

METAL RECORD OF Cu-BASED ANTIFOULING PAINTS IN SEDIMENT CORE FOLLOWING MARINA CONSTRUCTION AND OPERATION

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HIGHLIGHTS

- Sediment provenance changed following the marina construction.
- REEs coupled with Pb isotopes indicate disruption in sedimentary dynamics.
- Cu and Zn contamination from antifouling paints begins post marina operation.
- Cu enrichment in sediment is 15 times the local natural background.

ABSTRACT

Marinas are central hubs of global maritime leisure and transport, yet their operations can deteriorate the environmental quality of sediments. In response, this study investigated the metal contamination history associated with antifouling paint uses in a sediment core collected from Bracuhy marina (Southeast Brazil). Analysis target major and trace elements (Cu, Zn, Pb, Cd and Sn), rare earth elements (REEs), and Pb isotopes. The modification in Pb isotopic ratios and REEs pattern unequivocally revealed sediment provenance disruption following the marina construction. Metal distribution in the sediment core demonstrates that concentrations of Cu and Zn increased by up to 15 and 5 times, respectively, compared to the local background. This severe Cu and Zn contamination coincides with the onset of marina operations and can be attributed to the use of antifouling paints.

Key Words: Antifouling paints, sediment contamination, Pb isotopes, marine geochemistry

1 INTRODUCTION

Marinas bring numerous positive economic benefits to coastal and lakeside regions, including increased tourism revenue, job creation, support for small businesses, tax contributions, and opportunities for marine trades (Cruz Perez et al., 2021). Despite the socioeconomic benefits, the implementation and operation of marinas can degrade coastal ecosystems, altering sediment dynamics and introducing chemical contaminants derived from petroleum, antifouling paints, and sacrificial anodes used in vessels and marine constructions, in addition to dredging and wastewater discharges (Bird et al., 1996; Turner et al., 2008 and 2010; Guerra-García et al., 2021 and references within).

Specifically, the widespread use of antifouling paints containing toxic (Pb) or potentially toxic metals (Cu and Zn) as coatings on vessels has resulted in high levels of contamination of the water and sediments (Jones and Turner, 2010, Cassi et al., 2008; Burgin and Hardiman et al., 2011; Briant et al., 2013 and 2022; Ibabe et al., 2020; Hobbs et al., 2022; Jeong et al., 2023a). Lead-based paints were used in the past and replaced by arsenic, mercury, copper, and tributyltin (Gipperth et al., 2009). Today, Cu is currently the primary biocide used worldwide in antifouling systems and is commonly used as a booster biocide in zinc oxides and other chemical compounds like Diuron, Irgarol 1051, for example (Almeida et al., 2007; Amara et al., 2017)

Cu and Zn contamination in marinas has been recently reported worldwide (Guerra-García et al., 2021). Unfortunately, dimensioning metal contributions from antifouling paints remain elusive as its dispersion can be confused with several anthropogenic sources like industrial and urban wastes. This makes it difficult to differentiate multiple anthropogenic and natural metal sources and/or to determine if relatively low metal concentrations represent natural baseline levels. The assessments of sources and fates of metal contaminants are critical to support management strategies, either for remediation or to maintain emissions at sustainable levels (Richir et al., 2021). In the last decade, many endeavors have been addressed worldwide in implementing environmental regulatory policies for reducing the impacts of antifouling paints in the marine

environment (Ytreberg et al., 2021a; 2021b). It may pass by more accurate metal source quantification and ecological risk assessment associated with metals inputs in sediment. In Europe and Asia, it became the object of environmental contamination studies (Cassi et al., 2008; Burgin and Hardiman et al., 2011; Briant et al., 2013, 2022; Ibabe et al., 2020; Hobbs et al., 2022; Jeong et al., 2023a), but up to now, few studies most studies conducted in harbors and marinas in South America relies only on tributyltin (TBT).

The Bracuhy Marina in southeast Brazil began its operations in the 1970s in a tourist zone in Rio de Janeiro State. This Marina was artificially constructed to provide a safe mooring place for boats, characterized by low hydrodynamic energy, with minimal water circulation and renewal. This environment favors the retention of fine sediments rich in clay minerals and organic matter, thus promoting anoxic conditions in surface sediment that facilitate the trapping of trace metals by forming insoluble sulfide salts (Briant et al., 2022; Araújo et al., 2017b; Guerra-García et al., 2021; Huerta-Diaz and Morse, 1992). The marina was responsible for the safekeeping of approximately 500 vessels (Personal communication from the marina manager) in 2020, has never been dredged since its construction and does not face significant sources of pollution, such as sewage, urban waste, or industrial discharges. Therefore, it constitutes a natural laboratory to investigate the contamination dynamics related exclusively to the use of antifouling paints.

This study aims to reconstruct the trace metal contamination within the Bracuhy Marina and elucidate changes in sedimentary processes induced by marina operations over the past 40 years. To achieve this goal, the study focuses on geochemical, lead isotopic, and mineralogical analyses of a sediment core with a well-preserved geochemical profile covering the pre-construction period from 1978 until now. Additional samples, of soils and surface sediments were taken to represent the local terrestrial sources.

The findings of this research are expected to contribute substantially to the ongoing discussion regarding the release of metals from antifouling paints. Additionally, it aims to shed light on the broader implications of marina construction and operation on coastal ecosystems.

2 MATERIAL AND METHODS

2.1 Study site context

The Marina Bracuhy is situated in Bracuhy Cove, in the northeastern part of Ilha Grande Bay (see Fig. 1) and falls under the jurisdiction of the municipality of Angra dos Reis, in South Rio de Janeiro State. The area has well-preserved mangroves and restinga and boasting a diverse range of marine ecosystems (Creed et al., 2007). The climate of the region is classified as humid tropical, with temperatures ranging between 18 and 23°C and an average rainfall of 2,000 to 2,600 mm (Bidone et al., 1991; Cardoso et al., 2001). The Bracuhy River is the primary river flowing into Bracuhy Cove, and its drainage basin includes the Atlantic rainforest plateau (Mahiques, 1987; Bidone et al., 1991; Cardoso et al., 2001). During the construction of the Marina Bracuhy, a portion of the Bracuhy River's mouth was diverted, and the old river delta was excavated.

2.2 Sampling and sampling preparation

Samples from the sediment core, regional rocks, soils and fluvial sediments samples were collected along two sampling campaigns in 2020 and 2021.

Soil samples up to a depth of 20 cm were collected using a plastic shovel. After collection, they were air-dried, homogenized, and passed through a 2 mm sieve. Surface sediment samples were collected from the main river, estuary, surrounding mangroves, and the Bracuhy marina at a depth of 0-5 cm using a plastic shovel. These samples were then preserved in a refrigerator at 4°C until further preparation in the laboratory.

A scuba diver was used to access the inner Bracuhy's marina and retrieve a sediment core using a polycarbonate tube. The Bracuhy's marina core (hereafter labeled "Core") had a depth of 80 cm and was sliced every 2 cm. These slices were placed in plastic bags and stored at 4°C in the refrigerator before analysis. Core sub-samples and surface sediments were air-dried, crushed using an agate mortar, and sieved to obtain a fraction smaller than 63 µm which was used for elemental and isotopic analysis.

2.3 Sample preparation and elemental analysis

The total digestion and evaporation steps were carried out at Geoscience Institute (UnB) in a 1000-class clean room. Digestion was performed using double-distilled ultrapure acids (Merck, Germany) at sub-boiling temperatures in Teflon stills. Dilution was performed using high-purity water (N18.2 M Ω) produced by a Milli-Q (Nanop System®).

Aliquots of about 100 mg of powdered rocks, soils, sediments, and antifouling paints were digested in a Savillex® Teflon beaker on a hot plate using a multiple-step acid procedure with HF, HCl and HNO₃ (Tonhá et al., 2020). After total sample digestion, aliquots were taken for elemental and isotopes analysis. Major elements (Al, Ca, Fe, P, Ti, Mn) were analyzed using ICP-OES (5100, Agilent, USA) at Geoscience Institute (UnB) and trace elements (REEs, Th, Cu, Zn, Pb, Cd and Sn) using ICP-MS (iCAP Q-Thermo Scientific, USA) at OSU OREME, University of Montpellier.

The certified reference materials (CRMs) BCR-701 and Estuarine sediment 1646a and procedural blanks were included in every batch sample to assess the recovery of total concentration digestion (see Supplementary material) and accuracy of the analysis. The relative error between the measured elemental concentrations and the certified reference values was within 10%.

2.4 Pb isotopic analysis

Aliquots from the final digestion solution of sediment, rocks, soils, and antifouling paints were taken for Pb isotope analysis. This solution was purified using the ion-exchange chromatographic technique following the protocol of Babinski et al. (1999). Briefly, it consists of two steps which include a Bio-Rad® column packed with AG1- X8 200-400 mesh resin. The resin was conditioned in 0.7M HBr, the matrix was loaded and the resin was washed 3 times with 0.5 mL of 0.7M HBr. Pb was eluted using 1 mL 6M HCl and brought to dryness. The solution was redissolved in 0.7M HBr and the purification process was repeated. The final Pb purified solution was dried with one drop of H₃PO₄ on a hot plate. The purified Pb samples were then loaded onto a single Re filament with silica gel and measured by TIMS (Thermo Finnigan, Triton) at the Center of Geochronological Research (CPGeo) at São Paulo University. Lead isotopic compositions were

corrected for mass fractionation of 0.12 ‰ a.m.u⁻¹ based on repeated measurements of the NBS-981 in each analytical session during this study. Procedural blanks were 51 pg and had a negligible effect on the Pb isotope ratios of the measured samples.

Mineralogy Characterization

The mineralogical assemblage of the bulk sediments of sediment was determined by X-Ray diffraction (XRD) (Rigaku®, Ultima IV diffractometer) using Ni-filtered Cu-K α ($\lambda=1,5406 \text{ \AA}$) radiation and a graphite monochromator. The XRD patterns were recorded from 2θ values of 2–80° for the total, and clay minerals analysis, with a scanning speed of 2°/min. The XRD patterns interpretation was performed using the software Jade®.

2.5 Enrichment Factor and Statistical Analysis

The Enrichment Factor (EF) of trace elements was used to assess the degree of anthropogenic influences, adopting the combined physical (sieving) and geochemical (ratio to a conservative element) normalization approach (Kersten and Smedes, 2002; Le Cloarec et al., 2011):

$$EF = ([M]/[Th])_{\text{sample}} / ([M]/[Th])_{\text{background}}$$

Here, [M] represents the element of interest, and [Th] represents the reference element. The $([M]/[Th])_{\text{background}}$ value is estimated based on local values of Bracuhy watershed's pristine areas (see details in section 2.6). Thorium was selected as the reference element due to his conservative behavior during chemical weathering process, low solubility in the water and its association with finest particles and lithogenic sources (Sakaguchi et al., 2006). In addition, Th does not have any significant anthropogenic source in the region.

To identify potential associations among Fe, Al, Ti, Mn, P, Ca, Cu, Zn, Cd, Pb, Sn, Th, and REEs (Rare Earth Elements), a Principal Component Analysis (PCA) was conducted. Statistical analyses were performed using Statsoft software (Statistica, release 8.0). The PCA was carried out with Varimax rotation and retention of principal components whose eigenvalues were greater than unity (Tonhá et al., 2021).

2.6 Establishing local background concentrations.

The samples from the Bracuhy marina watershed's area was taken as representative of the local natural background as representative of the local natural background. This analysis aimed to estimate local background concentrations of metals and calculate the enrichment factor (as per Birch et al., 2017 and associated references). The locally estimated background concentrations, derived from mean values of bedrock samples (n=3), river sediments (n=3), and surface soil (n=4), are as follows: 35.2 (Th); 15.5 (Cu); 133 (Zn), 40.7 (Pb); 0.27(Cd); and 9.9 (Sn) mg kg⁻¹.

3 RESULTS AND DISCUSSION

The elemental and Pb isotopic data are summarized in Table 1S, 2S and 3S.

3.1 The physical textural and geochemical profiles of the Marina Bracuhy sediment (Core)

The sediment Core consists mainly of siliciclastic sediments without any faunal material (gastropod and bivalve shells or polychaeta tubes). The marina Bracuhy sediments are mainly composed of quartz, micas (biotite, muscovite), feldspars (anorthite, albite, orthoclase), clinocllore, stilpnomelane, sillimanite, kaolinite and gibbsite (Figure S1).

The textural profile illustrates an upper section (0 to 58 cm) characterized by layered dark clay shades, transitioning to a lighter gray, sandier bottom section (~60 to 85 cm). These two sections are demarcated by a fine transitional layer marked by interstratified clay minerals. Overall, the identified textural sedimentary sections reveal contrasting geochemical composition of sediment particles, expressed in terms of major elements (Fig. 2). The upper section of the Core shows an increase in Al content alongside a decrease in Ca, Ti, Mn and Th (Fig. 2). The higher concentration of Al in the upper section is attributed to the greater presence of aluminosilicates in finer particles. Similarly, the trace metal profiles also exhibit an abrupt shift from lower to higher concentrations when moving from the deeper to the upper sections.

The Marina sediment core has two distinct REEs patterns normalized to the Post Archean Australian Shale (PAAS) (Fig. 3a). The bottom section is enriched in LREEs over HREEs compared to PAAS. In contrast, sediment samples from the Marina operation period are similar to PAAS values. The watershed samples follow the same pattern as the bottom Core (Fig. 3b). The LREE/HREE ratio varies from lower ratios ($L/H < 63$), from 0.5 cm to 58 cm, and to a higher ratio ($L/H > 100$) in downward profile section identified as the pre-construction marina sediment, depth from 60 cm to 83 cm, and watershed bedrocks and Bracuhy river sediment.

As we will elucidate in further discussion, synchronous alterations in geochemical patterns and physical textural features observed between the upper and bottom sections of Core strongly indicate two distinct temporal periods. The first one, is attributed to the Marina pre-construction, and is characterized by the presence of both coarse and fine sediment and larger content of quartz, which is typical of estuary conditions. The second period section, described as the Marina operation period, is marked by the sedimentation of fine particles through decantation with a higher content of muscovite, kaolinite and gibbsite, which could have been resulted from man-induced reworking of terrigenous materials during marina construction.

3.2 Tracking sediment particle provenance

The La/Yb and Yb/Sm ratios are classical sediment provenance tracers (Fig. 4). In the Bracuhy system, they allow inferring the relative contributions between terrigenous and marine sources in sediment samples. To identify local terrigenous endmembers, we used the mean value obtained from rock, soil and river sediment. We also assess sediment from Ribeira Bay recorded in previous work of Gomes et al. (2019), which was retrieved in Bracuhy cove towards the open water. The bottom section of the core (60.5 to 83 cm), representing the pre-construction period, shows La/Yb and Yb/Sm ratios larger than 4 and lower than 0.3, respectively, which are similar to the river sediment, soil, and bedrock. On the other hand, the upper section of the core (0.5 cm to 58 cm), which corresponds to the marina operation period, displays La/Yb and Yb/Sm ratios lower than 3 and larger than 0.4, respectively, similar to those found in adjacent bays sediments, such as Ribeira bay. The sediment sources were local and

terrigenous during the pre-construction period, while fine sediment deposited during the marina operation period is likely marine sourced.

3.3 Trace metal and Enrichment Factors (EFs) profiles

The concentration of Pb and Sn show similar behavior in the two sections of the Core B (pre-marina and marina operating), with values of 34.5 ± 7.9 and 30.0 ± 2.2 mg kg⁻¹, respectively, for the pre-construction period, and 9.0 ± 5.3 and 7.0 ± 0.7 mg kg⁻¹, respectively, for the operation period of the marina. On the other hand, Cd concentrations are higher during the pre-construction period compared to the marina operation period, with values of 0.28 ± 0.05 and 0.11 ± 0.04 mg kg⁻¹, respectively. In contrast, during the marina operation period sediments contain higher concentrations of Cu and Zn compared to the pre-construction period, with values of 75 ± 8.8 and 144 ± 9.6 mg kg⁻¹, respectively, versus 18.5 ± 5.2 and 79 ± 8.7 mg kg⁻¹. Finally, the sediments between 60 and 58 cm, corresponding to the transition period, presents a high Cd concentration, reaching 0.80 mg kg⁻¹.

The calculated enrichment factors for all trace metals (Cu, Zn, Pb, Cd and Sn) studied in this work show an enhancement after the period of the marina construction (Fig. 4) at a depth 60 cm. Except for Cd, which had its peak of enrichment in the middle of the profile (41 cm), all trace metals showed an enrichment peak on the surface of the core (around 4 cm). The relationship between concentration and enrichment (Fig. 4) presented a notable correlation only for Cu, Zn and Cd. The Core sediments presented minor enrichment for Cd, Sn and Pb (EF < 4), moderate enrichment for Zn (EF > 4) and major Cu enrichment (EF up to 15). Comparing the metal concentrations and enrichment levels of the Core sediments with those obtained from previous studies conducted on Ilha Grande Bay (Bidone et al., 1991; Cardoso et al., 2001; Freret-Meurer et al., 2010; Chiappetta et al., 2016; Souza et al., 2021), we demonstrate that the metal concentrations obtained in the marina are higher, particularly for Cu, and to a lesser extent, Zn.

3.4 Lead isotopes

The local geogenic Pb isotopic signatures, obtained through rock analysis, exhibit a range of 1.190 to 1.233 for the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and 2.012 to 2.072 for the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio. These values fell within the range of the Upper Continental Crust (UCC) samples (1.19 to 1.21; Millot et al., 2004). Analysis of three commonly used antifouling paint brands in Brazil reveals remarkably $^{206}\text{Pb}/^{207}\text{Pb}$ ratios ranging from 1.187 to 1.192 (average of 1.189 ± 0.002), close to those reported for antifouling paints used in Korea (1.18 to 1.19; Jeong et al., 2023a).

The sediment core from Bracuhy Marina displays $^{206}\text{Pb}/^{207}\text{Pb}$ ratios ranging between 1.210 and 1.565 and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios from 1.995 to 2.040, with very radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (1.281 to 1.565) at the core's base. These findings suggest the presence of at least two geogenic endmembers within the marina sediments. Analysis of the sediment core highlights two distinct groups of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios: a more radiogenic group represented by the core's base (60 to 83 cm) and a less radiogenic group obtained on samples collected from 59 cm to the surface. From the inception of marina operations (59 cm) up to the present day, both Pb content and isotopic signatures have remained consistent (30 mg/kg and $^{206}\text{Pb}/^{207}\text{Pb} = 1.214 \pm 0.002$; Fig. 6). This Pb average ratio is comparable to those measured on unpolluted Atlantic shelf sediments (Mantovanelli, 2013), UCC ratios (Stacey & Kramers, 1975; Rudnick & Gao, 2003; Millot et al., 2004), and on sediments from Ilha Grande bay (Geraldés et al., 2015; Cunha et al., 2019). Notably, at around 60 cm depth, a sediment layer exhibits high Pb concentration and a radiogenic Pb isotopic signature (56 mg/kg and $^{206}\text{Pb}/^{207}\text{Pb} = 1.565$), which deviates from the local geogenic isotopic signature. Given its depth at the boundary between pre-construction and marina operation and the high Pb and Cd concentrations, it is possible to suggest that this sample represents a transitional phase. This sample showcases an intermediate geochemical signature in terms of major elements, REE and Th (Fig. 2 and 3).

The comparison of Pb isotope data determined on marina sediments, regional background rocks and antifouling paint, with major anthropogenic sources in Brazil, such as gasoline and diesel (Souto-Oliveira et al., 2019), antifouling paints (this study), urbanized rivers (Jeong et al., 2023b), and various anthropogenic sources in highly polluted Guanabara Bay (Geraldés et al., 2006), allow us to

suggest that the Pb source in Bracuhy Marina sediments is primarily geogenic (Fig. 7 and 8). However, due to the similarity of the antifouling paint's Pb isotopic signature with the geogenic signature, it is challenging to distinguish a potential contribution of Pb from antifouling paint leaching using this isotope tracer.

3.5 Metal fate and origin

The Principal Component Analyses (PCA) on the geochemical dataset (Fig. 9a and 9b), explained 96% and 84% of the total variance from the pre-marina period, respectively. In both PCAs, the grouping of the REE elements, Ti, and Th and Ca and Mn, form two clusters, likely related to heavy minerals and carbonates, respectively.

In the pre-construction sediment section, metals like Cu, Zn, Pb, Cd, and Sn were significantly correlated with the major elements Al and Fe, indicating that these metals are mainly associated with terrigenous materials such as clay minerals, aluminum, and iron oxides/hydroxides. This result is consistent with previous studies that have suggested that Fe oxides/hydroxides are important Cu carriers in both rivers and marine sectors in the studied area (Bidone et al., 1993)

In upper profile PCA, corresponding to the marina operation period, Pb, and Sn are also associated with the major elements Al and Fe, suggesting no source changes. In contrast, Cd is correlated with heavy mineral and carbonate group. Therefore, PCA indicate that these trace metals seem associated with terrigenous (Pb, Sn) and marine (Cd) particles, Cu and Zn form stand a part as a variable group negatively correlated with the others. As expected, this result confirms a common anthropogenic origin related to marina antifouling paint contamination for Cu and Zn.

As expected, the use of antifouling paints containing Cu and Zn, and sacrificial anodes for Zn resulted in elevated concentrations that surpass previous studies conducted elsewhere (Bird et al., 1996; Caplat et al., 2020; Briant et al., 2022;). Our results are consistent with Cu and Zn high contents observed in sediments from other marinas in Brazil (66 mg kg⁻¹ and 90 mg kg⁻¹, mean values for Cu and Zn respectively; Baptista Neto et al., 2005; Costa et al., 2016; Soroldoni et al.,

2018) and around the world (234mg kg^{-1} and 288 mg kg^{-1} , mean values for Cu and Zn respectively; Guerra-García et al., 2021 and references within; Jeong et al., 2023a).

3.6 Metal contamination Historical reconstruction

Our dataset allows us to analyze and reconstruct the contamination history, revealing two distinct periods during the marina's operation. The first period, from 1978 to 1995, was marked by a rise in metal contamination, while the second period, from 1995 to the present, exhibited a relatively constant level of metal contamination. These periods may be associated with the widespread use of Cu-based antifouling paint following the banning of other antifouling systems like TBT. Nevertheless, we cannot disregard the possibility that increased marina activities, such as heightened boat traffic due to tourism expansion, may have contributed to the observed trends in metal contamination.

The analysis of major and trace elements and as well as Pb isotopes, in the core retrieved from the marina, coupled with personal information provided by the marina manager, was helpful in providing a historical record of contamination. The construction of the marina involved a deviation of the Bracuhy River and the excavation of an ancient river delta in the mid-1970s (Barbosa, 2001) (Fig. S3). The marina began operations in 1978 (personal information), which resulted in a drastic increase in trace metal enrichment, mainly Cu and Zn (Fig. 5).

Now that the origin of the marine sediment is defined, with one sediment section corresponding to pre-construction and another to the marina operation, we can propose an age-depth model for the upper part of the date of the Core. Then, we can discuss the metal distribution in relation to the history of the Bracuhy marina. Based on the Bracuhy marina history and sediment geochemical tracing, it was determined that the marina operation deposit started in 1978 at a depth of 58 cm. A dating model was established by assuming a constant sedimentation deposition flux based on the homogeneous geochemical signature of the sediment section from 50 to 0 cm depth, indicating a sedimentation rate of 1.34 cm per year, leading to a 58 cm depth corresponding to 43 years.

Copper and Zn concentrations showed a linear increase from 60 cm to 30 cm, corresponding to the period from 1978 to 1995. After that, the Cu and Zn

concentrations remained relatively constant at around 80 and 150 mg kg⁻¹, respectively. The concentrations of Sn and Pb remained constant throughout the entire period, as did Cd, except for a high concentration at 41 cm. Although the enrichment factor (EF) of Pb, Cd, and Sn is moderate, it shows a slight increase after the marina operation, with values varying between 1 and 4 for Pb and 1 and 3 for Cd and Sn. The EF value of Zn is slightly higher, reaching 5, and the Cu-EF is classified as high, with a value reaching 16.

During the 1980s decade, there was also an increase in Sn enrichment due to the use of antifouling paints containing TBT, which was later banned in the 2000s. Copper and Zn concentrations continued to increase, peaking in enrichment in the middle of the 1990s, after which they tended to stabilize.

Finally, this study highlights the necessity of addressing hull coatings and devices that wash hazardous substances from ship exhausts into the water. To address the knowledge gap, further research may investigate other marina sediment cores and develop tracer tools, such as isotopic methods.

4 CONCLUSIONS

This study investigated the geochemical records of a sediment core in a Brazilian Marina to reconstruct the historical metal contamination associated with its establishment and operation since the late 1970s. Geochemical fingerprints, including major and trace elements, Pb isotopes, and Rare Earth Elements revealed synchronous patterns changes up 60 cm. This suggests a transition from (i) initial period associated with local terrigenous sources (rock weathering, soils), (ii) to subsequent period influenced by antifouling paints used in marina activities, as well as man-induced erosion and landscape modifications.

The Pb isotope analysis has confirmed the historical record of events inducing disturbances in sedimentary dynamics caused by human activities. The low Pb concentrations and Pb isotope diagrams indicate that the overwhelming majority of Pb is derived from geogenic origin with no significant influence from anthropogenic Pb source on its accumulation.

The sediment core collected at the marina exhibited significant contamination for all analyzed metals, especially copper, which displayed an enrichment factor of

up to 15 times the natural background. Multivariate statistics combined with geochemical tracers confirmed the Cu and Zn contamination by antifouling paint during the marina's operation. Their enrichment factor increased up to 15-fold during the initial 25 years after the marina operation.

Finally, the study highlights the potentially significant disturbance in the Cu and Zn cycles caused by antifouling paints in the Bracuhy marina. In a country like Brazil, with a coastline spanning 9,200 km and numerous marinas, it becomes crucial to quantify the contribution of antifouling paint usage more accurately in marina areas and the transfer of metallic contaminants to the surrounding marine environment. The use of geochemical tracers, such as isotopic tools, may aid in this environmental assessment. Our study underscores the limitations of Pb isotopes for source apportionment purposes in the Bracuhy marina area. We propose using new stable metal isotopes (Cu and Zn) as an alternative to better understand the impacts of metal contamination from antifouling paints on the cycles of these elements.

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TEXT FIGURES

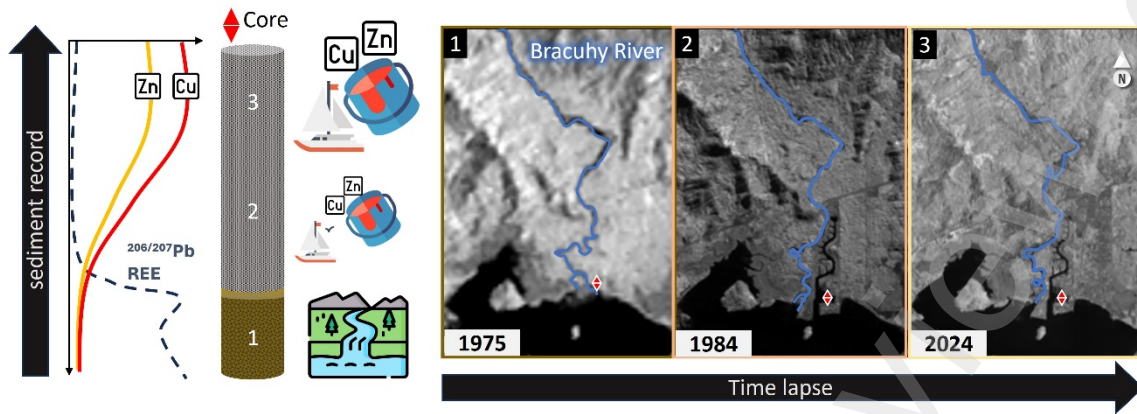


Fig. Graphical abstract

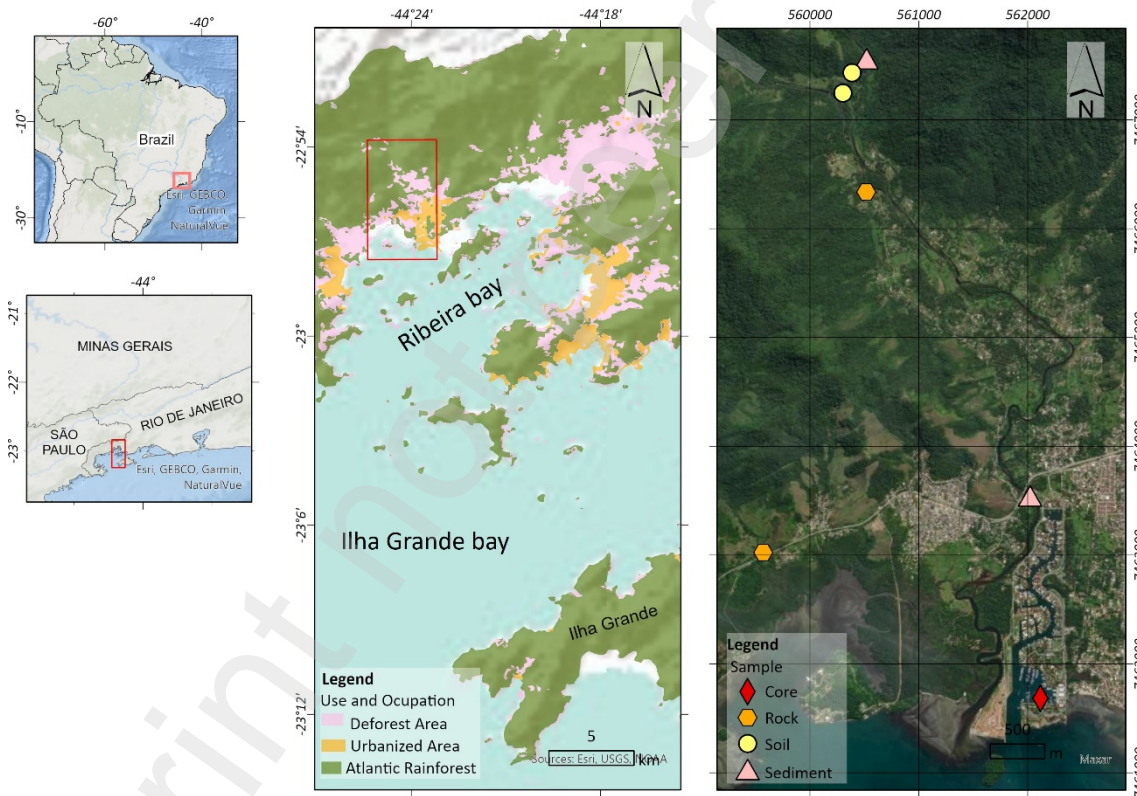


Fig. 1 The map and sampling sites location of the Bracuhy Watershed (Brazil).

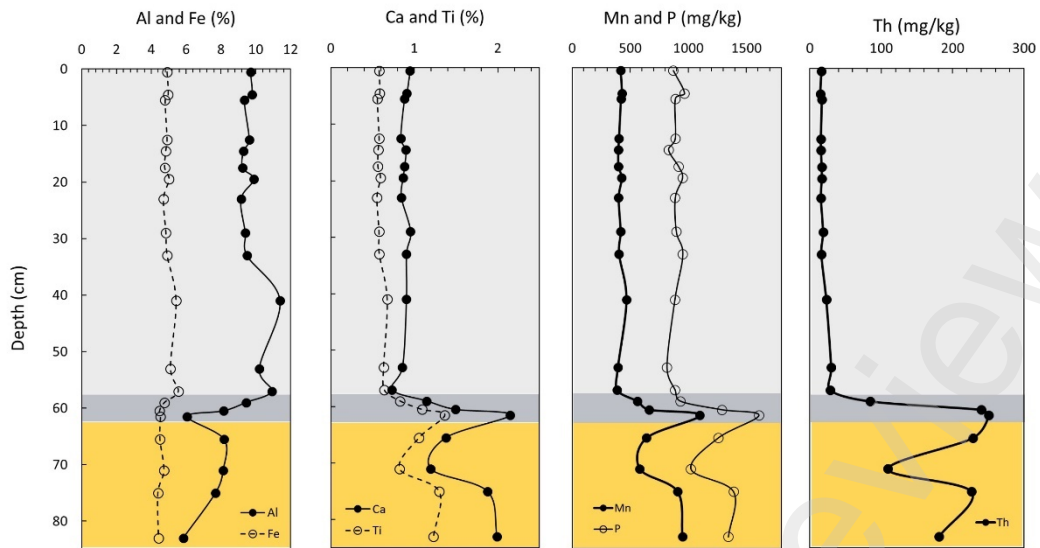


Fig. 2 Vertical distribution of Al, Fe, Ca, Ti (%), Mn, P and Th (mg kg^{-1}) concentrations in the sediment Core retrieved in the Marina Bracuhy. The colored layers represent the different textural sections and the three main periods of the marina evolution (see text for explanation).

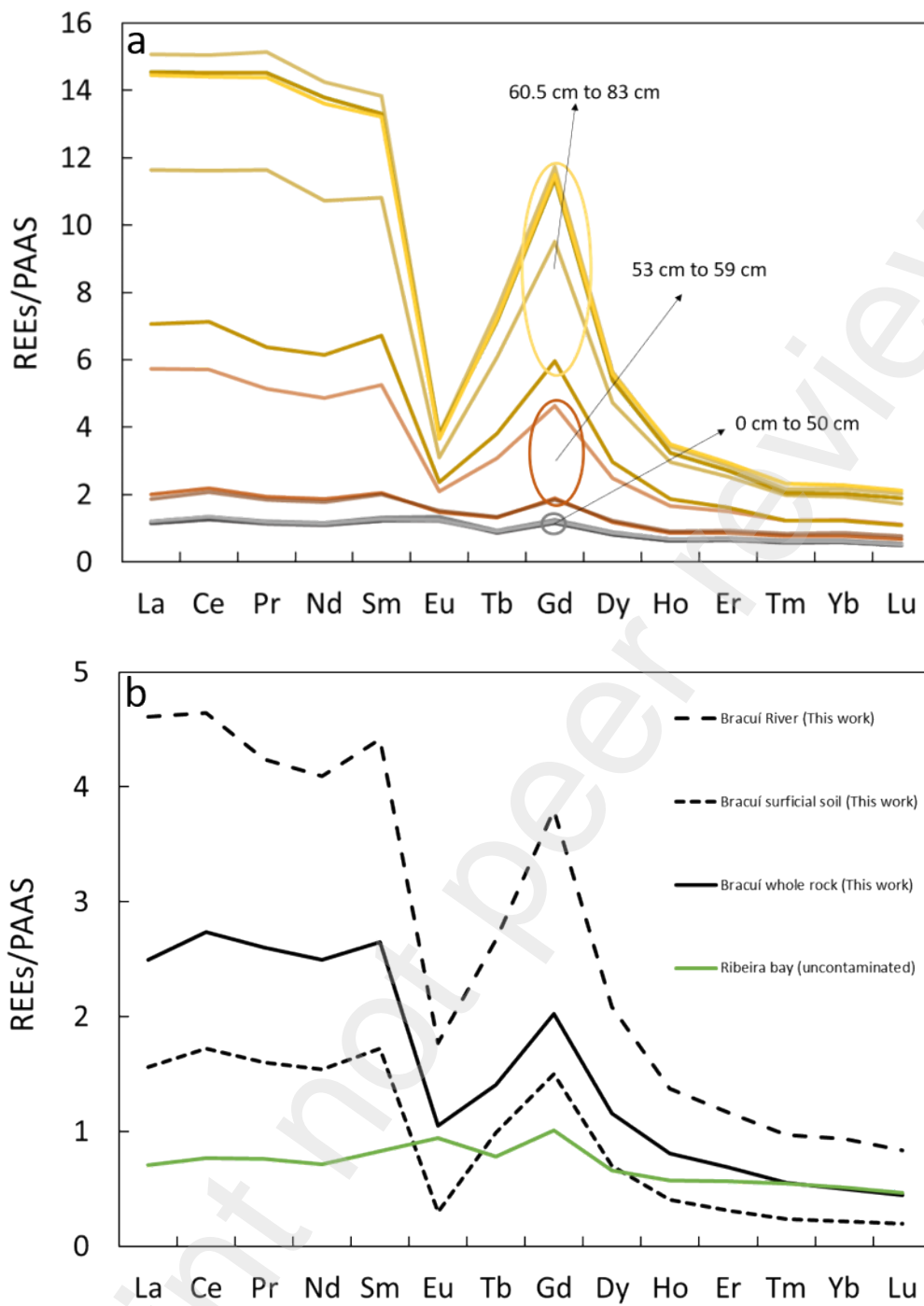


Fig. 3 Pattern of REEs normalized by PAAS in the two distinct textural sections of the core retrieved in the marina (a) and pattern of REEs for sediment sources (b). Ribeira bay Gomes et al., 2009

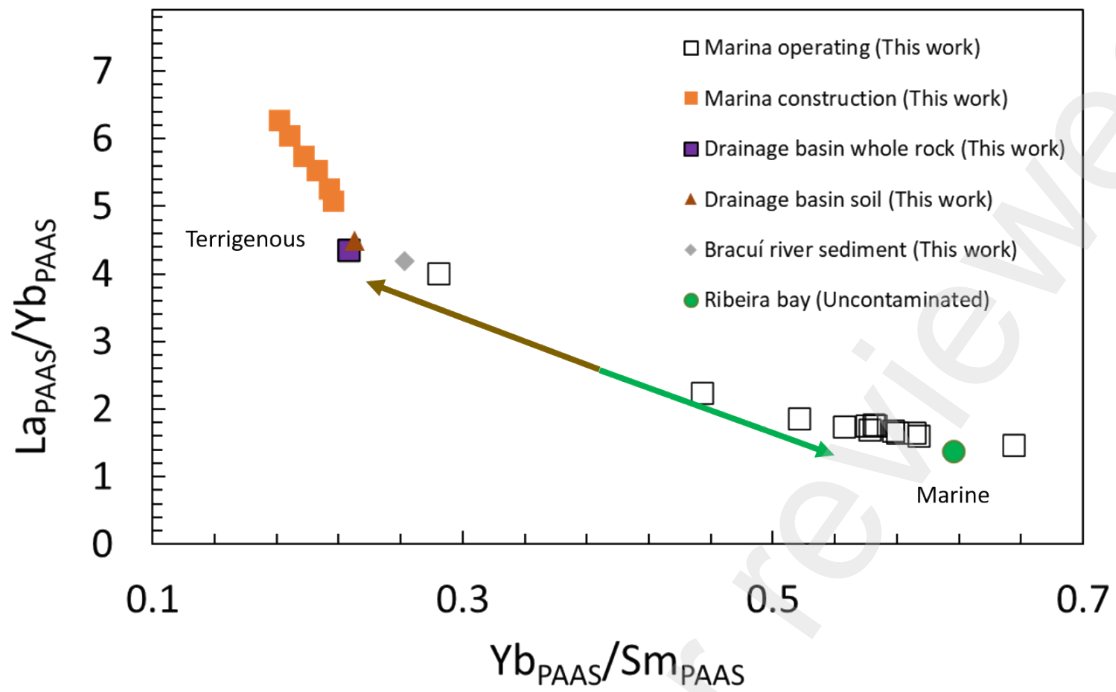


Fig. 4 Diagram of La/Yb Vs. Yb/Sm ratios normalized by PAAS for the Core sub-samples bedrock, soil, and river sediments. The sediment data from Ribeira bay (uncontaminated sediments) was compiled from Gomes et al. (2009).

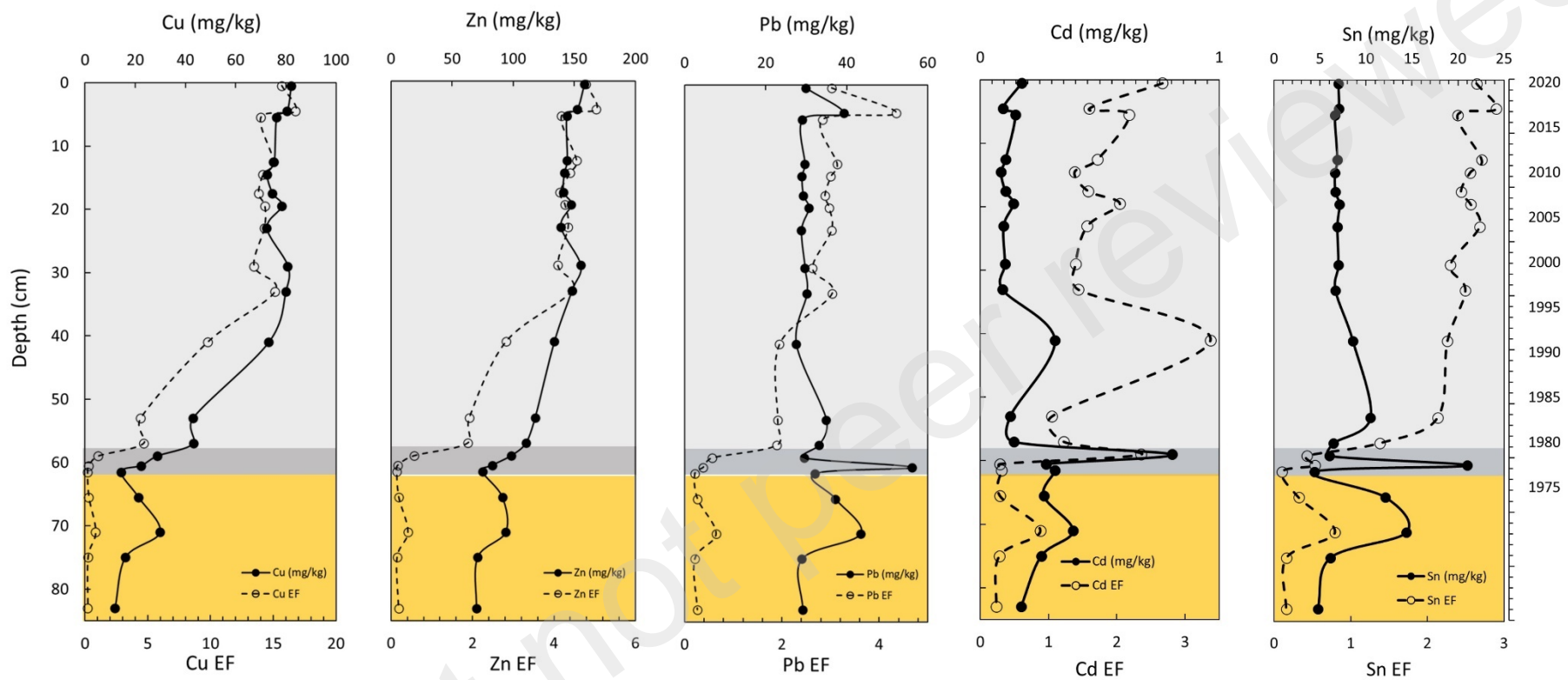


Fig. 5 Vertical distribution of Cu, Zn, Pb, Cd, and Sn (mg kg^{-1}) concentrations and enrichment in the marina Bracuhy cored sediments. The colored layers represent the different textural sections and the three main periods of the marina evolution (see text for explanation).

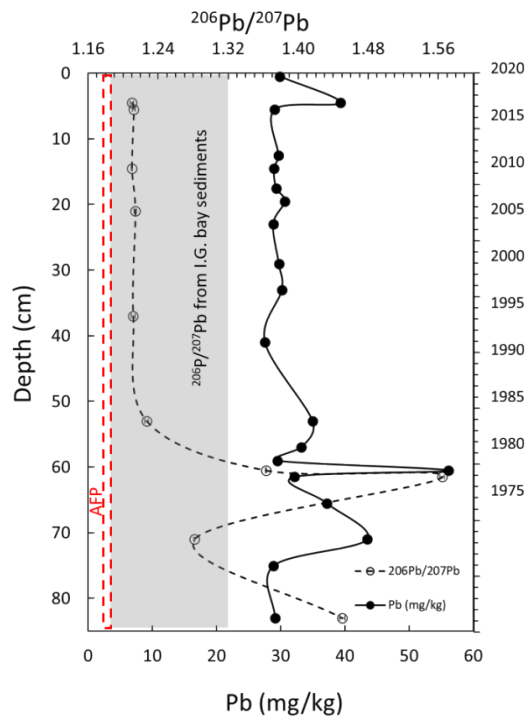


Fig. 6 Pb isotopic and Pb concentration vertical distribution for the marina Bracuhy core (Core B). The dashed red line represents the Pb isotopic signature of antifouling paints analyzed in this present work and the grey area represents the variability of Pb isotopic signatures in sediments from the Ilha Grande Bay (I.G. bay sediments, Geraldes et al., 2015; Cunha et al., 2018)

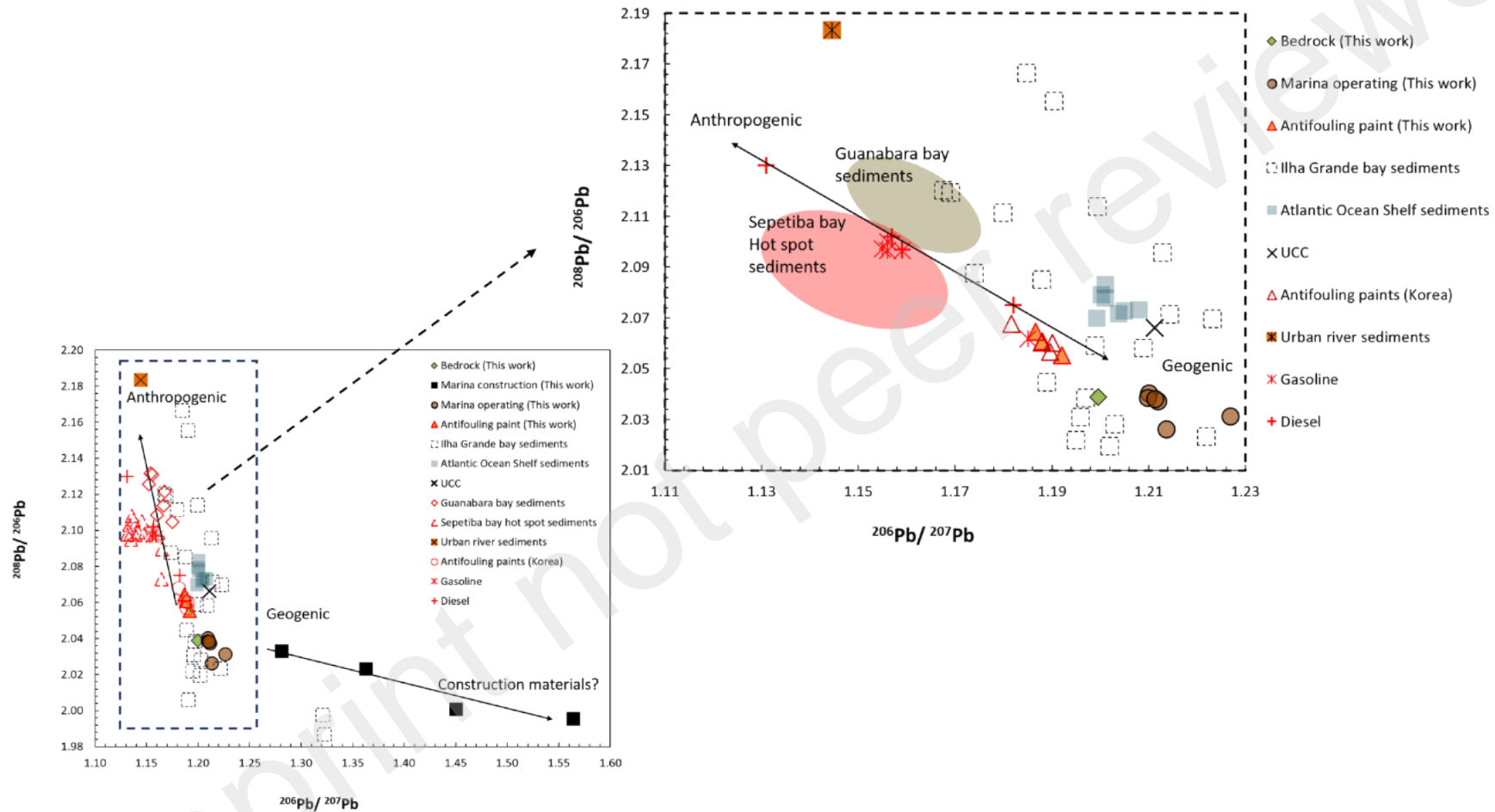


Fig. 7 Pb isotopic $^{206}\text{Pb}/^{207}\text{Pb}$ Vs. $^{208}\text{Pb}/^{206}\text{Pb}$ diagram from the core retrieved in marina Bracuhy and natural and anthropogenic sources from the (Ilha Grande bay sediments: Geraldés et al., 2015; Cunha et al., 2018; Atlantic Ocean Shelf sediments: Mantovanelli, 2013; UCC: Millot et al., 2004; Urban river sediments: Jeong et al., 2023b; Guanabara bay sediments: Geraldés et al., 2006; Antifouling paints: Jeong et al., 2023a; Gasoline and Diesel: Souto-Oliveira et al., 2019).

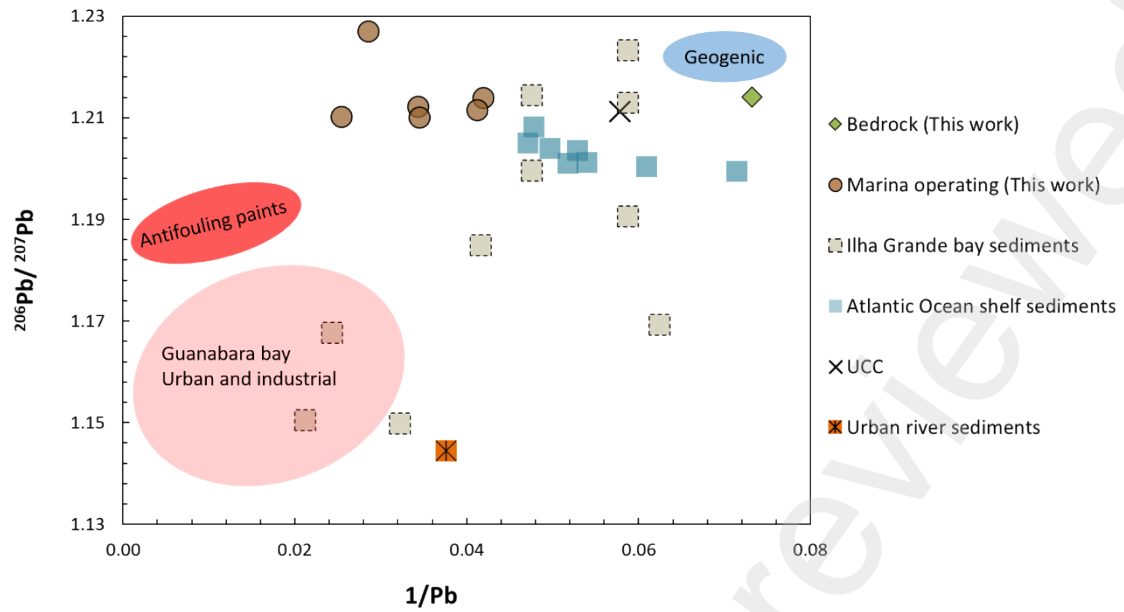


Fig. 8 Pb isotopic $^{206}\text{Pb}/^{207}\text{Pb}$ Vs. $1/\text{Pb}$ diagram from the core retrieved in marina Bracuhy (Core) and natural and anthropogenic sources from the literature (Ilha Grande bay sediments: Geraldes et al., 2015; Cunha et al., 2018; Atlantic Ocean Shelf sediments: Mantovanelli, 2013; UCC: Millot et al., 2004; Urban River sediments: Jeong et al., 2023b; Guanabara Bay sediments: Geraldes et al., 2006; Antifouling paints: Jeong et al., 2023a).

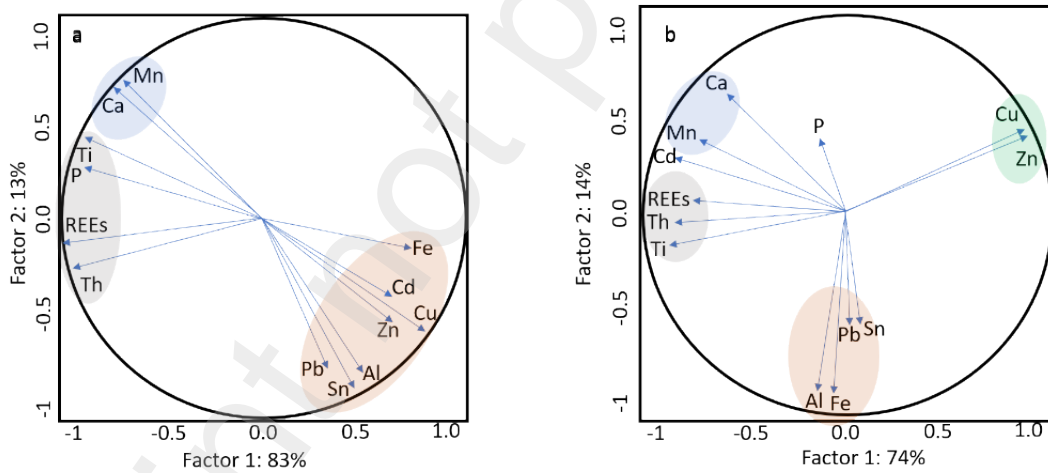


Fig. 9 Principal component analysis of Marina Bracuhy core sediments: (a) pre-construction and (b) marina operation periods

SUPPLEMENTARY MATERIAL

CERTIFIED REFERENCE MATERIALS (CRMS)

	Element	Measured value	Certified value	Recovery (%)
1646a				
(n=8)	Cu	9,21 ± 0,90	10.01 ± 0.34	92
	Zn	48,86 ± 0,75	48.9 ± 1.60	99
	Pb	10,8 ± 1,72	11.7 ± 1.2	92
	Al (%)	2,28 ± 0,011	2.297 ± 0.018	99
	Ca (%)	0,52 ± 0,032	0.519 ± 0.020	101
	Fe (%)	1,98 ± 0,025	2.008 ± 0.039	99
	Ti (%)	0,45 ± 0,025	0.456 ± 0.021	98

	Element	Measured value	Certified value	Recovery (%)
BCR-701				
(n=6)	Cd	7,49 ± 0,12	7,3 ± 0,4	103
	Cr	2,32 ± 0,26	2,26 ± 0,16	103
	Cu	55,05 ± 2,21	49,3 ± 1,7	112
	Ni	16,27 ± 0,95	15,4 ± 0,9	106
	Pb	2,95 ± 1,21	3,18 ± 0,21	93
	Zn	200,72 ± 1,98	205 ± 6	98

MAJOR ELEMENTS, Th and REEs

The major elements data from the watershed samples (bedrocks, soil, pristine mangrove sediments, and Bracuhy river sediments) displayed mean contents: Al 7%, Fe 3%, Ca 1.6%, Ti 0.5%, P 1017 mg kg⁻¹, Mn 490 mg kg⁻¹ and Th 46 mg kg⁻¹. In addition, trace elements concentration was 17 mg kg⁻¹ for Cu, 109 mg kg⁻¹ for Zn, 27 mg kg⁻¹ for Pb, 0.18 mg kg⁻¹ for Cd and 7 mg kg⁻¹ for Sn. These values agree with the Upper Continental Crust (UCC) (Rudnick and Gao, 2014).

Thorium contents and the sum of REEs concentrations (Σ REE) in the marina core varied largely (Fig. S2). As observed for major elements, the sediments corresponding to pre-construction and marina operation present significant differences. The Th concentration mean value is larger in the pre-construction sediment with 227±40 mg kg⁻¹ versus 17±4 mg kg⁻¹ in the marina operation period. Concerning the sum of REEs (Σ REE), the two sections are notably

different, with concentrations varying from 1,198 to 2,702 mg kg⁻¹ and 185 to 366 mg kg⁻¹, respectively, in the pre-construction and marina operation periods.

To trace the origin of sediments in both sections, we used geochemical tools and compared the geochemical signature to the watershed samples (bedrocks, soil, and Bracuhy river sediments), the regional samples (Ribeira bay), and the Post Archean Australian Shale (PAAS), commonly used to normalize oceanic sediments (McLennan, 1989).

HISTORICAL IMAGES FROM THE MARINA BRACUHY'S DRAINAGE BASIN

For the temporal analysis of the impact of the Bracuhy Port construction on the drainage system, images from the Landsat mission were employed. The images used were acquired on three different dates: February 16, 1975 (Landsat 2) with a spatial resolution of 60m, and May 21, 1984 (Landsat 5) and February 5, 2024 (Landsat 9), both with a spatial resolution of 30m. To enhance the differentiation between water bodies and land areas, histogram equalization was applied to the near-infrared (NIR) band.

Table S1 – Concentration of major and trace metals in sediments from the core retrieved in the marina Bracuhy (Core B) and local background samples in mg kg⁻¹

Mean Prof (cm)	Al	Ca	Ti	Fe	Mn	P	Th	Cu	Zn	Pb	Cd	Sn
0.5	97015	9493	5794	49022	417	869	16	82	158	30	0.17	7
4.5	97807	9103	5870	49707	428	966	15	80	152	39	0.09	7
5.5	93516	8821	5581	47921	419	886	17	76	144	29	0.15	7
12.5	96225	8377	5787	49021	402	886	15	75	144	30	0.11	7
14.5	92943	8973	5673	48232	397	828	16	72	142	29	0.09	7
17.5	92482	8834	5648	47679	398	915	17	75	141	29	0.11	7
19.5	98938	8652	5949	50145	426	948	17	78	147	31	0.14	7
23.0	91518	8448	5531	46973	400	886	16	72	139	29	0.10	7
29.0	94029	9553	5775	48350	416	895	18	81	155	30	0.10	7
33.0	94944	9061	5806	49060	403	951	16	80	148	30	0.09	7
41.0	113983	9045	6761	54169	467	883	23	73	134	28	0.31	9
53.0	102062	8577	6317	50976	393	814	30	43	118	35	0.13	10
57.0	109246	7285	6384	55463	385	884	29	43	110	33	0.14	6
59.0	94534	11492	8287	47564	560	932	85	29	98	29	0.80	6
60.5	81481	14920	10910	44685	662	1289	240	22	83	56	0.28	21
61.5	60526	21471	13654	45223	1099	1608	251	14	75	32	0.31	4
65.5	81839	13777	10578	44901	639	1256	228	21	91	37	0.27	12
71.0	81287	11946	8231	47235	582	1021	110	30	94	43	0.39	14
75.0	76949	18755	12969	43798	907	1389	226	16	71	29	0.26	6
83.0	58375	19926	12303	44056	949	1344	181	12	70	29	0.17	5
Rocks (n = 3)	60255	16065	2134	21214	588	350	29	13	49	18	0,06	3
Surface soil (n = 4)	45944	2136	2179	18791	147	400	16	10	136	8	0,07	3
River sediments (n = 3)	90473	33247	7485	39943	674	1922	64	21	161	73	0,48	18

Table S2 – Total concentration of REEs in sediments from the core retrieved in the marina (Core B) and local background samples in mg kg⁻¹

Mean Prof (cm)	La	Ce	Pr	Nd	Sm	Eu	Tb	Gd	Dy	Ho	Er	Tm	Yb	Lu
0.5	43.84	99.83	9.93	36.66	6.80	1.37	0.68	5.40	3.88	0.65	1.93	0.25	1.71	0.23
4.5	39.63	81.12	8.99	33.49	6.24	1.37	0.65	5.10	3.85	0.65	1.94	0.25	1.74	0.23
5.5	45.45	103.63	10.25	37.53	6.87	1.31	0.68	5.51	3.88	0.63	1.87	0.23	1.65	0.22
12.5	43.38	100.27	10.00	36.83	6.87	1.36	0.69	5.48	4.03	0.66	1.93	0.25	1.74	0.23
14.5	44.58	101.82	10.06	36.89	6.86	1.37	0.67	5.45	3.84	0.63	1.85	0.23	1.64	0.21
17.5	44.33	102.85	10.26	37.98	7.05	1.33	0.70	5.70	4.02	0.65	1.92	0.24	1.69	0.22
19.5	46.20	107.15	10.68	39.23	7.33	1.44	0.73	5.85	4.19	0.68	2.03	0.26	1.81	0.23
23	43.95	101.04	10.14	37.44	6.86	1.35	0.68	5.44	3.84	0.64	1.88	0.24	1.69	0.22
29	49.31	114.85	11.42	42.60	7.86	1.41	0.77	6.29	4.37	0.71	2.04	0.26	1.83	0.24
33	46.19	106.69	10.42	38.34	7.06	1.36	0.70	5.65	4.04	0.67	1.93	0.25	1.70	0.22
53	76.51	174.81	17.11	63.42	11.41	1.60	1.03	8.80	5.55	0.86	2.45	0.31	2.21	0.29
57	71.25	164.71	16.29	60.07	11.19	1.66	1.04	8.59	5.72	0.91	2.66	0.34	2.46	0.34
59	218.76	455.07	45.48	165.09	29.14	2.26	2.39	21.59	11.66	1.65	4.31	0.50	3.52	0.49
60.5	576.19	1197.34	133.67	483.06	76.77	4.13	5.82	54.65	26.40	3.40	8.16	0.88	6.14	0.87
61.5	599.01	1258.12	139.69	504.65	80.30	4.10	6.37	59.79	28.82	3.80	9.10	0.98	6.73	0.91
65.5	555.59	1156.32	128.18	467.22	73.93	4.08	5.57	53.10	25.23	3.21	7.75	0.83	5.71	0.82
71	270.24	567.03	56.22	208.77	37.28	2.55	2.96	27.85	13.94	1.85	4.58	0.50	3.43	0.47
75	551.81	1146.86	126.98	461.56	73.39	3.95	5.61	53.60	26.06	3.47	8.39	0.94	6.44	0.92
83	445.12	924.29	102.71	363.52	60.00	3.35	4.72	44.33	22.15	2.94	7.19	0.80	5.45	0.75
Rocks (n = 3)	41.87	91.39	9.71	35.67	6.19	1.08	0.55	4.25	3.29	0.62	1.99	0.29	2.20	0.32
Surface soil (n = 4)	32.12	69.44	7.47	27.59	5.04	0.25	0.42	3.72	1.86	0.24	0.57	0.07	0.44	0.06
River sediments (n = 3)	163.17	340.13	34.69	128.86	23.14	1.87	1.96	16.91	9.30	1.33	3.32	0.40	2.73	0.39

Table S3 – Pb isotopes in sediments from marina core, bedrock and antifouling paints commercialized in Brazil.

Mean Prof. (cm)	$^{206}\text{Pb}/^{204}\text{Pb}$	2SD	$^{207}\text{Pb}/^{204}\text{Pb}$	2SD	$^{208}\text{Pb}/^{204}\text{Pb}$	2SD	$^{206}\text{Pb}/^{207}\text{Pb}$	2SD	$^{208}\text{Pb}/^{206}\text{Pb}$	2SD
4.5	19.023	0.007	15.720	0.007	38.808	0.008	1.21	0.002	2.040	0.002
5.5	19.038	0.005	15.706	0.006	38.780	0.007	1.21	0.002	2.037	0.003
14.5	19.000	0.003	15.703	0.003	38.727	0.003	1.21	0.001	2.038	0.001
21	19.052	0.004	15.695	0.004	38.597	0.005	1.21	0.001	2.026	0.002
37	19.052	0.004	15.727	0.005	38.826	0.006	1.21	0.002	2.038	0.003
53	19.241	0.015	15.682	0.015	39.078	0.015	1.23	0.002	2.031	0.002
60.5	21.607	0.003	15.848	0.003	43.710	0.003	1.36	0.001	2.023	0.001
61.5	25.106	0.010	16.047	0.011	50.094	0.011	1.56	0.003	1.995	0.002
71	20.208	0.002	15.769	0.003	41.081	0.003	1.28	0.001	2.033	0.001
83	23.179	0.007	15.982	0.009	46.374	0.012	1.45	0.003	2.001	0.006
Bedrock 1	18.235	0.005	15.579	0.005	37.784	0.005	1.17	0.001	2.072	0.001
Bedrock 2	18.822	0.003	15.747	0.003	38.246	0.004	1.20	0.001	2.032	0.002
Bedrock 3	19.515	0.004	15.828	0.006	39.269	0.008	1.23	0.002	2.012	0.004
AF paint 1	18.639	0.014	15.637	0.014	38.310	0.013	1.19	0.002	2.055	0.002
AF paint 2	18.571	0.003	15.631	0.004	38.277	0.004	1.19	0.001	2.061	0.001
AF paint 3	18.535	0.009	15.621	0.009	38.269	0.009	1.19	0.002	2.064	0.001
NIST 8704 (n = 2)	19.036	0.007	15.697	0.010	38.887	0.013	1.213	0.004	2.043	0.007
NIST 2709a (n = 3)	18.907	0.004	15.665	0.005	38.569	0.006	1.208	0.002	2.040	0.003

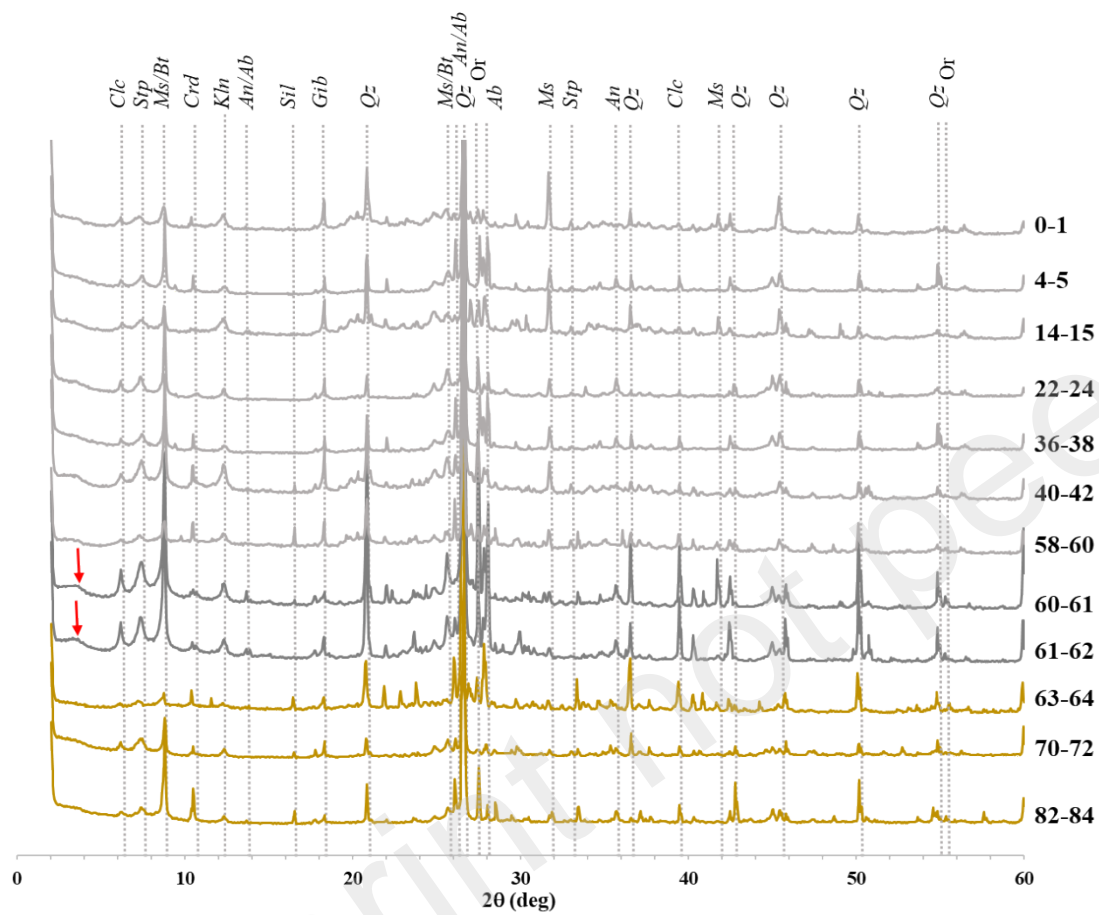


Fig. S1: XRD diffractograms of a sediment sample selection, from the core retrieved in the Marina Bracuhy. Minerals: Qz for Quartz, An for Anorthite, Alb for Albite, Or for Orthoclase, Bt for Biotite, Mus for Muscovite, Clc for Clinocllore, Stp for stilpnomelane, Sil, for Silimanite, Gib for Gibbsite, Kaol for Kaolinite. The red arrow highlights the interstratified clay minerals traces characteristic peak.

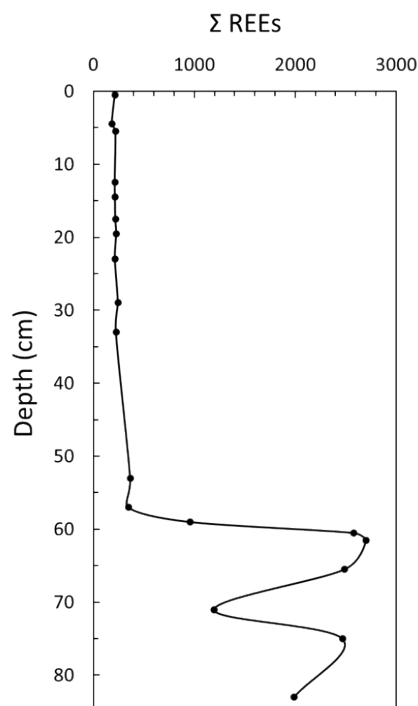


Fig. S2 Vertical distribution of the Sum of the REEs (mg kg^{-1}) on the sedimentary core retrieved in the Marina Bracuhy

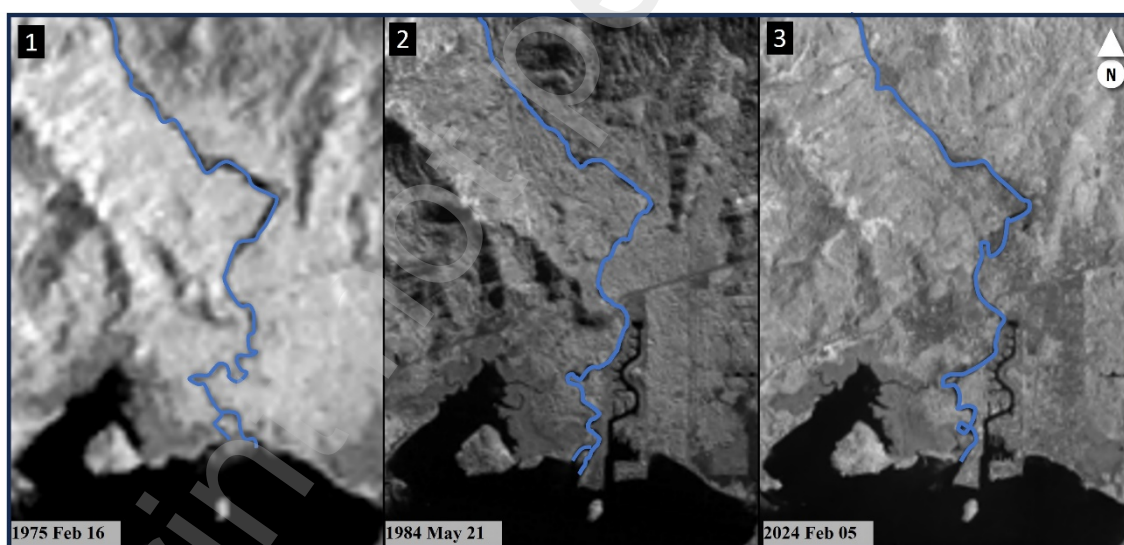


Fig. S3 Historical images of the impact of the Bracuhy Port construction on the drainage system. Bracuhy river depicted in blue: (1) Photo from 1975 showing Bracuhy river in a pristine condition and the ancient river delta; (2) Photo from 1984 show the complete deviation of the Bracuhy river and beginning of the marina operation; (3) Photo from nowadays with the Bracuhy marina in full capacity of operation