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LEAD SOURCE ASSESSMENT BY ISOTOPIC AND ELEMENTARY COMPOSITION IN THE TRANSITION FROM PRISTINE TO POLLUTED CONDITION OF COASTAL SEDIMENTS

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Abstract

The source assessments of metal contaminants are critical for a consistent management of coastal zones. In this work, lead (Pb) concentration and isotopic composition were determined in sediments from Angra dos Reis coast (Brazil) to evaluate the potential influence of contamination sources on Pb distribution. Estimated Pb enrichment factor up to 1.64 suggested natural source predominance. Diagrams of $^{206}Pb/^{207}Pb$ ratio plotted against $^{208}Pb/^{206}Pb$ and 1/Pb ratios indicated a binary source mixing that was explained by marine and terrigenous influences. Only some specific sites fall close to anthropogenic Pb isotopes signatures (e.g., from urban effluents and gasoline). The lower Pb concentrations were associated with a marine carbonate dilution effect, as indicated by a negative relationship between Pb and Ca. Past dredging activities contributed to explain a diffuse occurrence of anthropogenic Pb isotopic signature. The overall results reveal the beginning of a transition from pristine to slightly-polluted condition.

Keywords: Pb isotopes. Pollution assessment. Source identification. Coastal sediments.

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1 Introduction

Coastal regions host more than a half of the human population and most industrial activities, implying in frequent high levels of metal contamination induced by anthropogenic inputs, via atmosphere, groundwater and fluvial pathways (Mason, 2013). Multiple anthropogenic sources may cause lead (Pb) contamination, such as Pb ore mining and smelting, non-ferrous metal manufacturing plants, coal and alkyl-lead petrol burning, leaded fuels, waste incineration, production and storage of batteries, leaded oxide pigments, ferroalloys and metal fabricating industries and urban sewage (Nriagu and Pacyna, 1988; Monna et al., 1997; Véron et al., 1999; Heisterkamp and Adams, 1999).

The assessments of sources and fates of toxic metal contaminants, such as Pb, are critical to support environmental management strategies, either for remediation actions appropriately targeted as well as to maintain emissions at sustainable levels (Weiss et al., 2007). However, while areas heavily impacted are generally well diagnosticated by assessing anomalous metal concentrations and metal input from anthropogenic point sources (e.g., Moraes et al., 2004; Sivry et al., 2008; Rocha et al., 2010; Andrade Lima and Bernadez, 2011; Araújo et al., 2017), the detection of anthropogenic influences in sites potentially affected by diffuse contamination sources, as occur in many coastal regions, tend to be a challenging task. For example, it may be difficult to differentiate anthropogenic and natural metal sources and to determine if relative low metal concentrations represent or not natural baseline levels (Shiel et al., 2013).

This is the case of Angra dos Reis coast (ARC), located in the Ilha Grande Bay, SE Brazil (Fig. 1). This area is known as economically important for touristic activities, showing well preserved coastal ecosystems, including coves, sandy beaches, and mangroves (Belo et al., 2002; Creed et al., 2007). Despite the use of ARC areas as reference sites for trace metal concentrations in coastal sediments in the last decades (Cardoso et al., 2001; Freret-Meurer et al., 2010; Chiappetta et al., 2016), some anthropogenic activities may be affecting the sediment quality of this coastal region.

These potential pollution sources include: (i) the growing urban occupation in the watershed; (ii) the presence of marinas, the biggest shipyard in Brazil (operating since the 1960s) and discharges of wastes related to shipping and boating activities (e.g., anti-fouling paints); and (iii) oil terminals and storage (Pinheiro et al., 2006; Quadros et al., 2009; Vasconcelos et al., 2011). Sediment dredging was also carried out in this area to support navigation and oil transport, which may have implied in metal remobilization from the sediments. Moreover, high trace metal concentrations were observed in bivalves found in the ARC inner area (Vannuci-Silva et al., 2017).

The isotope fingerprints techniques are useful to trace anthropogenic sources in the environment (Weiss al., 2007; Cunha et al., 2009; Araújo et al., 2017; Gioia et al., 2017), even in remote areas (e.g., Antarctica; Rosman et al., 1994). Unique relative Pb isotopes abundances for different sources are produced by the radioactive decay of the parent radionuclides, depending on the initial parent-to-product elemental ratios and time. Therefore, Pb isotopic composition of anthropogenic emissions (e.g., fossil fuel combustion, smelting, and refining, sewage, atmospheric deposition) reflects the isotopic composition of the source. On the other hand, crustal Pb isotope compositions reflect the initial parental composition and new radiogenic Pb accumulated from the radioactive decay of U and Th since the time of formation. These abundances of isotopes define signatures, allowing the use of the isotopic ratios as an efficient tracer system to distinguish natural or polluting sources in the environment (Marcantonio et al., 1999; Landmeyer et al., 2003; Babinski et al., 2003; Gioia et al., 2006, 2017; Ettler et al., 2006; Komarek et al., 2008).

Since the ARC region seems to represent a transition from a natural baseline condition to an anthropogenically-influenced condition in relation to trace metals (Mayer-Pinto and Junqueira, 2003; Chiappetta et al., 2016), it requests careful attention to be assessed. In this work, previously reported $^{206}Pb/^{207}Pb$ ratios (Souza et al., 2014) are combined with new elemental concentration (i.e., P, Mn, Fe, Ti and Ca concentrations) and $^{208}Pb/^{206}Pb$ ratios data from the same sediment samples, in order to assess potential contributions of anthropogenic Pb sources in the ARC region.

2. Materials and methods

Surface sediments were sampled in 10 stations using a Van Veen grab in 2011 (Fig. 1). Sample preparation was performed at the Laboratório Geológico de Preparação de Amostras from Universidade do Estado do Rio de Janeiro (LGPA-UERJ) and included: (i) drying; (ii) sieving (<200 mesh); (iii) weighting; (iv) total dissolution ($HF+HNO_3$) in a hot plate; (v) solution analysis for total lead concentration, chemical elements and isotopes (HR-ICP-MS) in ActLabs Canada (ISO 17025). The mass bias was corrected with a calibration against a Pb isotopic standard (NIST981). The standard error for Pb ratios was 0.05%.

Some sedimentary chemical elements were chosen and applied in this study as proxies for redox processes (Mn, Fe), terrestrial (Ti) and marine (Ca) sources (Carvalho et al., 1993), as well as urban effluent input (P), as reported for nearby areas (e.g., Luiz-Silva et al., 2008; Borges et al., 2009; Chiappetta et al., 2016).

Principal Component Analysis (PCA) was performed to identify possible associations between the mentioned elements and Pb isotopic composition. Statistical treatments were performed using a Statsoft software (Statistica, release 8.0).

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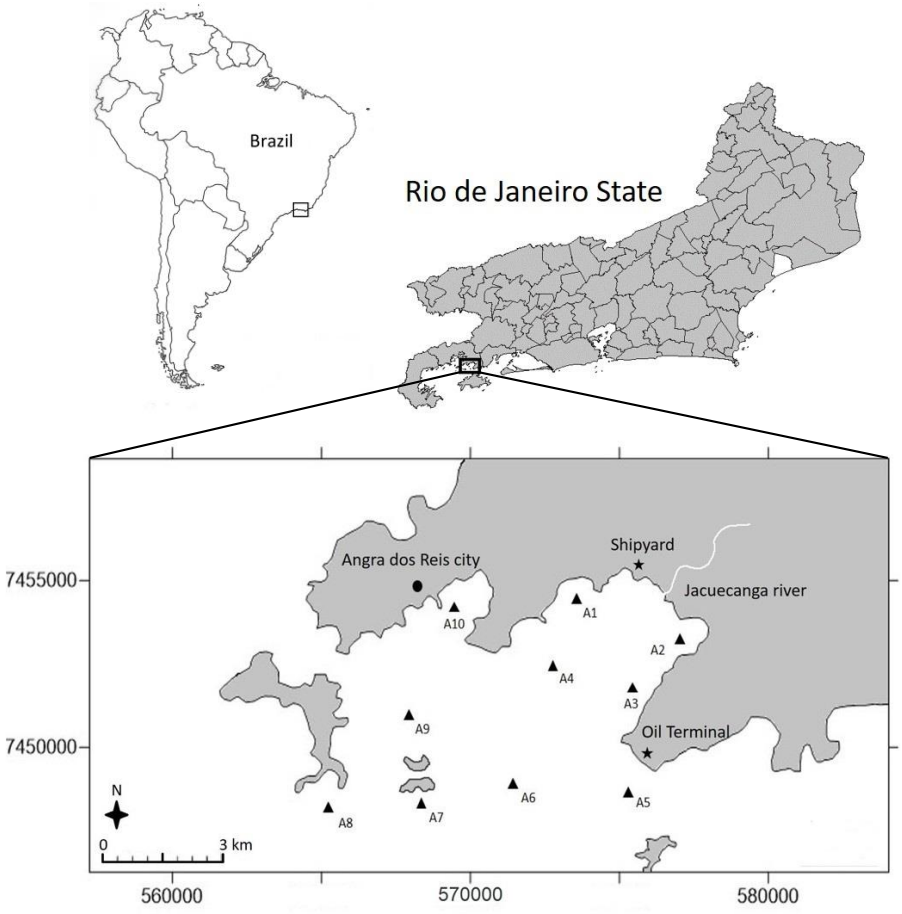

Fig. 1. Location of sampling stations in Angra dos Reis coast, SE Brazil.

A trace element Enrichment Factor (EF) was used to identify and estimate anthropogenic influences, adopting the combined physical (sieving) and geochemical (ratio to a conservative reference element) normalization approach (Kersten and Smedes, 2002). EF values were calculated as follows:

$$EF = ([M]/[Ti])_{sample} / ([M]/[Ti])_{reference}$$

where [M] is the metal of interest and [Ti] is the conservative reference element, with no significant anthropogenic source. Regional background concentrations reported for coastal sediments by Gomes et al. (2009) were used for these calculations.

3. Results and Discussion

All datasets of Pb concentration, isotopic composition and enrichment factors and major elements concentrations are showed in Table 1. Samples located near the continental source (Fig. 1) had the highest concentrations of Fe (A1, A2, A3), P (A1, A2, and A10) and Ti (A1, A2, A3, A4, A9 and A10). The observed higher P levels (~1,000 mg/kg) were comparable to those reported for nearby coastal sediments under the influence of eutrophicated coastal water bodies (e.g., Borges et al., 2009).

Samples A5, A6, A7 and A8 had the highest Ca concentrations, indicating a major influence of contributions of marine carbonates. The Mn and Pb concentrations of the analysed samples varied from 315 to 556 mg/kg and 16 to 47 mg/kg, respectively. The highest Pb contents were found at stations A2 and A10, with 47 mg/kg and 41 mg/kg, respectively. The estimated Pb EF values, ranging from 0.57 to 1.64, indicate that the Pb contents variability was mainly associated with natural sources. Only slightly high Pb concentrations related to pollutants were observed in specific sites (Table 1). The overall $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios in the studied ARC sediments varied from 1.15 to 1.22 and 2.07 to 2.19, respectively (Table 1). To help the source identification, the Pb isotopic compositions of ARC sediments were compared with those from anthropogenic and natural sources ("end-members") reported in previous studies (Fig. 2).

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Tab. 1. Total concentrations of the analyzed chemical elements and Pb enrichment factors and isotopic composition ratios.

Sample	UTM		Ti (%)	Fe (%)	Ca (%)	P (mg/kg)	Mn (mg/kg)	Pb (mg/kg)	Pb EF	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$
	LAT	LONG									
A1	575350	7455474	0.56	4.65	0.44	1100	363	31	0.83	1.1497	2.1592
A2	579139	7454323	0.43	5.24	0.29	1300	554	47	1.64	1.1504	2.1988
A3	576539	7453313	0.55	4.08	1.47	930	315	21	0.57	1.2144	2.0712
A4	572910	7452753	0.52	1.68	2.66	780	369	24	0.69	1.1848	2.1664
A5	577647	7450095	0.24	3.81	8.83	490	556	17	1.06	1.1905	2.1552
A6	572254	7449261	0.37	3.23	6.44	600	359	16	0.65	1.1692	2.1192
A7	568921	7448113	0.32	3.25	6.74	510	510	17	0.80	1.2232	2.0696
A8	566310	7448429	0.24	1.68	7.94	200	356	17	1.06	1.2129	2.0955
A9	568687	7451665	0.52	3.25	4.34	710	443	21	0.61	1.1995	2.1138
A10	569851	7454388	0.56	3.85	1.98	1060	330	41	1.10	1.1676	2.1203

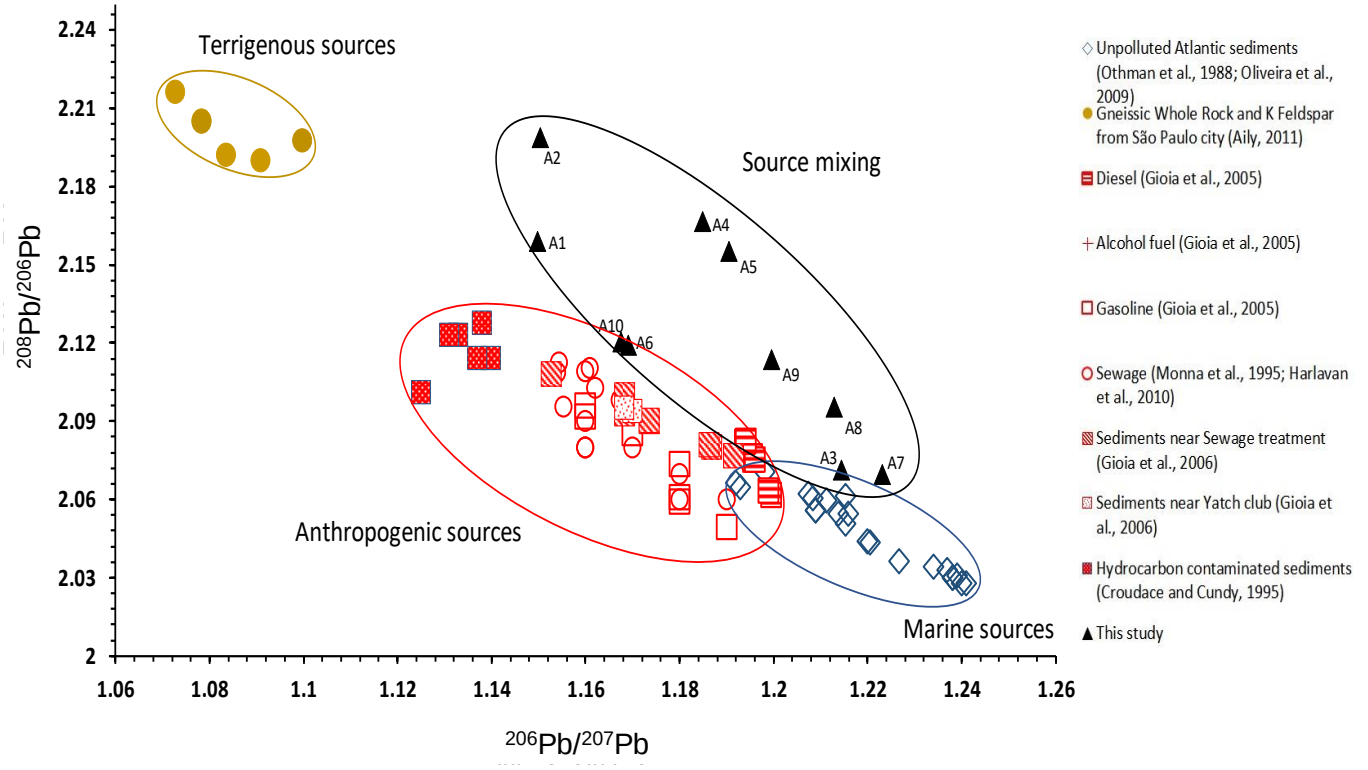

Fig. 2. Plot of $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{206}Pb$ ratios, comparing Angra dos Reis coast results with anthropogenic and natural sources signatures available in the literature.

Four groups of different Pb isotopic composition trends were distinguished: (i) the terrestrial source data, represented by gneissic rock and K-feldspar from São Paulo, SE Brazil (Aily, 2001); (ii) anthropogenic sources (e.g., fuels used in Brazil, sewage and contaminated sediments by boating activity; Croudace and Cundy 1995; Monna et al., 1995; Gioia et al., 2005, 2006; Harlavan et al., 2010); (iii) natural marine Atlantic sediments (Othman et al., 1989) and coastal lagoon sediments located in a remote site (Fernando de Noronha Island; Oliveira et al., 2009); and (iv) ARC sediments, displaying a source mixing trend between terrestrial, anthropogenic and marine inputs. Samples A1

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and A2, collected near the continental sources (Fig. 1), showed Pb isotopic ratios closer to those of terrestrial signature. The samples A3, A7 and A8 showed Pb isotopic ratios with stronger similarity to those from non-polluted marine sediments. Only two samples (A6 and A10) displayed a similarity with the anthropogenic sources signatures reported in the literature (e.g., from urban effluents and gasoline; Fig. 2).

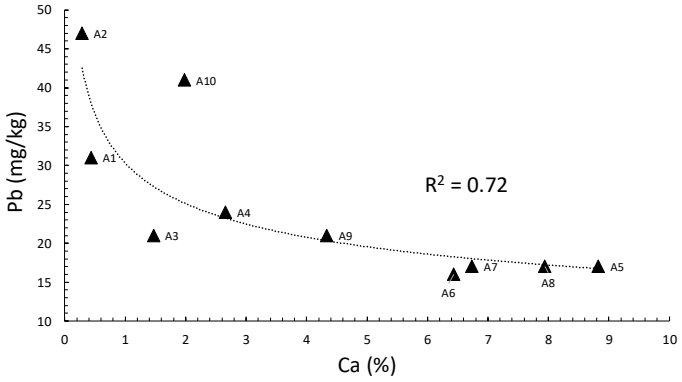

Fig. 3. Plot of Pb vs. Ca total concentrations.

The sample A10 has an anthropogenic signature explained by its location inside an area with known exposure to anthropogenic contamination (e.g., sewage pollution due to urbanization; Mayer-Pinto and Junqueira, 2003). However, no local contamination source is known for the sample A6 location, suggesting possible anthropogenic Pb transport and (re)deposition induced by past dredging activities, or the influence of Pb diffuse emissions from terrestrial sources, marinas and ships.

Note that A6 sample presented the lowest Pb concentration (16 mg/kg) and relatively high level of Ca and low Ti content (Table 1). The low Pb concentration in A6 may be partly explained by carbonate dilution, as suggested by the inverse correlation (R^2 = 0.72) between Pb and Ca, illustrated in Fig. 3. If the A6 sample is not considered, a high linear correlation is observed between $^{206}Pb/^{207}Pb$ ratios and 1/Pb (R^2 = 0.74) for A6 sample suggests a binary source mixing (Fig. 4). Since both Pb contents and isotopic data evidenced a natural source dominance, it should be hypothesized that this binary source mixing is mainly explained by natural terrigenous and marine end-members influences.

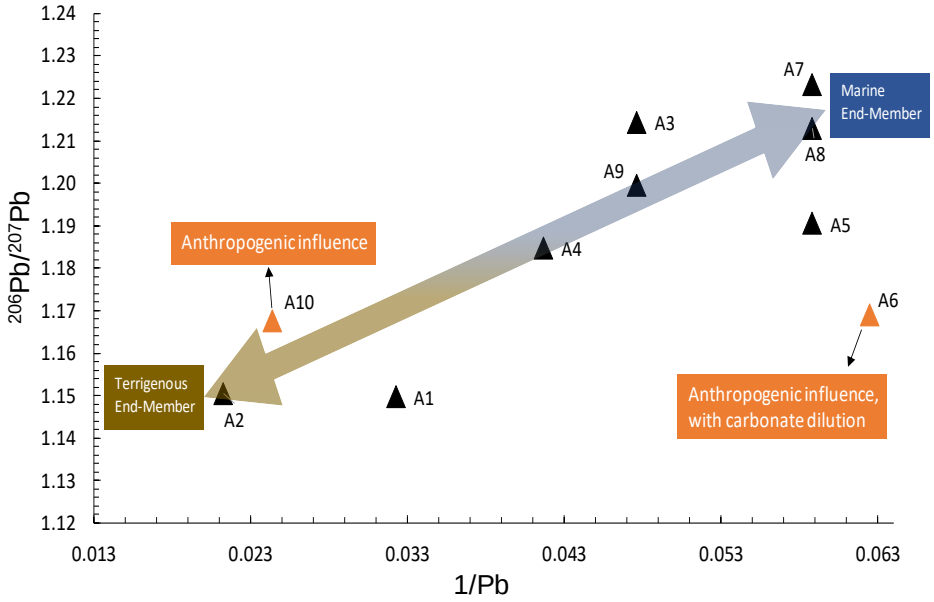

Fig. 4. Plot of $^{206}Pb/^{207}Pb$ ratios vs. 1/Pb concentrations. Note that the station A6 data was not considered for the correlation analysis (see text).

Principal Component Analysis (PCA) based on the entire dataset produced two factors, which explained ~81% of data variability (Fig. 5). The Factor 1 was mainly associated with the distribution trends of terrestrial, marine and sewage proxies (Ti, Fe, Ca and P), Pb concentrations and $^{206}Pb/^{207}Pb$ ratios. Lead concentrations and isotopic compositions were associated with proxies of terrigenous and sewage inputs (Fe and P, respectively). Calcium was negatively correlated with these elements, which is consistent with its marine origin. The Factor 2 is mainly associated with Mn and Ti distribution trends, reflecting the inverse relationship between the known conservative behavior of Ti and the highly redox-sensitive behavior of Mn (Burdige, 1993). Though Mn compounds are recognized as potential geochemical carriers for trace metals in coastal sediments (Shaw et al., 1990), the PCA evidences that the Pb distribution trends was not driven by the redox-sensitive Mn behavior. Therefore, the PCA results suggest that Pb

concentrations and isotopic signatures association are more related to the influence of natural and diffuse anthropogenic input, than by biogeochemical processes, such as diagenetic redistribution following Mn diagenesis.

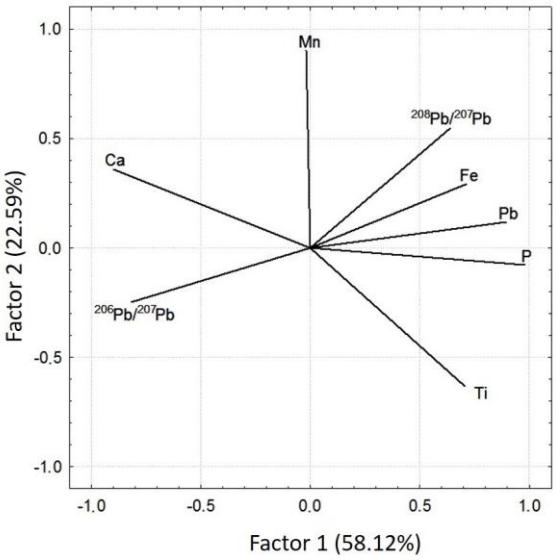

Fig. 5. Principal Components Analysis of elemental and isotopic dataset.

5. Conclusion

The studied ARC sediments show low Pb EFs, suggesting no significant contamination in most of the study sites. The Pb isotopic ratios and $^{206}Pb/^{207}Pb$ vs. 1/Pb diagrams evidenced a general mixing between two major sources, interpreted as the natural continental and marine sources. However, the sedimentary Pb isotopic composition indicate that two sites (A10 and A6) may be slightly affected by anthropogenic activities (e.g., sewage and nautical activities pollution, and dredging-driven dispersion of anthropogenic Pb). The A6 station presented remarkably low Pb concentrations and EF, as it was partly explained by a marine carbonate dilution process.

This study demonstrates that the combined use of isotope fingerprint techniques and geochemical dataset analysis assisted by multivariate statistics is useful to provide more comprehensive assessments of Pb sources, even in the case of low polluted environments.

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