Metal levels and foraminifera occurrence in sediment cores from Guanabara Bay, Rio de Janeiro, Brazil

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Guanabara Bay, located at Rio de Janeiro, is an example of an impacted coastal environment due to the high influx of industrial and domestic effluents. Four sediment cores were sampled in areas with different levels of pollution and were analyzed for trace elements and foraminifera for abundance. Instrumental neutron activation analysis (INAA) was used to determine As, Ba, Co, Cr, Fe, Sb, Sc, and Zn. The effects of metal concentrations in the benthic foraminifera were studied. The low concentrations of the benthic foraminifera and the dominance of opportunistic species in coastal regions such as *Ammonia* may be correlated to natural stress or anthropogenic impact.

Introduction

Guanabara Bay represents the second largest bay on the Brazilian coast. Located at the State of Rio de Janeiro (RJ), Brazil, the Guanabara Bay (22° 37' and 22° 57' S – 43° 02' and 43° 16' W) covers a perimeter of 130 km and an area of 370 km^2, approximately. The water volume is in average $1.87 \cdot 10^9$ m^3. The bay measures approximately 28 km from West to East and 30 km from South to North.[1]

Guanabara Bay is one of the most important centers of focus for environmental concern due to the constant aggression it has suffered. Dredging continuously takes place in the port area to a depth of 17 m in support of shipping and docking activities. The alteration in the drainage basin initiated at the beginning of the 19th century led to modifications in the eutrophic conditions,[2] to high sedimentation rates,[3] to elevated concentrations of toxic metals and hydrocarbons in sediments and also to changes in the pelagic and benthic communities.[4] The bay receives 45 tributaries, 6 of which are responsible for 85% of the runoff (100±59 m$^3 \cdot$s^{-1}) of total annual average freshwater discharge. It receives inputs of untreated domestic and industrial wastes (including organic matter, oil, and heavy metals) from Rio de Janeiro, the second largest industrialized region of Brazil, which comprise around 10,000 plants (chemical, metallurgic, and oil refiners), two harbours, shipyard, and oil terminals.[5]

The sand bank, located at the bay entrance, greatly influences the inner water circulation due to the current channeling.[1] The bottom topography is influenced by tidal currents that drain through the central channel, and by strong input sediment as a result of activities in the drainage basin.[2] Near the bay entrance, BAPTISTA NETO et al.[6] mapped to a scale of 1 : 25,000 extensive silty clay deposits, demonstrating the existence of a sandy mud transition zone at a depth of 5 m. The sediments are comprized of sand, muddy sand, sandy mud, and mud.[7]

The study of sediment cores has shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments. A number of recent works have used sediment profiles to describe contamination history of different environments.[8–10] Most of the contaminants can leave their fingerprint in the sediments. The only necessary condition for this to happen is stability within the sedimentary column, i.e., no or insignificant post-depositional mobility is allowed. Metals that are more widely applied in the industry like cadmium, chromium, copper, iron, mercury, nickel, lead, and zinc constitute the bulk of the works presented in the literature.[10]

Heavy metals are one of the main problems in the Guanabara bay.[11] High concentrations of Cu, Hg, Cd, and Pb have been found in bottom sediments mostly in the Northern area, due to the discharge of polluted rivers.[12]

Granulometry, pH, and heavy metals are some abiotic factors that can cause decrease in the diversity and abundance of benthic foraminifera, which are small organisms living in sediments.[13] These microorganisms are used as bioindicators to evaluate natural changes or anthropogenic pollution due to their high diversity and abundance, short life histories, their fast response to environmental changes, and species characteristic responses to ecologic conditions.[14]

In this work, As, Ba, Co, Cr, Fe, Sb, Sc and Zn were analyzed by instrumental neutron activation analysis (INAA) in four core sediments from the Guanabara bay. Foraminifera present in the sediments were analyzed for species occurrence and abundance related to metal concentration.

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Experimental

Sampling and sample preparation

Four sediment cores were hand sampled in the Guanabara Bay during the summer of 2001, in areas with different anthropogenic influences (Fig. 1). Core C1 was sampled near Niterói city, at the entrance of the bay, an area submitted to domestic and industrial sewages. Core C5 was located in the central area, near Rio de Janeiro city. Core C0 was sampled at the northwest area, which includes the Duque de Caxias oil refinery zone (REDUC), and core C3 at the northeast, which includes the Guapimirim region, considered a highly degraded mangrove. Sampling was carried out by using one meter long polyethylene tubes that were sliced in 2 cm layers. The samples were stored in polyethylene bags at fridge temperature (4 °C) and transported to the laboratory, where they were frozen to –20 °C. They were then dried out in a oven at 50 °C for analysis (granulometric, faunal and INAA).

Instrumental neutron activation analysis

One hundred to one hundred fifty mg of the sediment samples were accurately weighed in polyethylene bags. Elemental synthetic standards of the analyzed elements were prepared by pipetting convenient aliquots of standard solutions (SPEX) onto 1 cm^2 pieces of Whatman No. 40 filter paper. The standards were then sealed in polyethylene bags. Samples and standards were irradiated at the IEA-R1 nuclear reactor at the Instituto de Pesquisas Energéticas e Nucleares (IPEN) for 16 hours at a neutron flux of 10^{13} $n \cdot cm^{-2} \cdot s^{-1}$. The measurements of the induced gamma-ray activity were carried out in a Canberra GX20190 hyperpure Ge detector. An 8192-channel Canberra S-100 plug-in-card in a PC computer multichannnel analyzer was used. The gamma-ray spectra were processed by using the VISPECT program. The accuracy and precision of the method were verified by the analysis of the Buffalo River Sediment (NIST SRM 2704) reference material, showing analytical precision and relative errors better than 10% (Table 1).

Foraminifera analysis

The sediment was dried and the foraminifera fauna was picked off in each sample using a fine brush. Samples yielding less than 300 foraminifers were taken in their entirety. All samples from the core were examined and faunal groups were identified and counted. Foraminifera species were identified according to BOLTOLSKOY et al.[15] and LOEBLICH and TAPPAN.[16]

Results and discussion

The results obtained are presented in Tables 2 to 5. Considering the comparison with element concentration levels in shale,[17] the mean concentration in earth crust for sedimentary rocks, only As, Zn, and Cr can suggest contamination. The comparison with shale values is a well known criterion used to verify whether a particular element can be considered "natural". This criterion presents some restrictions, since the sedimentary rocks considered to achieve shale values can be quite different from the rocks found in tropical countries. Zinc presented higher values than the value accepted for shale (95 $\mu g \cdot g^{-1}$) in all cores analyzed and mainly in core C0. Chromium showed concentrations higher than in shale (90 $\mu g \cdot g^{-1}$) in core C5, in the upper 20 cm and more than 10 times higher than shale in core C0, in depths from 30 to 48 cm. Arsenic exhibited higher levels than shale (13 $\mu g \cdot g^{-1}$) only in the first 8 cm of core C5. The concentrations of Ba, Sb, Sc, Co and Fe were not elevated in comparison to shale, indicating that these elements may be originated from the neighboring lithologies.

It can be observed in Tables 2 to 5 that the total foraminifera specimens were very low in all cores. The foraminiferal assemblages had distinct diversity patterns related to the different regions of Guanabara bay. Foraminifera dominant species were *Ammonia* sp. and *Triloculina* sp., which are cited in the literature as opportunistic in coastal regions under stressed environment conditions caused by anthropogenic pollution.[13,14] These species are more adaptable to environmental changes.

Fig. 1. Guanabara Bay and sampling sites

Table 1. Results obtained for the Buffalo River Sediment certified reference material (NIST 2704) (in $\mu g \cdot g^{-1}$)

Element	Buffalo River Sediment SRM 2704	Certified value*
As	23.2 ± 0.8	23.4 ± 0.8
Ba	408 ± 14	414 ± 12
Br	5.3 ± 0.3	–
Co	14.0 ± 0.7	14.0 ± 0.6
Cr	135 ± 1	135 ± 5
Cs	5.8 ± 0.1	(6)
Fe	42100 ± 600	41100 ± 1000
Hf	8.06 ± 0.08	(8)
Rb	102 ± 2	(100)
Sb	3.77 ± 0.06	3.79 ± 0.15
Sc	12.3 ± 0.3	(12)
U	3.0 ± 0.2	3.13 ± 0.13
Zn	476 ± 5	438 ± 12
La	30.0 ± 0.2	(29)
Ce	66 ± 1	(72)
Nd	28 ± 2	–
Sm	6.9 ± 0.3	(6.7)
Eu	1.25 ± 0.01	(1.3)
Tb	0.90 ± 0.02	–
Yb	2.91 ± 0.03	(2.8)
Lu	0.58 ± 0.01	(0.6)

* National Institute of Standards and Technology (NIST), Certificate of Analysis Standard Reference Material – Buffalo River Sediment 2704, NIST, Gaithersburg, 1990.
Figures in parenthesis are information values. Reference material uncertainties are 95% confidence limits and data uncertainties are one standard deviation of six replicates.

In core C5, the concentrations of As, Cr, and Zn were higher in the top of the sediment core (0–15 cm), indicating an anthropogenic contamination, originated probably from the industrial park of Rio de Janeiro city. In this sediment core, the dominant species was also *Ammonia* sp., which is known as an opportunistic species in areas under stressed conditions.

In the northwestern area (C0), near to the REDUC (oil refinery), the diversity was very low and dominant species abundance was higher (*Ammonia tepida*) in the first 5 cm of the core. High concentrations of Cr and Zn were obtained along the core (Table 2). For Cr, a tendency of increasing concentration with depth was observed. In this core, high metal concentrations and absence of benthic foraminifera were observed. Similar behaviour was observed by VILELA et al.[18,19] in the Guanabara bay. On the other hand, at lower latitudes (Mediterranean, Caribbean, and Arabian Seas), *Ammonia beccarii forma tepida* has been reported to dominate in areas close to outfalls discharging sewage,[20] chemical and thermal effluents,[21] fertilizer byproducts,[22] and heavy metals,[23–25] as it was observed in the first 5 cm of core C0.

In core C1, the concentrations of Cr and Zn were lower than in cores C0 and C5, and were similar to literature values in this area.[19] On the other hand, the diversity of foraminifera species was higher and *Triloculina* sp. was dominant in this region.

In core C3, which includes the Guapimirim region, a highly degraded mangrove area, the concentrations of Cr and Zn were relatively high, considering the low percentage of mud in the core samples (less than 43%). The granulometry consists of a good control of the element concentrations, as far as elements are associated with the fine grained portion of the sediments (fraction smaller than 63 μm).[10,26] In this core, few foraminifera were found, which indicates stressed environment conditions. These results show that high metal concentrations in the study area and other factors such as the dynamic of the region, pH, Eh and organic matter may strongly influence the diversity and the presence of benthic foraminifera in coastal areas.

Table 2. Metal levels and foraminifera occurrence in core C0; lat (S)/lon(W): 22°80'98"/43°24'49"; water depth: 1 m

	Core depth, cm											Total fossilizing
	0–2	4–6	6–8	12–14	16–18	18–20	24–26	32–34	40–42	42–44	46–48	
Abundances of foraminifera dead assemblages												
Ammonia tepida		535			1					20	9	566
Bolivina spp.		3										3
Elphidium spp.		10										11
Triloculina spp.		13			3							16
Specimens	0	561	0	0	4	0	0	0	0	20	9	596
Granulometry, %												
Sand	38.21	25.65	30.56	14.84	31.8	28.79	34.24	26.57	21.86	26.3	41.07	
Mud	61.79	74.35	69.44	85.16	68.2	71.21	65.76	73.43	78.14	73.7	58.93	
Metal, μg/g												
As	5.8 ± 0.6	n.d.	5 ± 0.5	3.9 ± 0.2	n.d.	6.6 ± 0.3	6.3 ± 0.3	5.6 ± 0.4	17 ± 1	n.d.	9.9 ± 0.7	
Ba	223 ± 3	n.d.	278 ± 3	319 ± 11		360 ± 12	326 ± 11	333 ± 26	342 ± 26	n.d.	256 ± 20	
Sb	0.74 ± 0.07	n.d.	0.79 ± 0.07	0.72 ± 0.01	n.d.	0.85 ± 0.01	0.66 ± 0.01	0.81 ± 0.05	0.91 ± 0.06	n.d.	0.60 ± 0.05	
Cr	248 ± 20	n.d.	201 ± 16	205 ± 16	n.d.	403 ± 31	591 ± 46	1461 ± 9	1107 ± 85	n.d.	1632 ± 10	
Sc	13.3 ± 0.8	n.d.	14.0 ± 0.8	14.4 ± 0.5	n.d.	13.6 ± 0.5	12.8 ± 0.4	15.2 ± 0.08	14.1 ± 0.8	n.d.	14.1 ± 0.8	
Zn	346 ± 5	n.d.	327 ± 15	318 ± 14	n.d.	288 ± 14	299 ± 15	403 ± 4	331 ± 3	n.d.	443 ± 5	
Co	8.1 ± 0.4	n.d.	8.4 ± 0.5	9.15 ± 0.04	n.d.	9.22 ± 0.04	10.20± 0.05	11.81± 0.01	13.09± 0.01	n.d.	16.70± 0.01	
Fe, %	4.73 ± 0.14	n.d.	4.76 ± 0.14	4.76 ± 0.05	n.d.	4.97 ± 0.05	1.23 ± 0.01	5.52 ± 0.16	5.80 ± 0.17	n.d.	5.64 ± 0.17	

nd: Not determined.

Table 3. Metal levels and foraminifera occurrence in core C1; lat (S)/lon(W): 22°48'37"/43°08'25"; water depth: 3 m

	Core depth, cm							Total
	0–2	6–8	8–10	10–12	12–14	14–16	24–26	
Abundances of feraminifera dead assemblages								
Ammonia tepida	1			3				12
Elphidium spp.	3	3	3	2		7		18
Triloculina spp.		25	20	23	20	15		103
Specimens:	4	30	24	28	23	24		133
Granulometry, %								
Sand	49.81	69.94	49.52	68.8	36.34	84.24	74.87	
Mud	50.39	30.06	50.48	31.2	63.66	15.76	25.13	
Metal, μg/g								
As	4.6 ± 0.2	13.9 ± 0.5	n.d.	n.d.	12.5 ± 0.4	n.d.	13.9 ± 0.5	
Ba	348 ± 13	276 ± 13			261 ± 13		292 ± 14	
Sb	0.17 ± 0.01	0.57 ± 0.03	n.d.	n.d.	0.59 ± 0.04	n.d.	0.85 ± 0.05	
Cr	15.8 ± 0.8	49 ± 3	n.d.	n.d.	51 ± 3	n.d.	73 ± 4	
Sc	4.6 ± 0.1	10.5 ± 0.3	n.d.	n.d.	10.9 ± 0.3	n.d.	13.8 ± 0.4	
Zn	125.6 ± 0.5	279 ± 1	n.d.	n.d.	241 ± 1	n.d.	80.1 ± 0.3	
Co	3.58 ± 0.02	6.57 ± 0.04	n.d.	n.d.	6.73 ± 0.04	n.d.	9.21 ± 0.06	
Fe, %	1.63 ± 0.01	3.64 ± 0.03	n.d.	n.d.	3.72 ± 0.03	n.d.	4.38 ± 0.03	

nd: Not determined.

Table 4. Metal levels and foraminifera occurrence in core C3; lat (S)/lon(W): 22°47'68"/43°05'40"; water depth: 2.5 m

	Core depth, cm								Total
	0–2	6–8	12–14	18–20	40–42	46–48	52–54	62–64	
Abundances of feraminifera dead assemblages									
Ammonia tepida	1		1			10		6	18
Bulimina marginata						10			10
Cassidulina minuta						8			8
Elphidium spp.								7	7
Pararotalia cananaensis						35			35
Specimens	1		1			63		13	78
Granulometry, %									
Sand	69.3	57.64	58.24	61.76	57.02	71.72	77.89	86.8	
Mud	30.7	42.36	41.76	38.24	42.98	28.28	22.11	13.2	
Metal, μg/g									
As	10.8 ± 0.5	11.8 ± 0.6	11.6 ± 0.6	9.8 ± 0.5	11.2 ± 0.8	n.d.	10.5 ± 0.8	10.7 ± 0.8	
Ba	238 ± 8	274 ± 9	267 ± 9	232 ± 8	333 ± 26	n.d.	342 ± 26	256 ± 20	
Sb	0.64 ± 0.01	0.82 ± 0.01	0.82 ± 0.01	0.69 ± 0.01	234 ± 18	n.d.	222 ± 17	250 ± 19	
Cr	59 ± 5	67 ± 5	72 ± 6	70 ± 5	80 ± 1	n.d.	78 ± 6	75 ± 6	
Sc	12.8 ± 0.4	12.7 ± 0.4	13.9 ± 0.5	13.1 ± 0.4	14.1 ± 0.8	n.d.	14.5 ± 0.8	13.9 ± 0.8	
Zn	170 ± 8	168 ± 8	174 ± 8	187 ± 9	170 ± 2	n.d.	129 ± 1	139 ± 1	
Co	8.81 ± 0.04	11.40 ± 0.05	11.60 ± 0.05	11.22 ± 0.05	10.9 ± 0.01	n.d.	11.55 ± 0.01	12.08 ± 0.01	
Fe, %	3.87 ± 0.01	2.07 ± 0.02	4.71 ± 0.05	4.44 ± 0.04	4.88 ± 0.14	n.d.	5.21 ± 0.15	5.01 ± 0.15	

nd: Not determined.

Table 5. Metal levels and foraminifera occurrence in core C5; lat (S)/lon(W): 22°95'04"/43°18'19"; water depth: 4 m

	Core depth, cm									Total
	0–2	6–8	12–14	18–20	24–26	28–30	42–44	54–56	64–66	
Abundances of foraminifera dead assemblages										
Ammonia spp.	46	25	25				28	7	14	145
Bolivina translucens	15	3	19				9	1		47
Buliminella elegantissima							35	10	3	48
Elphidium spp.	5	2	2		6	1	47	30	33	126
Textularia sp.						10				10
Triloculina sp.		19								19
Specimens:	66	49	46		6	11	119	48	50	395
Granulometry, %										
Sand	58.98	65.88	67.96	73.99	96.59	91.38	90.84	88.33	84.34	
Mud	41.02	34.12	32.04	26.02	1.79	0	2.79	11.67	15.66	
Metal, μg/g										
As	18 ± 1	18 ± 1	12 ± 1	8.9 ± 0.9	4.2 ± 0.5	4.4 ± 0.1	0.83 ± 0.09	2.22 ± 0.08	5.8 ± 0.2	
Ba	298 ± 4	275 ± 3	321 ± 4	346 ± 4	230 ± 3	253 ± 10	61 ± 5	146 ± 6	282 ± 12	
Sb	0.80 ± 0.08	0.84 ± 0.08	1 ± 0.09	0.84 ± 0.09	0.76 ± 0.07	0.56 ± 0.03	0.06 ± 0.01	0.15 ± 0.01	0.57 ± 0.03	
Cr	180 ± 14	227 ± 18	279 ± 22	189 ± 11	49 ± 4	31 ± 2	2.7 ± 0.4	6.8 ± 0.4	30 ± 2	
Sc	9.2 ± 0.5	9.4 ± 0.5	9.1 ± 0.5	9.3 ± 0.05	5.3 ± 0.3	4.3 ± 0.1	0.58 ± 0.04	1.63 ± 0.04	6.0 ± 0.2	
Zn	369 ± 6	368 ± 6	288 ± 4	180 ± 3	90 ± 1	55.1 ± 0.2	8.4 ± 0.4	6.64 ± 0.03	24.9 ± 0.1	
Co	6.2 ± 0.3	6.1 ± 0.3	6 ± 0.3	6.1 ± 0.3	3.6 ± 0.2	2.88 ± 0.02	0.39 ± 0.02	0.93 ± 0.01	3.07 ± 0.02	
Fe, %	3.31 ± 0.10	3.20 ± 0.10	1.83 ± 0.01	1.71 ± 0.01	1.42 ± 0.01	1.07 ± 0.01	0.197 ± 0.009	0.403 ± 0.003	1.29 ± 0.01	

Conclusions

The area studied in this work presented poor benthic foraminifera occurrence. The diversity of the species varied in the different regions, and opportunistic species such as *Ammonia* sp. were dominant in all studied cores, which could demonstrate a stressed environment. Heavy metal pollution may be related to foraminifera absence and poor diversity but other factors such as organic matter and physical and chemical parameters must be considered in the foraminifera assemblage in the study region.

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