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Pb isotope signatures of sediments from Guanabara Bay, SE Brazil: Evidence for multiple anthropogenic sources

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Abstract

Sediments from Guanabara Bay and two rivers were analyzed for Pb isotope composition. The results define linear groups interpreted as different sources of Pb. The samples from Iriri and Surui rivers present different Pb compositions probably resulting from two active pollutants which are transported in the waters to the Guanabara Bay, where they are mixed. The $^{206}Pb/^{207}Pb$ values of 1.151 and 1.091 presented here are in the range of Brazilian galena ore signature.

Keywords: Pb isotopes; Sediments; Guanabara Bay

1. Introduction

Over the last 6000 years, anthropogenic Pb has been introduced into the global environment through atmospheric transport (Niagru, 1989; Hong et al., 1994). Prior to the industrial revolution, anthropogenic lead was emitted solely as a by-product of mining and smelting of lead, silver, and copper ores. By the mid-18th century, combustion of Pb-containing coal had become the primary source of industrial lead emissions into the atmosphere (Marcantonio et al., 2002). Since the 1920s, automobile exhaust, with Pb additives (alkyl lead), has exceeded all other sources of anthropogenic Pb emitted into the environment. Nowadays, more than 95% of lead deposited in the environment is of anthropogenic origin (Alfonso et al., 2001).

Total Pb concentrations alone may be insufficient for separating pollution from natural background because Pb concentration is often highly variable due to natural processes (Helland et al., 2002; Luck and Othman, 2002). Pb isotopic analysis has been used with great success to trace the source of elements in recent sediments, to distinguish different sources, to trace elements from source to burial, and to assess the effect of remedial actions to reduce atmospheric emissions from a specific polluter (Verón et al., 1999; Rosman et al., 2000). In addition, establishing reference sites is a critical factor in determining the baseline of contaminant background and the remediation of impacted landscapes (Niagru, 1989; Monna et al., 2000). This contribution aims to present preliminary results of Pb isotope in sediments from Guanabara Bay (Fig. 1), Rio de Janeiro-Brazil to constrain the signature of Pb sources in the region and pollutant transport.

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2. Methods

Guanabara Bay is an estuary of 380 km^2 between the cities of Rio de Janeiro, Niterói, Duque de Caxias, Magé, Guapimirin, Itaboraí e São Gonçalo, with a population about 11 million. Industries, oil refineries, shipyards and domestic sewage represent the principal sources of pollution of surface sediments (Rego et al., 1993).

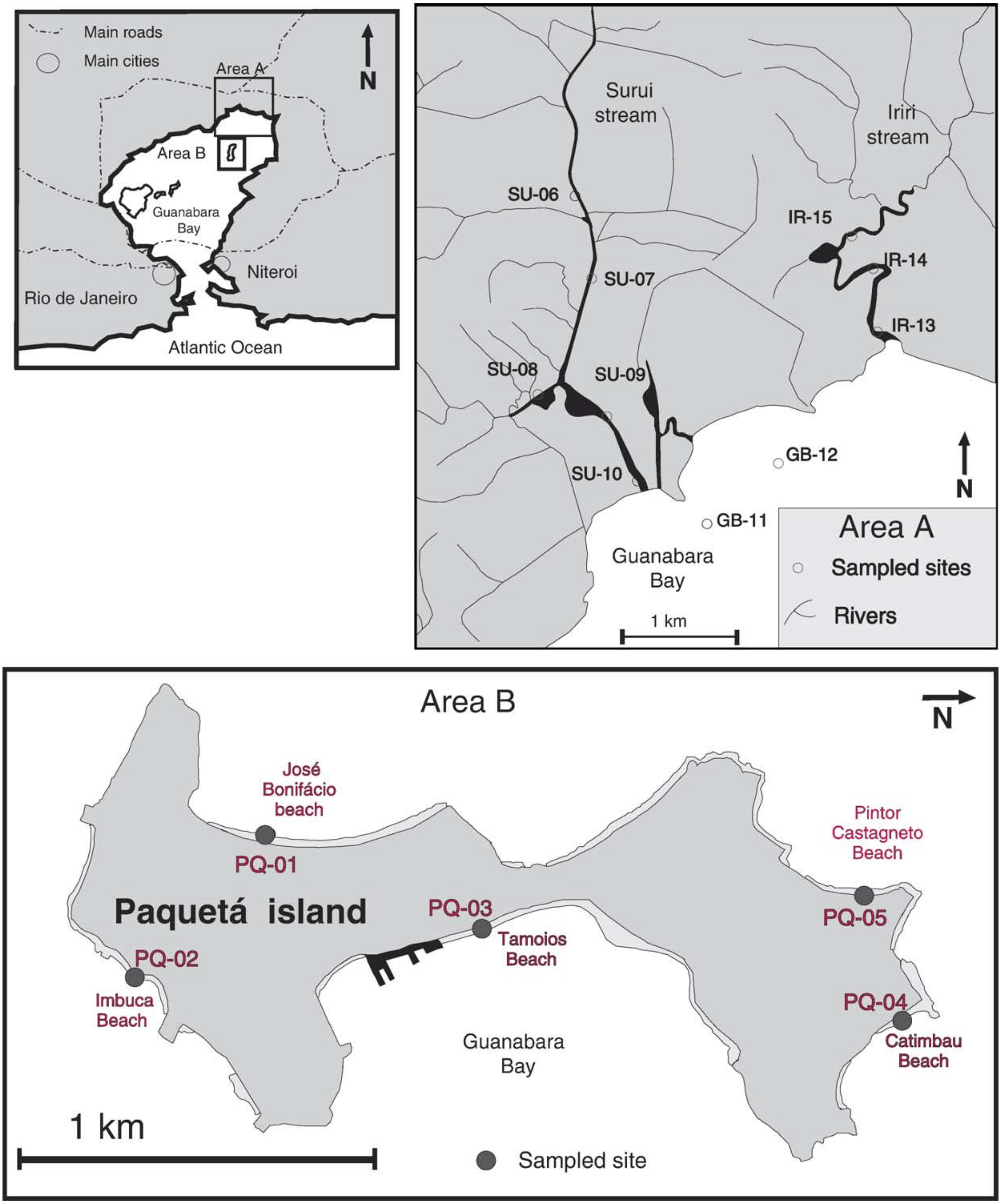

Fig. 1. Location map of the Guanabara Bay and cities of Rio de Janeiro and Niteroi, SE Brazil. Area A: NE sector of the Guanabara Bay. Area B: Paquetá Island.

Table 1
Pb isotope and concentration results of sediments from Guanabara Bay (GB), Surui and Iriri streams (SU and IR) and Paquetá Island (PQ)

Sample	207/206	208/206	Pb (ppm)
PQ01	0.8511	2.1047	38
PQ02	0.8566	2.1216	24
PQ03	0.8680	2.1256	65
PQ04	0.8620	2.1086	86
PQ05	0.8666	2.1317	340
SU06	0.8636	2.1332	49
SU07	0.8651	2.1424	13
SU08	0.8583	2.1140	12
SU09	0.8687	2.1430	27
SU10	0.9153	2.1422	82
GB11	0.8652	2.1309	66
GB12	0.8572	2.1139	47
IR13	0.8619	2.1209	17
IR14	0.8588	2.0792	18
IR15	0.8646	2.1330	39

The studied samples have been chosen in the NE sector of the Bay (Fig. 1), including the Surui (samples SU-06, SU-07, SU-08, SU-09 and SU-10) and Iriri rivers (IR-13, IR-14 and IR-15); bay area (GB-11 and GB-12) and Paquetá Island (PQ-01, PQ-02, PQ-03, PQ-04 and PQ-05). Sample preparation included: (a) drying and granulometric separations; (b) weighting and oxidation of organic material; (c) sequential extraction procedure using nitric acid at 0.1 N, 0.2 N, 1.0 N and 2.0 N obtaining respectively the leaching solutions L1, L2, L3 and L4; (d) leaching solution analysis for Pb concentration (Atomic Absorption) and Pb isotope compositions (ICP-MS).

3. Results

Anomalous Pb concentrations were found in part of the samples. Pb values in sediments vary from 12 ppm to 340 ppm and are consistent with data reported in the literature (40–117 ppm according to Rego et al., 1993). The Pb isotopic compositions were carried out only in the L3 leaching of the finest fraction (<0.12 mm) of each sample because these solutions presented the highest Pb concentration from all leaching. The Pb isotope ratios $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ (Table 1) show a variation from 0.851 to 0.915 and from 2.079 to 2.143, respectively. When plotted in the $^{207}Pb/^{206}Pb$ versus $^{208}Pb/^{206}Pb$ diagram, the data define a linear trend interpreted as a mixture of different sources of Pb (Fig. 2).

The four sites of sampling define different Pb signatures. In the case of the Surui and Iriri rivers, Pb

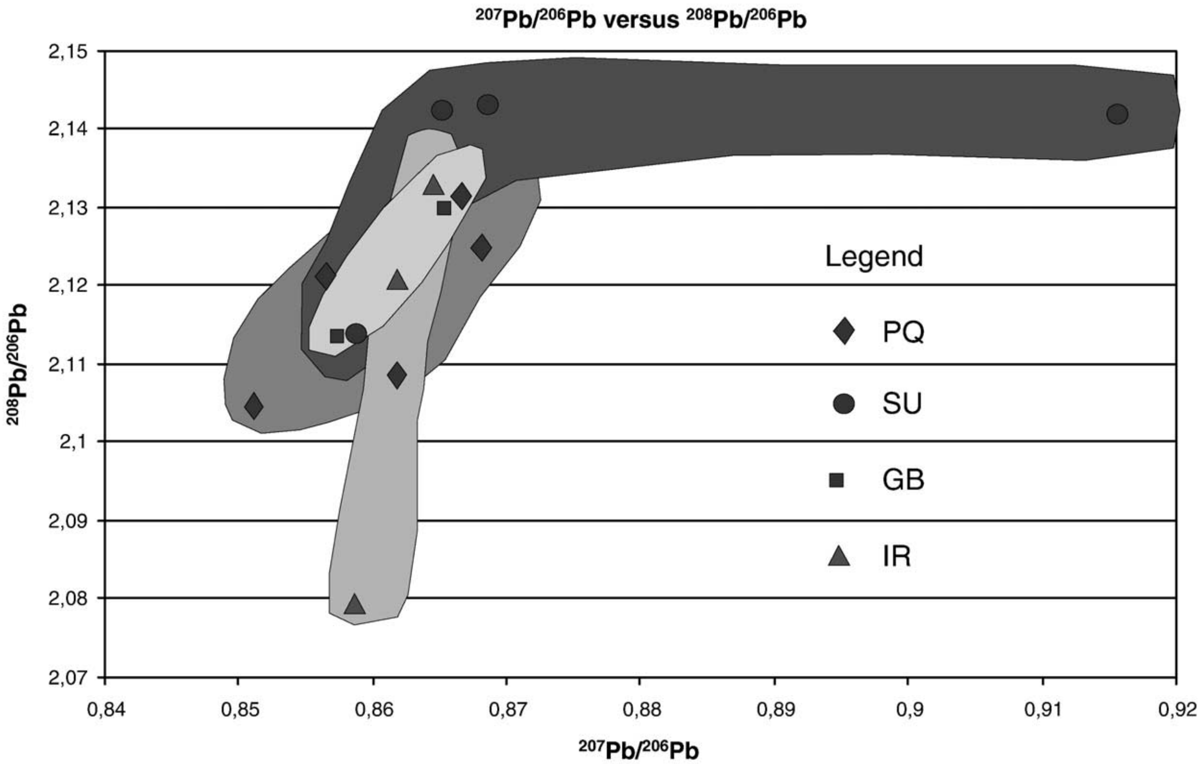

Fig. 2. $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ diagram of the samples: GB = Guanabara Bay; IR = Iriri river; SU = Surui river, and PQ = Paquetá island.

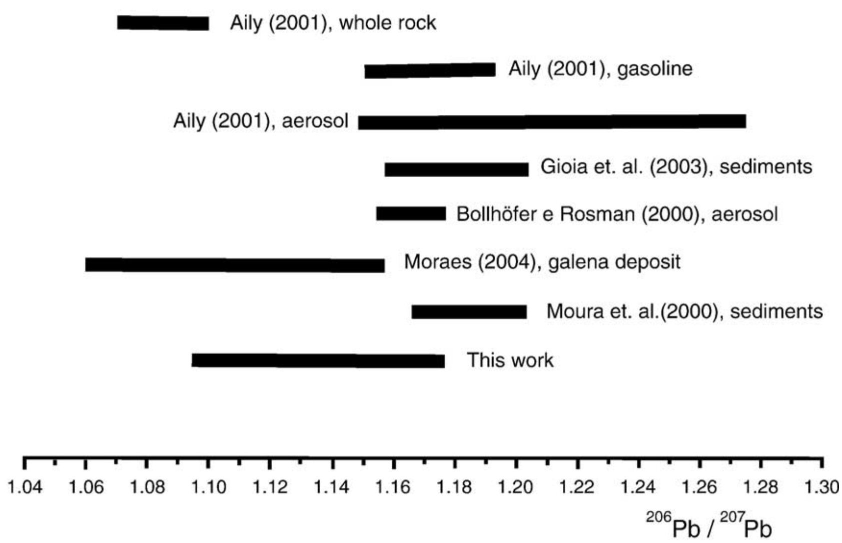

Fig. 3. $^{206}Pb/^{207}Pb$ ratios obtained in this study and from the literature (Aily, 2002; Bollhöfer et al., 1999; Moraes et al., 2004).

isotope values indicate different signatures and may be interpreted as a contamination by two different pollutant sources and samples SU-10 and IR-14 define possible end members. Without these points, the two rivers show similar Pb signature and may be interpreted as result of a unique anthropogenic source. In addition, the Pb signature of the sediments collected in the Paquetá Island are similar to the signature of the sediments of the Guanabara Bay, but high values of Pb concentration may suggest a third source within the island.

Pb isotope compositions of the samples collected in bay bottom (GB-11 and GB-12) present a coincident area in the plot of the diagram (Fig. 2). If we take into account samples SU-10 and IR-14, the samples GB-11 and GB-12 may represent the result of the mixing environment represented by the waters of Guanabara Bay where Iriri and Surui river get together. Corroborating this hypothesis, the Pb signature of the samples collected in the Guanabara Bay coincides with the signature of the Surui and Iriri sediments with tidal influence.

The $^{206}Pb/^{207}Pb$ values ranging from 1.092 to 1.151 presented here can be compared to the anthropogenic signatures reported in other investigations in Brazil (Fig. 3). Two studies using Pb isotope signatures of aerosols have been reported: The first study (Bollhöfer and Rosman, 2000) reported aerosols Pb signatures from Brazil (9 samples), Argentina (3 samples) and Chile (9 samples) and show $^{206}Pb/^{207}Pb$ values from 1.147 to 1.177. Studies on the Pb isotope composition of the São Paulo city atmosphere (Aily, 2002), collected daily during 14 months (August 1999–September 2000), indicated $^{206}Pb/^{207}Pb$ values from 1.142 to 1.273. The values are related to contribution of Pb additives and industrial activities. In addition, investigations on Pb isotopes analysis in mining waste (galena massive vein hosted in Neoproterozoic carbonates), and river channel sediments in a transect downstream from the mine dump, identified the mines as a highly pollutant (Moraes, 1997). Pb isotope studies in sediments are reported also in Brasilia (DF) and Belém (PA) where $^{206}Pb/^{207}Pb$ values range respectively between 1.1526 and 12028 (Gioia et al., 2003) and between 1.1622 and 1.2031 (Moraes et al., 2004) and characterize anthropogenic sources interpreted as sewage and industrial polluters.

4. Conclusion

The Pb isotope data obtained from sediments collected in Guanabara Bay area here reported are coherent with a hydrodynamic model where two active Pb pollutants (represented in the sediments of Surui and Iriri rivers) are transported along the fluvial waters and are mixed within the waters of the Guanabara Bay. In addition, the Pb signature of the sediments collected in the Paquetá Island are similar to the signature of the sediments of the Guanabara Bay, but high values of Pb concentration may suggest a third source present within the island or reconcentration process associated to mineralogical variations, local hydrodynamic or sedimentologic processes. The $^{206}Pb/^{207}Pb$ values presented here range from 1.092 to 1.151 and are similar to galena deposits suggesting Brazilian ore origin.

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