

# SOURCES OF POLLUTANTS IN THE NORTHERN/NORTHEAST AREA OF GUANABARA BAY (SE, BRAZIL) SINCE THE LATE NINETEENTH CENTURY USING LEAD ISOTOPES AND METAL CONCENTRATIONS

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#### Abstract

The coastal areas, the most populated regions in the world, are those which have undergone the greatest human influence. In Brazilian southeastern coast, the region around Guanabara Bay (GB) is one of the most densely populated, with large cities, such as Rio de Janeiro and Niteroi, and is highly industrialized. Due to anthropic activities tones of effluents, waste and sewage is daily released in GB. Despite, several works have been performed aiming to study the current and past human influence in GB, the sources of pollutants that have impacted this bay since the late nineteenth century. This work is a new contribution aiming to identify the main sources of pollution in the northern/northeast region of GB using stable isotopes of lead (Pb) and metal concentrations during the last decades. It analyses results obtained along the core T3 collected in the northeast region of Guanabara Bay, near the Guapimirim Environmental Protected Area (known as Apa de Guapimirim), a mangrove fringe. Twenty-two sediment samples collected along this core were submitted to grain size, total organic carbon content (TOC), elemental concentrations (Ag, Ca, Cu, P, Pb, S and Zn) and stable isotopes of lead (Pb) analyses. The sediment accumulation

#### 1. Introduction

Stable isotopes of lead (<sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb, <sup>208</sup>Pb) are generated from decay of <sup>238</sup>U (<sup>206</sup>Pb), <sup>235</sup>U (<sup>207</sup>Pb) and <sup>232</sup>Th (<sup>208</sup>Pb) isotopes (Faure, 1986; Turekian and Holland, 2013).

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rate was estimated by <sup>210</sup>Pb. Results of core T3 were compared with similar data acquired in core T8, collected in Guanabara Bay, at north of Paquetá island. The comparison of the geochemical results allowed to verify that both cores recorded the same reality. Previous works have shown that the northern/northeast region of Guanabara Bay is low polluted by metals, however, since the ≈1950 a marked increase in eutrophication and metal contamination and another noticeable pulse after  $\approx$ 1970, were recorded in both cores studied in this work. The 206Pb/207Pb values suggest that the main source of pollutants to northern/northeast region of GB since the second half of the 20th century have been related to deforestation and landfill and embankment engineering works preformed around the GB, in addition to mineral products applied in industrial goods, as well as oil, agricultural and organic loads.

Keywords: Metal Concentrations. Pb isotopes. Contamination. Pollutant sources. Coastal area. Anthropogenic record.

The <sup>204</sup>Pb, originated during the solar system formation, is the only natural radioactive isotope considered stable (Austin, 2005). It is therefore used as a reference for the standardization of other isotopes of this element



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( $^{206}Pb/^{204}Pb$ ,  $^{207}Pb/^{204}Pb$  and  $^{208}Pb/^{204}Pb$ ) due to its long half-life (>1.4 x 10<sup>17</sup> years; Machado et al., 2004).

According to Oh et al. (2004) and Duzgoren-Aydin and Weiss (2008), the isotopic composition of a lead ore is dependent on the original concentrations of Pb, U and Th, and the age of deposition. The industrial materials of this ore carry its isotopic signature. Similarly, lead in several nonmineral materials, such as coal and soil, also has a particular isotopic composition due to the presence of U and Th (Bacon et al., 2006; Tserenpil et al., 2016). Thus, lead released into the atmosphere by combustion, melting and other processes keeps the original isotopic composition (Doucet and Carignan, 2001; Clarke et al., 2004; Simoneit et al., 2004). Since, the normal chemical and physical processes do not affect the original isotopic composition, it is possible to estimate Pb sources in aerosols through isotopic composition analysis (Komárek et al., 2008; Widory et al., 2010).

Environmental studies conducted since the 1960s demonstrated the applicability of lead isotopic ratios in pollution assessment, since Pb scattered in the environment, from natural or anthropic processes, has the same isotopic characteristics of the source material (Patterson, 1965; Bindler, 2011; Ignacio et al., 2019; Potratz et al., 2019). Thus, the isotopic composition of Pb in a contaminated environment will be identical to that of the contaminating source (isotopic signature), allowing its identification when the isotopic compositions of different materials that compose a certain area of study are well known (e.g., Chow and Patterson, 1962; Patterson and Hirao, 1974; Shirahata et al., 1980). As the natural environment (bay or river) is submitted to the influence of several natural and anthropogenic sources, it is necessary to discriminate isotopically all possible and most important sources of lead, so that calculations of mass balance allow to characterize the contribution of each one and to separate the natural lead from the anthropogenic one (e.g., Bacon et al., 1995, 1996, 2006; Farmer et al., 1996, 2002; Shotyk et al., 1998; Weiss et al., 1999; Kaste et al., 2003; Watmough et al., 2004; Le Roux et al., 2005; Steinnes et al., 2005; Graham et al., 2006; Cloy et al., 2008).

Recent studies of lead isotopes have shown that it is possible to trace their origin in several environments, such as water and sediments of rivers, lakes, oceans, aerosols, lichens and mosses, rainwater, and fuels such as alcohol, gasoline and diesel (Babinski et al., 2005; Díaz Morales, 2019a; Ignacio et al., 2019; Potratz et al., 2019). Its most common applications to identify sources of pollution have been focused on surface water, groundwater, atmosphere and soil surface layers (e.g. Gulson et al. 1992; Rosman et al. 1994; Kober et al. 1999; Miller et al. 2002, 2005; Bollhöfer et al. 2005; Leybourne et al., 2009; Souza et al., 2017).

Sedimentary records collected in calm environments of bays and lakes naturally concentrate fine sediments and organic matter (Borges and Nittrouer, 2016; Delavy et al., 2016; Laut et al., 2016, 2019; Dias et al., 2017; Alves Martins et al., 2018; Pregnolato et al., 2018). These materials have great affinity to heavy metals (Alves Martins 2015; Martins et al., 2015, 2017; Suzuki et al, 2016; Zaaboub et al., 2016; Díaz Morales et al., 2019b) and can provide temporal information regarding the beginning of anthropic influence in the environment (Vilela et al., 2014; Bueno et al., 2019), which is one of the objectives of this research.

Ferrand et al. (1999), analyzing stable isotopes of lead in 24 cores (0-50 cm) of several transects in the Gulf of Lion (France), observed that lead concentrations (23-85 ppm) and isotopic signatures  $^{206}$ Pb/ $^{207}$ Pb (1.174 – 1.188) in the surface sediments, clearly evidenced the impact of polluting lead, which contributed for 22-80% of the lead accumulated in the first centimeter of the sediments in the studied sites.

Desenfant et al. (2006) reconstructed the transport of pollutant Pb and its entry into the Caribbean basin in relation to past weather changes and industrial activities, based on geochemical data obtained from massive corals collected in 1998 in Mona Island. A striking relationship was found between the isotopic impressions of lead and the North Atlantic oscillation index for two specific periods (1914-1929 and 1965-1997), characterized by distinct isotopic signatures of the main pollutant emitter of Pb to the North Atlantic troposphere, North America and Western Europe (Nriagu, 1990). Thus, variations of radiogenic isotopes can provide independent and useful information in studies of sedimentary and environmental geology, being useful to: i) investigate the sources and transport of dissolved and particulate materials in the hydrological, sedimentary and biogeochemical cycles in ecosystems; ii) to reconstruct temporal changes in the ocean water chemistry and; iii) to point out changes in studies of stratigraphic correlation.

Several studies investigated long-term trends both in water (e.g., Mayr, 1998; Paranhos et al., 1995; Contador and Paranhos, 1996) and in sediment records (e.g. Barth et al., 2004; Pereira et al., 2007; Borges e al., 2009; Vilela et al., 2014; Baptista Neto et al., 2017) of negative impacts in Guanabara Bay. However, the main determinant sources of pollutants for the north/northeastern area of GB, which is considered less polluted by metals (Baptista Neto et al., 2006; Potratz et al., 2019) during the last decades are not yet known.

The main aim of this work is to find geological records of the anthropic influence in Guanabara Bay (SE, Brazil), including increasing of organic matter and contamination by metals, in two cores collected in the innermost northern/northeast region of this coastal system. It also intends to identify sources of pollutants using lead isotopes.

### 1.1 Study Area

Guanabara Bay (southeastern Brazil) is located between the latitudes 22°24' and 22°57 'S and longitudes 42°33' and 43°19' W. It practically encompasses the entire metropolitan

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region of Rio de Janeiro and, despite being of incontestable historical, economic, cultural, scientific, social and environmental importance, it is one of the most degraded coastal environments in the country (Baptista Neto et al., 2013). It is a complex ecosystem which includes for instance forests, mangroves, marshes, wetlands, lagoons, dunes, beaches, rivers, estuaries, coves, islands, slabs, pinnacles, rocky outcrops and cliffs (Amador, 1997).

Guanabara Bay has approximately 381 km<sup>2</sup> of surface or water mirror, carrying a volume of  $\approx$ 3 billion cubic meters of water (Amador, 1997). It measures 28 km long in a northsouth direction and a maximum east-west width of 27 km. The depth reaches a maximum of 50 meters near the entrance and an average of 7.6 meters. The main channel, in a north-south direction, measures approximately 20 km in length, with an average depth of 15 to 20 meters and a width of 3 km (SEMADS, 2001). Its internal area is shallower with depths <3.0 m near the margins. GB has a narrow entrance of about 1.6 km wide (Kjerfve et al., 1997). The lower stretches of many rivers have been modified since the late nineteenth and early twentieth centuries through drainage works performed by federal, state and municipal public agencies.

Situated in the middle of an intertropical area and squeezed between sea and mountain, the climate of the region is generally hot and humid. The annual average temperature is  $\approx 24^{\circ}$ C, reaching maximum values >40 °C. The average annual total precipitation ranges between 1,000 and 1,500 mm. In winter there is a tendency for a dry season, while summer is characterized by torrential rain.

The factors that determine the circulation pattern in Guanabara Bay are: tidal range, coastal morphology, bathymetry (Catanzaro et al., 2004), wind regime and freshwater input from river basins. Circulation governed by tidal ebb and flow is predominant, with a semi-diurnal regime (INEA). Because the bottom topography, it has in its central part a natural deeper channel; the flow is all induced to this area, generating more intense currents (INEA). In the innermost part of the Bay, where the depths are lower, there is a progressive loss of currents velocity, causing a mixture of oceanic and inland waters.

Around the Bay live about 10 million inhabitants distributed among 16 municipalities: Duque de Caxias, Mesquita, São João de Meriti, Belford Roxo, Nilópolis, São Gonçalo, Magé, Guapimirim, Itaboraí, Tanguá and partially Rio de Janeiro, Niterói, Nova Iguaçu, Cachoeiras de Macacu, Rio Bonito and Petrópolis. The 4,081 km<sup>2</sup> river basin houses 25 basins and sub-basins, considered the most representative, whose main waterways carry most of the pollution generated on the mainland to the Bay.

The anthropic impact in this bay reflect different stages of industrial expansion, with the larger development of the urban-industrial occupation in the last decades which has been triggering a progressive and marked environmental degradation (Amador, 1997; Barth et al., 2004; Pereira et al., 2007; Vilela et al., 2014; Baptista Neto et al., 2017). Its landscape of tropical paradise was altered, initially with the exploration of Brazil wood, then with its occupation and defense, that would lead to the creation of the City of São Sebastião do Rio de Janeiro by the Portuguese colonizers, ongoing with the economic cycles of sugarcane, mining, coffee and, lastly, industrialization (Amador, 1997).

Nowadays, Guanabara Bay holds the country's second industrial park, an exceptionally large refinery (REDUC), two commercial ports (Rio de Janeiro and Niterói), 16 maritime oil terminals and 12 shipyards, all of which are major sources of pollution. Guanabara Bay produces 18.6 m<sup>3</sup>/s of raw sewage from  $\approx$ 9 million inhabitants, and 470t of organic load, 64t of industrial waste, 0.3t of heavy metals, 7t of oil and 6t of garbage are dumped daily. The main sources of pollution are the 6,000 industries. In Guanabara Bay, approximately 13,000 t/day of garbage is generated, and 4,000 t/day is not collected, being leaked on vacant lots, rivers and canals.

# 2. Materials and methods

### 2.1 Cores location

This study analyses grain size and geochemical results obtained in cores T3 (Latitude 22°41'10" S, Longitude 43°04'7.9" W, 1 m deep; 197 cm long) and T8 (Latitude 22°44'28" S, Longitude 43°06'45" W, 4 m deep; 242 cm long) collected in the north-northeast part of Guanabara Bay (SE, Brazil; Fig. 1). These cores were collected in 2001 by percussion drilling using PVC pipes (7 cm in diameter), by a team from the Marine Geology Laboratory of Universidade Federal Fluminense (LAGEMAR/UFF, Rio de Janeiro State, Brazil).

Core T8 also was previously studied by Vilela et al. (2014) for TOC and foraminifera content and Baptista Neto et al. (2017) comparing foraminifera, pollen, TOC and metals, for paleoenvironmental reconstruction for the last 5000 years. This work mostly compares results of the upper 197 cm of cores T3 and T8 and analyses stable isotopes of lead and geochemical data (TOC and elemental concentrations) aiming to identify the main sources of pollution in the N/NE area of GB, since the late nineteenth century.

Core T3 was retrieved near the Guapimirim Environmental Protected Area (known as Apa de Guapimirim), a mangrove fringe where several rivers flow, and close the Iriri river mouth, a meandering river with low competence to transport sediment (Fig. 1). Core T8 was recovered at north of the Paquetá island (Fig. 1), in an area protected from strong hydrodynamics caused by cold fronts that sometimes reach Guanabara Bay (GB) from south to north, acting very effectively on their water and sediment dynamics. For this work, along the cores T3 and T8 were collected 22 and 20 samples, respectively, of 2 cm thicknes Baptista Filho et al.





Fig. 1. Location of the studied cores T3 and T8, in Guanabara Bay (SE, Brazil). Adapted from a satellite image of NOOA.

### 2.2 Sediment grain size and geochemical analysis

Particle size analysis was carried out using a Malvern Mastersizer Microplus MAF 5001 of the Laboratory of Particulate Systems, of PEQ/COPPE/UFRJ, which determines the distribution of particle sizes in the diameter range 0.5-550  $\mu$ m. This analysis provides the relative abundance of particles for size classes and statistical sedimentological parameters such as the sediment mean grain size.

Total organic carbon content was determined in each sample using the CS infrared analyzer (model Eltra Metalyt 1000CS) from the Leibniz Institute for Baltic Sea Research Warnemünde, Germany.

Elemental concentrations and lead isotopes were analyzed in the section 1-197 cm, of cores T3 and T8. Elemental concentrations (Ag, Ca, Cu, P, Pb, S and Zn) were determined in fine fraction (sediment fraction <0.062 mm) according to the methodology described by Baptista Neto et al. (2017). Samples were digested with aqua regia under pressure using a Perkin Elmer microwave digestion system (USEPA 3051a). Elemental analysis was carried out using a Perkin Elmer Analyst 200 atomic absorption spectrophotometer. Sample blanks and a reference sediment WQB-1 from the National Laboratory for Environmental Testing, Burlington, Canada, were used at regular intervals to monitor quality control.

A concentration factor was estimated for the analyzed elements by dividing the concentration of each element ( $C_{metal}$ ) in the sediments of the studied cores by the respective baseline concentration ( $C_{baseline}$ ), proposed by Pinto et al. (2019):

$$CFmetal = \frac{C_{metal}}{C_{baseline}}$$

Lead isotopes were analyzed in 42 layers of core T3 (22 samples) and core T8 (20 samples). About 2 grams of the sediment fraction <0.062 mm was sent to the Activation Laboratories LTD, in Ontario, Canada. The analyzes, with the error calculated in duplicate and using the reference NIST981 for calibration, followed the following steps: (i) Total digestion of the sediment sample using nitric, hydrochloric, hydrofluoridic and perchloric acids; (ii)

Determination of concentrations using the Plasma Induction Mass Spectrometry (ICP-MS) for the elemental concentration analysis and; High-resolution Plasma



# Induction Mass Spectrophotometer (HR ICP-MS) for lead isotopes, in the samples with lead concentrations $\geq$ 15 mg kg<sup>-1</sup>.

## 2.3 Age control

The age control in core T3 was based on <sup>210</sup>Pb data activities, determined by gamma-ray spectrometry, by collecting sediment samples at  $\approx$ 5 cm intervals down to a depth of 180 cm. Gamma-ray measurements were performed using a semi-planar intrinsic germanium high purity coaxial detector with 40% efficiency. This was housed in a lead shield and coupled to a multichannel analyzer. Activity was calculated according to Patchineelam and Smoak (1999). The sedimentation rate was calculated by dividing the <sup>210</sup>Pb decay constant by the slope of the log-linear plot of unsupported <sup>210</sup>Pb *versus* depth (Appleby and Oldfield, 1992).

## 2.4 Statistical Analyses

Elemental concentrations, TOC contents and  $^{206}Pb/^{207}Pb$  values obtained along the cores T3 and T8 were transformed by log (x + 1) and submitted to Principal Components Analysis (PCA). The PCA was carried out aiming to explain the variance-covariance structure of the studied data and to select the principal components with the largest variance. Pearson correlations between the analyzed variables also were determined. These statistical treatments were performed using a Statsoft software (Statistica 12). Depth plots and bi-plots and linear regression lines and respective R<sup>2</sup> were performed with the Microsoft Excel software.

# 3. Results

# 3.1 Age model

According to the results presented in Fig. 2, the sediment accumulation rate of core T3 is 0.67 cm yr<sup>-1</sup>, between the top and level of 70 cm. Based on <sup>210</sup>Pb geochronology we can estimate that the section below 150 cm was deposited before 1900 AD (AD: *Ano Domine*), between 75-0 cm was deposited after ≈1950 AD; the section between 45-0 have sediments deposited after ≈1970 AD.

# 3.1 Sediment Mean Grain Size and Total Organic Carbon

Both T3 and T8 cores are essentially fine-grained sequences. Core T3 is composed by a muddy sedimentary sequence, with sediment mean grain size (SMGS) ranging from 5.4-8.3  $\Phi$  (Table 1). Small oscillations of SMGS around the mean value (7.0±0.6  $\Phi$ ) are observed along this core. In core T8, SMGS is more variable ranging from 0.6 to 9.9  $\Phi$  (mean 5.4±2.7  $\Phi$ ) (Table 1).

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Total organic carbon (TOC) content (Table 1 and Fig. 3) varied in core T3 between 1.0-5.8 % (mean  $3.2\pm1.6$  %) and in core T8 between 1.4-5.4 % (mean  $3.4\pm1.2$  %). In both cores, TOC values are lower in the section below 80 cm and increase progressively to the top until reaching values >5% (Fig. 3).



**Fig. 2.** Estimated sediment accumulation rate for core T3, based on  $^{210}$ Pb. The trend lines for two sections of this core are represented in dash red. The R<sup>2</sup> of the upper section trend line and the estimated sediment accumulation rate are presented.

## 3.2 The isotopic signature of Pb in sediments

Lead isotope data of cores T3 and T8 were included in Table 2 and Appendix 1. The  $^{206}Pb/^{207}Pb$  ratios oscillated in core T3 between 1.15 and 1.20 (mean 1.18) and in core T8 from 1.14 to 1.20 (mean 1.17). The depth plots of  $^{206}Pb/^{207}Pb$  ratios along the cores T3 and T8, presented in Fig. 3, show that these ratios tend to decrease in the upper sections of both cores.

## 3.3 Elemental concentrations along the cores T3 and T8

The results of elemental concentrations (Ag, Ca, Cu, P, Pb, S and Zn) in cores T3 and T8 are presented in Table 3. In core T3 they ranged for: Ag from 0.29-1.60 mg kg<sup>-1</sup> (mean 0.47 mg kg<sup>-1</sup>); Ca from 0.41-2.30 % (mean 1.11 %); Cu from 12-70 mg kg<sup>-1</sup> (mean 37 mg kg<sup>-1</sup>); P from 0.067-0.132% (mean 0.080%); Pb from 16-73 mg kg<sup>-1</sup> (mean 48 mg kg<sup>-1</sup>); S from 0.75-1.61 % (mean 1.03 %) and; Zn from 71-238 mg kg<sup>-1</sup> (mean 146 mg kg<sup>-1</sup>).



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In core T8 the elemental concentrations ranged for: Ag from 0.29-1.80 mg kg<sup>-1</sup> (mean 1.07 mg kg<sup>-1</sup>); Ca from 0.41-2.49 % (mean 1.16 %); Cu from 11-84 mg kg-1 (mean 54 mg kg<sup>-1</sup>); P from 0.0670-0.1510% (mean 0.1011%); Pb from 14-70 mg kg-1 (mean 50 mg kg-1); S from 1.00-1.70 % (mean 1.46 %) and; Zn from 68-248 mg kg<sup>-1</sup> (mean 190 mg kg<sup>-1</sup>).

Tab. 1. Sediment mean	grain	size ( $\phi$ )	and	total	organic	carbon
(TOC; %) along the cores	s T3 a	nd T8. S	D –	Stand	ard devia	ation.

	Sedime	ent Mean	Total Organic		
Depth	Grain	Size (Φ)	Carbon (TOC; %)		
(cm)	Core	Core	Core	Core	
4	T3	T8	T3	<u>T8</u>	
1	/.1	/.6	5./	4.6	
3	7.5	8.6	5.8	5.4	
5	6.9	8.1	4.8	4.9	
7	6.7	6.8	4.8	4.3	
9	7.2	7.1	4.5	5.4	
15	7.1	8.9	4.8	5.1	
21	7.5	7.5	4.4	5.1	
25	7.3	9.9	4.2	4.5	
31	6.9	5.1	4.9	4.4	
35	6.8	9.5	4.4	3.9	
41	6.6	7.4	4.5	3.6	
45	6.9	6.2	3.8	3.9	
51	6.7	5.5	3.9	4.2	
61	8.1	5.5	3.0	3.5	
71	8.3	0.7	3.7	3.0	
81	6.8	3.2	1.8	2.4	
91	7.4	0.8	1.5	2.5	
101	7.0	1.4	1.6	2.6	
111	6.4	0.6	1.6	1.4	
121	7.6	2.5	1.3	2.7	
131	7.0	4.8	1.2	2.6	
141	5.8	5.0	1.0	2.1	
151	5.4	4.4	1.3	2.2	
161	7.6	3.9	1.5	2.3	
171	6.3	4.9	1.9	2.2	
181	6.4	5.5	2.0	2.2	
197	6.8	5.6	1.9	2.2	
Maximum	8.3	9.9	5.8	5.4	
Minimum	5.4	0.6	1.0	1.4	
Mean	7.0	5.4	3.2	3.4	
SD	0.6	2.7	1.6	1.2	

The depth plots for the analyzed chemical elements are presented in Fig. 4. This figure shows that concentrations of Ag, Cu, P, Pb, S and Zn are relatively low in the lower section of the analyzed cores and increase significantly in the upper 80 cm. Calcium contents have an opposed pattern, decreasing in the upper section of these cores. These trends are more marked in core T8, where Ag, Ca, Cu, P, S and Zn reach higher maximum and mean concentrations than core T3. Depth plots of CF of the analyzed elements (Ag, Ca, Cu, P, Pb, S and Zn) along the cores T3 and T8 also evidence similar trends (Fig. 5).

Tab. 2. Results of  $^{206}$ Pb/ $^{207}$ Pb along the cores T3 and T8.

Depth	Core T3	Core T8
(cm)	<sup>206</sup> Pb/ <sup>207</sup> Pb	<sup>206</sup> Pb/ <sup>207</sup> Pb
1	1.18	1.16
5	1.16	1.16
9	1.15	
13	1.16	1.16
17	1.17	1.16
21	1.17	1.16
25	1.17	1.15
29	1.18	1.16
33	1.15	1.17
37	1.17	1.16
41	1.16	1.17
45	1.18	
49	1.17	1.16
53	1.20	1.15
57	1.19	1.14
61	1.20	1.17
65	1.17	1.17
69	1.19	1.17
81	1.19	1.18
97	1.20	1.18
145	1.20	1.20
197	1.20	1.20
Maximum	1.20	1.20
Minimum	1.15	1.14
Mean	1.18	1.17

# 3.4 Statistical results

The results of the PCA based on <sup>206</sup>Pb/<sup>207</sup>Pb values and TOC and elemental concentrations (Ag, Ca, Cu, P, Pb, S and Zn) in cores T3 and T8 is presented in Fig. 6 and Table 4. Factor 1 (71%) and Factor 2 (14%) explain most part of data variability (85%). The biplot of Factor 1 versus Factor 2 evidence that, in both cores <sup>206</sup>Pb/<sup>207</sup>Pb and Ca (Group I) are opposed to the enrichment of Ag, Cu, P, Pb, S and Zn and TOC (Group II).

This relationship is also evidenced by Pearson correlations (Appendix 2): the analyzed chemical elements have significant positive correlations with each other and TOC, in both cores, except with Ca and <sup>206</sup>Pb/<sup>207</sup>Pb values. The depth plots presented in Figs. 3-5 and the statistical



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results evidence that core T8 has similar geochemical results in the analyzed section (0-197 cm) to core T3.

## 4. Discussion

The accumulation rate recorded in core T3 (0.67 cm yr<sup>-1</sup>) is the same determined by Baptista Neto et al. (2013) in a core collected near this one and is higher than that reported by Amador (1980) and Godoy et al. (1998), of 0.19 cm yr<sup>-1</sup>, due to its location near the river Iriri outflow and others

rivers mouth at the Apa de Guapimirim. This accumulation rate is also higher than that estimated by Peixoto (2005) for Guarapina lagoon (in Rio de Janeiro State) of 0.27 cm yr<sup>-1</sup>. Amador (1980) reported sediment accumulation rates for two periods comparing nautical charts, for the bathymetric range of 5 to 10 m (close to the area where the core T8 was collected). This author calculated silting rates of 15.1 cm.100 yrs<sup>-1</sup> and 41.6 cm.100 yrs<sup>-1</sup> for the periods 1849-1922 and 1938-1962, respectively. These values indicate a tendency to increase the accumulation rate toward the recent.

Tab. 3. Elemental concentrations (Ag, Ca, Cu, P, Pb, S and Zn) in cores T3 and T8.

Core T3							
Depth	Ag	Ca	Cu	Р	Pb	S	Zn
(cm)	mg kg-1	%	mg kg-1	%	mg kg-1	%	mg kg-1
1	1.60	0.62	70	0.132	62	1.21	238
5	0.70	0.41	61	0.100	60	1.61	232
9	0.70	0.49	65	0.078	63	1.30	207
13	0.80	0.64	60	0.083	65	1.41	200
17	0.70	0.50	67	0.080	65	1.32	210
21	0.50	0.54	59	0.077	65	1.17	190
25	0.50	0.62	70	0.080	70	1.25	202
29	0.29	0.44	39	0.075	65	1.18	178
33	0.60	0.64	36	0.083	73	1.11	183
37	0.40	0.73	61	0.082	73	1.02	194
41	0.29	0.72	46	0.077	64	0.92	169
45	0.29	1.74	25	0.073	52	0.91	106
49	0.29	1.51	21	0.078	45	0.78	107
53	0.29	1.60	19	0.079	39	0.86	97
57	0.30	1.60	18	0.073	30	0.76	82
61	0.29	1.41	15	0.077	27	0.77	90
65	0.29	1.87	21	0.078	40	0.75	107
69	0.29	1.24	16	0.075	33	0.80	94
81	0.29	1.72	15	0.072	16	0.93	83
97	0.40	1.65	12	0.069	17	0.84	82
145	0.29	1.52	16	0.067	16	0.82	79
197	0.29	2.30	12	0.069	16	0.99	71
Maximum	1.60	2.30	70	0.132	73	1.61	238
Minimum	0.29	0.41	12	0.067	16	0.75	71
Medium	0.47	1.11	37	0.080	48	1.03	146
			Core	Т8			
Depth	Ag	Ca	Cu	Р	Pb	S	Zn
(cm)	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
1	1.60	1.36	84	0.1510	70	1.54	229
5	1.60	1.10	73	0.1470	58	1.37	225
13	1.50	0.78	75	0.1210	52	1.50	238
17	1.50	0.82	60	0.1080	49	1.61	218
21	1.80	0.76	68	0.1210	56	1.60	245
25	1.60	0.77	74	0.1140	54	1.65	248



Core T8							
Depth	Ag	Ca	Cu	Р	Pb	S	Zn
(cm)	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
29	1.50	0.85	66	0.1040	52	1.54	234
33	1.70	1.09	72	0.1040	62	1.53	236
37	1.60	0.75	73	0.1050	55	1.68	239
41	1.00	0.41	68	0.0930	52	1.63	236
49	1.10	0.67	72	0.1040	61	1.70	243
53	0.90	0.93	62	0.1080	57	1.65	218
57	0.80	0.90	39	0.0880	64	1.50	191
61	0.60	1.05	41	0.0940	65	1.65	186
65	0.60	1.15	42	0.0890	64	1.55	178
69	0.60	1.36	46	0.0850	66	1.21	140
81	0.29	1.72	15	0.0770	22	1.00	84
97	0.40	2.49	13	0.0710	17	1.00	79
145	0.29	1.89	16	0.0670	15	1.19	73
197	0.50	2.35	11	0.0700	14	1.15	68
Maximum	1.80	2.49	84	0.1510	70	1.70	248
Minimum	0.29	0.41	11	0.0670	14	1.00	68
Medium	1.07	1.16	54	0.1011	50	1.46	190

## Table 3 (cont.). Elemental concentrations (Ag, Ca, Cu, P, Pb, S and Zn) in cores T3 and T8.



**Fig. 3.** Depth plots of TOC (%) and  $^{206}Pb/^{207}Pb$  ratio along the cores T3 and T8. Estimated ages based on  $^{210}Pb$  geochronology are presented. AD – *Anno Domini*. The trend lines and respective R<sup>2</sup> are presented, as well as the mean value for the TOC depth plots are presented in both cores. The section between 80-0 cm has been shaded; it is characterized by the sharp increase in TOC values and decrease of  $^{206}Pb/^{207}Pb$  ratios; these trends also were marked with arrows.





**Fig. 4.** Depth plots of elemental concentrations (Ag, Ca, Cu, P, Pb, S and Zn) along the cores T3 and T8. Estimated ages based on  $^{210}$ Pb geochronology are presented. AD – *Anno Domini*. The regression line and respective R<sup>2</sup> value are also presented. The section between 80-0 cm has been shaded to mark the sharp increase of Ag, Cu, P, Pb, S and Zn concentrations and decrease of Ca concentrations.

The analyzed cores are located in an area of low hydrodynamism (Amador, 1980), where presently tidal currents are not intense, favoring the accumulation of finegrained sediments enriched in organic materials (Delavy et al., 2016; Alves Martins et al., 2018).

Both cores (T3 and T8) have similar distribution patterns of TOC and elemental concentrations and <sup>206</sup>Pb/<sup>207</sup>Pb values. This similarity indicates that both cores although located in distinct areas of Guanabara Bay record the same reality.

# 4.1 Long-term trends of eutrophication in the Northern/Northeast Area of Guanabara Bay

The analyzed cores have TOC contents ranging from 1 to 6% (Table 1). Several studies have shown that organic matter contents in Guanabara Bay vary inversely with the increasing of sediment grain size, that is, where the percentage of sand and gravel tends to decrease towards the interior of the bay, the percentage of organic material tends to increase (e.g. Catanzaro et al., 2004; Alves Martins et al., 2018). According to Catanzaro et al. (2004) percentages of TOC <1% occur in the entrance and central channel of GB, associated to coarser grained sediments, stronger tidal currents and, consequently, greater water oxygenation, which favor organic matter degradation. The high levels of organic matter, such as those presented in the inner part of the bay and in more sheltered areas, are in general related to reducing sedimentary conditions and consequently lower rate of degradation (e.g. Delavy et al., 2016; Alves Martins et al., 2018).

As shown in Fig. 3, TOC contents increased significant and continuously since the 50's in core T3. Similar trend is observed in core T8, corresponding probably to the same period. This trend was attributed to the growing process of eutrophication in protected environments due to anthropic action, which has been causing a progressive and marked environmental degradation.



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Phosphorus is a nutrient which enhances primary production (Pace and Lovett, 2013; Misailidis et al., 2018). The increase in P contents associated with the rising of TOC (Fig. 6), especially since the 50's, may be related to agricultural fertilizers and launching of domestic sewage in GB, enhancing the primary productivity in this ecosystem.

The opposite pattern of Ca and TOC contents should indicate carbonate dissolution (poor preservation) due to the production of acids following organic matter degradation (e.g. Delavy et al., 2016; Martins et al., 2016 a, b). On the other hand, in coastal environments mollusks and foraminifera with carbonate shells and tests are relatively abundant. The reduction of Ca values may also indicate a decline in the presence of these organisms due to processes of oxygen depletion in the bottom water and sediment, due to eutrophication processes (e.g. Delavy et al., 2016; Baptista Neto et al., 2017). In these sediments, it is frequent to observe the presence of living foraminifera with poorly calcified and dissolved tests (Martins et al., 2016 a, b). This means that these organisms have difficulty of calcify their shells and tests in this environment. The presence of high sedimentary organic matter content is being a stressing and unfavorable factor for the life of these protozoans (Martins et al., 2016 a, b) and mollusks as well.

Positive correlations between TOC and S, may suggest the production of sulfides. Pyrite was found in the sediments of the inner area of Guanabara Bay, related to initial processes of diageneses (Pennafirme et al., 2015). Another effect of high accumulation of organic matter in the inner area of GB is the presence of gas seeping (Catanzaro et al., 2004; Delavy et al., 2016). The release of biogenic methane from the sediments was identified in some areas of the northern region of GB (Catanzaro et al., 2004; Delavy et al., 2016).



**Fig. 5.** Depth plots of CF of the analyzed elements (Ag, Ca, Cu, P, Pb, S and Zn) along the cores T3 and T8. Estimated ages based on <sup>210</sup>Pb geochronology are presented for core T3. AD - Anno Domini. The regression line and the respective R<sup>2</sup> value are also presented. The section between 80-0 cm, where the increase or decrease of several CF values is more prominent, has been shaded.





Fig. 6. Biplot of Factor 1 against the Factor 2 of PCA based on TOC, <sup>206</sup>Pb/<sup>207</sup>Pb and (Ag, Ca, Cu, P, Pb, S and Zn) in cores T3 and T8.

# 4.2 Anthropic impact in the Northern/Northeast Area of Guanabara Bay

Depth plots of Ag, Cu, P, Pb and Zn concentrations as well as the CF values (Fig. 5) reveals continuous increases of these metals in the upper sections of cores T3 and T8. The increase in both cores of Cu and Zn, for instance, is positively correlated with Pb (Fig. 7). Similar trends were also observed by Baptista Neto et al. (2013, 2017).

The PCA results presented in Fig. 6 indicate that the metals increase, namely Pb, in both cores is followed by the decreasing of <sup>206</sup>Pb/<sup>207</sup>Pb. The same is indicated by the biplots presented in Fig. 7. The range of <sup>206</sup>Pb/<sup>207</sup>Pb values presented in this work for cores T3 and T8 (Fig. 8) were compared with that obtained in several investigations, such as Geraldes et al. (2006), in addition to the results obtained by Bollhöfer and Rosman (2000), Aily (2001), Moura et al. (2004), Moraes et al. (2004), Gioia et al. (2006) and Saliba et al. (2011). Geraldes et al. (2006) and Saliba et al. (2011) analyzed several surface bottom sediment samples spread along the innermost area of GB, as well as in Suruí and Magé rivers, thus encompassing our area.

According to the information compiled in Fig. 8, rocks and products of mining activity are characterized by lower <sup>206</sup>Pb/<sup>207</sup>Pb values. Based on the results presented in Fig. 9 the anthropic activities left a marked influence characterized by increased TOC and potentially toxic metals concentrations mostly since the second half of the 20<sup>th</sup> century, which agree with the observations of Baptista Neto et al. (2013). Thus, Guanabara Bay, which receives the sediment load from its boundary basin since it functions as a natural space for sediments accommodation, began to receive a much higher sediment load due to anthropic interventions (Baptista Neto et al., 2017).

The occupation of the surroundings and the islands of the Guanabara Bay, characterized by the removal of much of the natural vegetation including that of the Atlantic forest and mangroves may have caused this effect, namely the landfill, both in the islands for the construction of airports, and in the waterfront, such as those carried out from Caju to Copacabana, between 1902 and 1906, and from the 1950s onwards for the construction of Avenida Brazil, Flamengo embankment, Rio-Niterói bridge, Niterói-Manilha highway and Red Line. The filling and retreatment of some river channels, among other interventions, were formally implemented with the "sanitarista" conception in the 18th century and intensified since the beginning of the 20th century. The purpose of such interventions would be to provide support for urban and industrial expansion. However, such expansions eventually became disorganized due to population growth on a geometric scale.

In addition, resulting from the expansion of activities in its surroundings GB also started to receive an increase of domestic waste and sewage and industrial effluents and products, namely mining materials applied in industrial goods as well as oil, metals and organic load (as evidenced by the results of this work; Figs. 3, 4, 5, 7, 9).





Fig. 7. Biplots of lead concentrations *versus* Pb<sup>206</sup>/Pb<sup>207</sup> and *versus* Zn and Cu concentrations in cores T3 and T8. The trend lines and respective equation and R<sup>2</sup> were included (blue dashed line) in each graphic.





Fig. 8. Range of values of <sup>206</sup>Pb/<sup>207</sup>Pb noticed in several investigations, including data of this work.



**Fig. 9.** Depth plots of: PCA Factor Score 1 and  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratios along the cores T3 and T8. The mean values of  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratios in two sections (1-70 cm and 80-197 cm) the first section representing the last 100 years and the second one the previous period, of the cores T3 and T8 are presented at dashed in different colors for each section. The red arrows at the top of the figure result from the interpretation of the PCA results (relative to data of Table 4) and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios (in association with data shown in Figs. 3, 5 and 8).

Tab. 4. Correlations between the analyzed variables and the	Factor
1 and Factor 2 of the PCA (Fig. 6).	

Variables	Factor 1	Factor 2
T3- <sup>206P</sup> b/ <sup>207</sup> Pb	0.78	-0.02
T3-Ag	-0.59	0.67
Т3-Са	0.86	-0.28
T3-Cu	-0.91	0.28
Т3-Р	-0.62	0.47
T3-Pb	-0.97	-0.07
T3-S	-0.66	0.61
T3-Zn	-0.92	0.31
Т3-ТОС	-0.96	-0.11
T8-TOC	-0.94	-0.09
T8-206Pb/207Pb	0.75	0.42
T8-Ag	-0.94	0.11
Т8-Са	0.78	0.53
T8-Cu	-0.96	-0.22
Т8-Р	-0.89	0.27
T8-Pb	-0.80	-0.43
T8-S	-0.77	-0.49
T8-Zn	-0.94	-0.33
Explained Variance	0.71	0.14

According to Baptista Neto et al. (2006) and Potratz et al. (2019) the regions where cores T3 and T8 were collected are low polluted by metals in GB. However, changes in sedimentological characteristics, metal concentrations and stable isotopes of lead along the cores T3 and T8 evidence

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an increasing trend eutrophication and metal pollution in this region northern/northeast of Guanabara Bay clearly marked since the 50's, with another pulse after the 70's, related to anthropic activities.

## 5. Conclusion

Stable isotopes of lead, namely the <sup>207</sup>Pb/<sup>206</sup>Pb results in cores T3 and T8 indicate that rocks erosion and mining products applied to industrial goods is a substantial source of pollution and lead released in Guanabara Bay. The increase of eutrophication and metal pollution evidenced in the results obtained in cores T3 and T8, is clearly related to anthropic activities. Deforestation and landfill and embankment engineering works, domestic and industrial effluents, large amount of waste and sewage released daily (including mining materials applied in industrial products, as well as oil, heavy metals, toxic substances and organic load) together with the restricted circulation are causing a steadily increasing of negative impact especially since the second half of the 20th century. This negative impact affects not only the region of the Guapimirim Environmental Protected Area (known as Apa de Guapimirim), a mangrove fringe but also central northern area of Guanabara Bay, at north of Paquetá island which have been considered low polluted areas of this coastal system.

# Appendices 1-2 are attached as supplementary materials (SM1-SM2) in: http://www.e-publicacoes.uerj.br/index.php/jse/article/view/45786

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