (Atlantic Ocean)	*Crassostrea gigas*	1.1775	2.0941			2.7		Shiel et al., 2013