



## Ecological risk evaluation of sediment metals in a tropical Eutrophic Bay, Guanabara Bay, Southeast Atlantic



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### ABSTRACT

Surface sediments were collected from Guanabara Bay, at 14 stations distributed in five sectors, over three sampling campaigns. Analyses of metals, grain size fractions and total organic carbon analyses were performed. The geo-accumulation index and the enrichment factor were estimated to assess contamination status based on background values. Additionally, the sediment quality guidelines were applied to evaluate the adverse biological effects. Results show that there was no seasonal variation in sediment quality based on any methodology, and all methods utilized showed that NW sector and HRJ sector were the worst affected and that the NE sector had the best conditions. The sediments of GB are polluted mainly by Cr, Pb and Zn. According to  $\Sigma$ SEM/AVS, these metals are not available to the biota, although toxicity tests dispute this. Among the various methods employed, those using background values for the area seem to best reflect the local historical contamination.

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### 1. Introduction

Sediments act as a sink for pollutants of diverse sources that can be re-released to overlying water via natural or anthropogenic processes, potentially having adverse outcomes for ecosystems (Adams et al., 1992; Essien et al., 2009). Geochemical study of sediments is crucial to obtain information regarding the potential risk pollutants represent to aquatic organisms (Maia et al., 2006), becoming a primary issue for the management of aquatic ecosystems.

Trace metals are dangerous pollutants in the environment due to their potential toxicity, persistence and bioaccumulation. Metals generated by anthropogenic activities cause more environmental pollution than naturally-occurring ones because they are discharged in greater amounts into the environment. Trace metal contamination has become a serious problem in marine ecosystems throughout the world. Such metals enter ecosystems through industrial, agricultural and urban effluents (Feng et al., 2012). The main factors affecting the concentrations of metals in sediments include, grain size; the presence of oxides and hydroxides of Fe, Al and Mn; the presence of organic matter, with which they can form organometallic compounds; and co-occurrence

of clay minerals, which form clay-pollutant complexes that can be remobilized by erosion events (Maia et al., 2006).

In this context, Guanabara Bay (GB), located in the littoral region of Rio de Janeiro, Brazil, is a heavily polluted environment that represents one of the most important embayments of the Brazilian coastline, with a high ecological value and socio-economic relevance. Many stakeholders share the bay's environment with fishing, tourism, industries, harbors, wharfs, marinas, domestic and industrial landfills, mariculture, oil refineries, shantytowns and sewage outfalls all occurring (Maranhão et al., 2009). Burgeoning urban occupation and industrial development have increased the quantity of contaminants being discharged into GB and its tributaries, which are responsible for 85% of contaminant input into the bay (Kfoury et al., 2005). Thus, large amounts of solid waste, organic matter, trace metals, organic pollutants and hydrocarbons are introduced into the bay and may potentially accumulate in the sediments.

GB has been extensively studied regarding its environmental quality (Carreira et al., 2002; Xavier de Brito et al., 2002; Azevedo et al., 2004; Baptista-Neto et al., 2006; Silva et al., 2007; Vieira et al., 2007; Mendes et al., 2007; Maranhão et al., 2009, 2010; Soares-Gomes et al., 2010; Soares-Gomes et al., 2016), but a multi- and inter-disciplinary approach is still lacking. Considering the ecological and socioeconomic importance of the bay, our study is the first attempt to make an evaluation risk analysis of the bay, searching for an integrative diagnosis of its sediment quality by applying several indexes of sediment quality.

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## 2. Study area

GB is a 384 km<sup>2</sup> eutrophic coastal bay located in Southeast Brazil. The rivers and channels that discharge into the bay cross greatly urbanized areas, receiving all kinds of effluents (Faria and Sanchez, 2001; Fonseca et al., 2014; Borges et al., 2014). Its drainage basin receives polluted effluents from about 6000 industries, 2 airports, 2 commercial harbors and 15 oil terminals located in its vicinity (Kjerfve et al., 1997). Furthermore, there are inputs of untreated domestic sewage from diffuse sources. Mostly, those inputs come from the rivers of the vast watershed (about 45 rivers and innumerable streams), six of which are responsible for 85% of the total runoff (Kjerfve et al., 2001). At river inflow points, internal estuaries are formed and deltas are present, which are occupied by mangrove ecosystems at the mouths of the main rivers, mainly in the northeast portion of the bay (Silva et al., 2015). Trace metals, petroleum hydrocarbons, pesticides and other toxic chemical compounds enter the bay daily, especially at its inner area, accumulating in the sediments (Xavier de Brito et al., 2002; Ventura et al., 2002; Baptista-Neto et al., 2006; Silva et al., 2007).

The water quality of the bay exhibits considerable variability, both spatially and temporally, governed by hydrology, pollutant hotspots and rainfall (Kjerfve et al., 1997). Tides and winds control circulation, allowing water inflow from the ocean through the lower water layers. According to Kjerfve et al. (2001), the worst water quality is indicated by average faecal coliform counts higher than 1000 mL<sup>-1</sup> and by the average chlorophyll concentration exceeding 130 µg L<sup>-1</sup> in the inner bay, the most critical zone, in response to high nutrient loading. Dissolved oxygen concentration reaches 300% of saturation in the daytime due to phytoplankton blooms, but can drop below 1 mL L<sup>-1</sup> in the lower water layers (Wagener et al., 1988, 1990). Concentrations range from anoxia to 7.26 mL L<sup>-1</sup> for the more restricted water circulation in the inner bay area (Paranhos et al., 2001; Pereira Neto et al., 2004).

The sedimentation rate in GB has increased over the last 50 yrs from 0.19 cm y<sup>-1</sup> to 0.86–2.20 cm y<sup>-1</sup> (Lima, 1996; Godoy et al., 1998), and the flux of organic matter in the last 100 yrs changed from 4.2 mol C m<sup>-2</sup> y<sup>-1</sup> to 41.7 mol C m<sup>-2</sup> y<sup>-1</sup> for some areas of GB (Carreira et al., 2002). Those increments in particle settling have promoted an increase in the organic loads of GB's sediments, favoring anoxic conditions and accumulation of pollutants.

Sediments are not evenly distributed, with mud predominating at the inner bay areas and fine sand near the mouth (Baptista-Neto et al., 2006). Soft-bottom macrobenthos studies have revealed three main sectors in GB: inner, intermediary and outer. Within those sectors, an increasing gradient of biodiversity is observed, ranging from the azoic and impoverished inner sector to a well-structured community in terms of species composition and abundance in the outer sector (Soares-Gomes et al., 2012; Santi et al., 2006; Santi and Tavares, 2009; Mendes et al., 2007).

## 3. Material and methods

### 3.1. Sampling design

For this work, GB was compartmentalized according to the main sources of contamination, resulting in five sectors. Sector 1 is located in the northwestern zone of GB, between Governor's Island and the city of Duque de Caxias (Fig. 1), and receives a contaminant load primarily from industrial and urban loads sources. Sector 2 is a transition zone between the northwestern and northeastern zones, which shows the widest variability. Sector 3, located in the northeastern zone, is semi-enclosed and exhibits better environmental conditions due to the preservation of mangrove swamps and possesses lower heavy metal concentrations. Sector 4 is located in Jurujuba Sound, Niterói, and is considered one of the most polluted sites (Baptista-Neto et al., 2000;

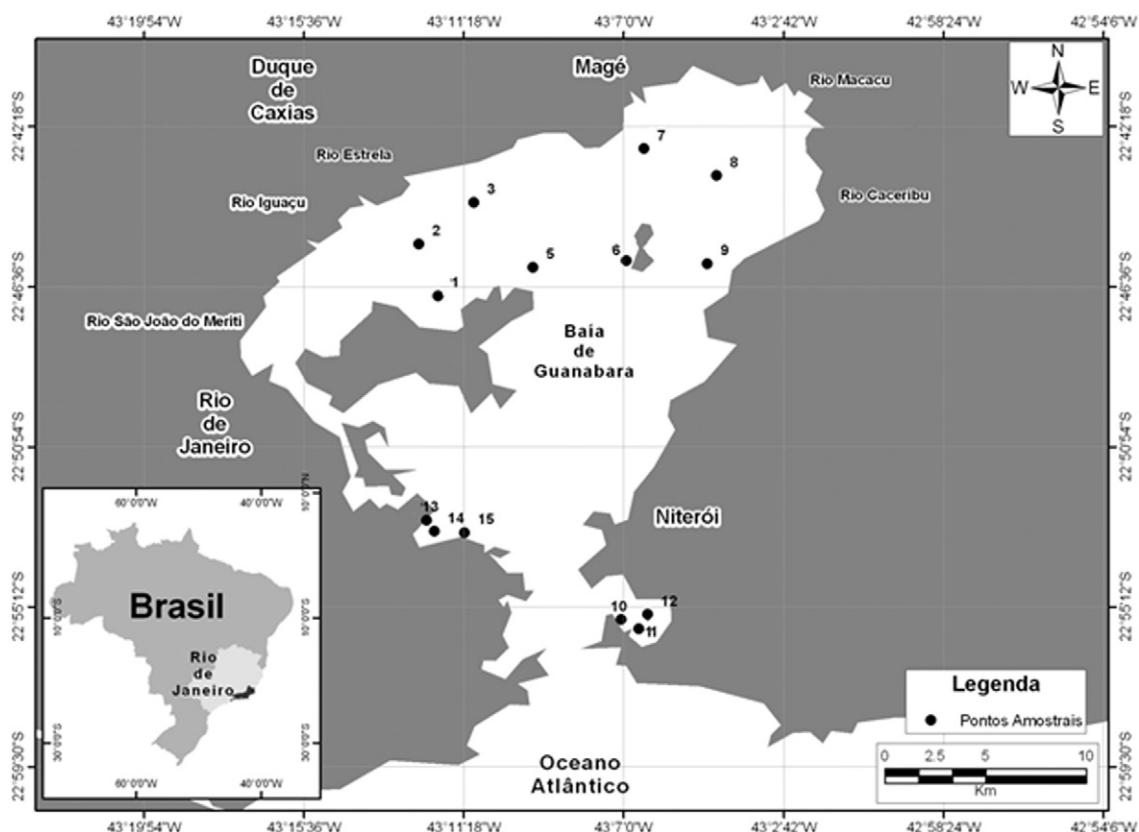


Fig. 1. Location map of the study area and sampling sites (Sector 1: 1, 2 and 3; Sector 2: 5 and 6; Sector 3: 7, 8 and 9; Sector 4: 10, 11 and 12; Sector 5: 13, 14 and 15).

**Table 1**

Results obtained from analysis of certified NIST material (Industrial Sludge 2782), limits of detection, accuracy and precision of metal determinations on certified material ( $\mu\text{g g}^{-1}$ ) (average  $\pm$  standard deviation,  $n = 3$ ).

		Al	Ba	Fe	Mn	Ni	Pb	Zn
NIST 2782	LD	0.1	0.02	0.1	0.02	0.02	0.04	0.02
	Certified value	1553	152 ( $\pm 11$ )	254,000 ( $\pm 16,000$ )	258 ( $\pm 15$ )	95.9 ( $\pm 4.7$ )	554 ( $\pm 36$ )	1167 ( $\pm 57$ )
Campaign 1	VD	2369 ( $\pm 67.4$ )	147 ( $\pm 4.09$ )	246,066 ( $\pm 4186$ )	228 ( $\pm 4.10$ )	88 ( $\pm 0.772$ )	435 ( $\pm 5.98$ )	1022 ( $\pm 30.6$ )
	CV (%)	2.85	2.78	1.70	1.80	0.877	1.37	2.99
	R (%)	153	96.6	96.9	88.2	91.8	78.5	87.6
Campaign 2	VD	1519 ( $\pm 19.5$ )	104 ( $\pm 0.469$ )	82,247 ( $\pm 774$ )	202 ( $\pm 1.31$ )	91 ( $\pm 4.45$ )	381 ( $\pm 2.83$ )	1082 ( $\pm 8.35$ )
	CV (%)	1.28	0.451	0.941	0.649	4.89	0.744	0.772
	R (%)	97.8	68.4	<b>32.4</b>	78.3	95.0	68.7	92.7
Campaign 3	VD	1456 ( $\pm 45.0$ )	102 ( $\pm 1.80$ )	87,650 ( $\pm 2051$ )	197 ( $\pm 5.08$ )	85.3 ( $\pm 8.67$ )	424 ( $\pm 14.0$ )	1054 ( $\pm 23.3$ )
	CV (%)	3.09	1.77	2.34	2.57	10.2	3.30	2.21
	R (%)	93.8	66.8	<b>34.5</b>	76.4	88.9	76.6	90.3

LD = limit of detection, VD = value determined, CV = coefficient of variation, R = recovered.

Sabadini-Santos et al., 2014) mainly due to domestic effluent, besides the presence of yacht clubs and mariculture activities. Sector 5 is located in the Harbor of Rio de Janeiro (HRJ), where trace metal concentrations are associated with shipping activities and the outlet of one of the most polluted rivers of the catchment basin (Borges et al., 2014).

In order to verify temporal and spatial differences in the distribution of metals in sediments, samples were taken at fourteen sampling stations distributed in distinct sectors of the bay (Fig. 1). Triplicate sediment samples were taken using a Birge Ekman stainless steel grab at each of the stations in each of the three campaigns (except for station 12 that was not sampled in campaign 1): campaign 1 between December 2006 and January 2007 (wet season); campaign 2 in August 2007 (dry season); and campaign 3 in March 2008 (wet season). Location of sampling stations was determined in accordance with previous studies regarding contaminant distribution in GB sediments. Samples were transferred to plastic bags and placed in an isothermal box at 4 °C to be transported to the laboratory where they were then stored at –20 °C for further analysis.

### 3.2. Sample analyses

The grain sizes of sediment samples were determined after sediment dispersion in  $\text{Na}_4\text{P}_2\text{O}_7$  and 10 min sonication. A particle analyzer with laser diffraction (Cilas 1064 model) was employed to quantify 0.04–500  $\mu\text{m}$  particle size fractions. Data generated was processed using the program GRADISTAT version 4.0 (Blott and Pye, 2001).

Total organic carbon (TOC) was determined with a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer after removing the inorganic carbon with hydrochloric acid.

Extraction of acid-volatile sulfides (AVS) was conducted using the purge and trap technique described by Allen et al. (1991), with some modifications made by Machado et al. (2004). Wet samples were subjected to acid distillation with cold 6 mol  $\text{L}^{-1}$  HCl and the released  $\text{H}_2\text{S}$  was trapped in 0.5 mol  $\text{L}^{-1}$  NaOH, using argon as a carrier gas. Sulfide concentrations were determined by spectrophotometry in FEMTO equipment (model 700 PLUS). Acid sediment suspensions were filtered for the determination of simultaneously extracted metals (SEM) (Fe, Cd, Cu, Ni, Pb and Zn) by optical emission spectrometry with inductively coupled plasma source ICPOES. The sum of concentrations of simultaneously-extracted metals of environmental concern (Cd, Cu, Ni, Pb and Zn) was denoted as  $\Sigma\text{SEM}$ . According to Di Toro et al. (2005), the application of the reason  $\Sigma\text{SEM}/\text{AVS}$  for evaluating the toxicity of these metals has proven to be quite successful at predicting the lack of toxicity in sediments.

The digestion methodology to analyze Al, Ba, Cd, Cr, Fe, Mn, Ni, Pb and Zn was based on the USEPA Method 3051A (USEPA, 2007). In brief, 0.5 g of dry sediment sample was placed in 10 mL of analytical-grade Merck nitric acid in a Microwave Sample Preparation System (CEM Corp, Matthews, NC). Acidified sediment extracts were filtered

and diluted to 25 mL with ultrapure water. Metal concentrations were determined using a Jobin–Yvon Ultima 2 sequential ICPOES (Longjumeau Cedex, France) with software Analyst JY5.2. All water used throughout the experimental work was obtained from a Simplicity Milli-Q Water System (Millipore, Milford, MA, USA). Analytical quality assurance was evaluated by simultaneous analysis of a reference material (NIST Industrial Sludge 2782) using four replicates. The results obtained and the accuracy, precision and detection limits are shown in Table 1. The results obtained for the analysis of certified reference material showed good precision (CV % of 0.88–2.85) and accuracy (82–97% recovery).

### 3.3. Data analysis

Differences in metals and organic carbons concentration between stations and seasons were tested separately using non-parametric Kruskal–Wallis ANOVA. Spearman rank correlation was employed to evaluate the relationship between variables. Sample sizes were  $n = 39$  (13 stations \* 3 samples) for campaign 1, and  $n = 42$  (14 stations \* 3 samples) for Campaigns 2 and 3. Station 12 was not sampled in campaign 1 for operational reasons.

Toxicity tests data were checked for normality by Shapiro Wilk's and Bartlett statistical tests, and the homogeneity of variances were checked by the F-test. After, Student's *t*-test (ZAR, 1996) were applied to compare the samples with their respective controls. Toxstat 3.5 program (Gulley, 1995) was used for these analyses. In the acute toxicity test, the data for each sample was compared to the control and to the other samples. The samples were designated as significantly different (SD), when results were significantly different from the controls but, showed levels  $\text{NH}_3 > 0.05$  mg L. They were classified as non-toxic (NT) when the samples were significantly different from control, but exhibited embryonic development rates close to those of control (>80%) (Maranho et al., 2010).

### 3.4. Geochemical indexes

In order to obtain a measure of the sediments' toxicity mean quotients in case of existence of multiple contaminants (Violintzis et al., 2009), the following quotients were introduced according to the equations:

$$\text{ERMQ} = \frac{\sum_{i=1}^n \frac{M_i}{\text{ERM}_i}}{n} \quad \text{PELQ} = \frac{\sum_{i=1}^n \frac{M_i}{\text{PEL}_i}}{n}$$

where  $M_i$  is the metal concentration in the sediment sample,  $\text{ERM}_i$  and  $\text{PEL}_i$  the guideline values for the element  $i$  and  $n$  the number of metals. These mean quotients can be used ERMQ values of <0.1, 0.11–0.5, 0.51–1.5 and >1.5 are related to 12%, 30%, 46% and 74%, respectively, that sediments present toxicity in amphipod survival bioassays. Similarly, PELQ

**Table 2**  
Enrichment factor (EF) values.

EF	Description
$0.5 \leq EF \leq 1.5$	The metals may be completely derived from natural or lithogenic processes.
$EF > 1.5$	A large portion of trace metal is derived from non-natural processes or anthropogenic sources.
$EF < 2$	Metal contamination might be entirely from natural sources.
$2 \leq EF < 5$	A moderate portion of trace metals originated from an anthropogenic source or non-natural process.
$5 \leq EF < 20$	A significant portion is from anthropogenic sources.
$20 \leq EF < 40$	A high portion of contamination is derived from anthropogenic sources.
$EF \geq 40$	An extremely high portion of contamination

values of <0.1, 0.11–1.5, 1.51–2.3 and >2.3 coincide with 10%, 25%, 50% and 76% of toxicity respectively (Long and MacDonald, 1998). Four relative levels of contamination have been created (high, medium high, medium low, low) (McCready et al., 2006).

The enrichment factor (EF) is a useful tool for differentiating anthropogenic from natural sources of metal enrichment (Tavakoly Sany et al., 2013; Likuku et al., 2013). This evaluation technique is undertaken by normalizing metal concentrations considering the dissimilar sedimentological characteristics of sediments. Aluminum is a major metallic element found in the earth's crust; its concentration is somewhat high in sediments and is not affected by man-made factors.

$$EF = \frac{\left(\frac{C_{\text{metal}}}{Al}\right)_{\text{sediment}}}{\left(\frac{C_{\text{metal}}}{Al}\right)_{\text{background}}}$$

where  $(C_{\text{metal}}/Al)_{\text{sediment}}$  is the metal concentration in the sediment sample and the  $(C_{\text{metal}}/Al)_{\text{background}}$  value is the natural background ratio of the trace metal to Al (normalizing element). When the EF of a metal is >1, the metal in the sediment originates from anthropogenic sources. Table 2 shows the categories of enrichment factors used (Tavakoly Sany et al., 2013; Likuku et al., 2013).

To evaluating the degree of pollution of surface sediments, was considered the Total Enrichment Factor (TEF). This is average EF values, of all EF (n) indicator metals (in this case, Cd, Cr, Mn, Ni, Pb and Zn; n = 6), calculated for the each station.

The baseline used as a background reference for normalizing metals was that proposed by Monteiro et al. (2012) (Table 3). The background values ( $C_{\text{metal}}$  and Al) used in the calculation of EF were determined by the average of the sample dating from periods prior to the European colonization process in three profiles of sediments from different sectors of the GB. Figueiredo et al. (2014) discuss about the sedimentation process and the chronologies of the cores used to extract the background values. The BG28 core from the northwestern sector (22°45'54.11"S, 43°12'4.87"W) was a 565 cm long sediment core dated back 5465 yr cal BP; BG 08 core from the western-center sector (22°51'34.58"S, 43°10'43.89"W) was a 300 cm length core, dated back 5900 yrs BP; and

**Table 3**  
Background levels of metals (mg kg<sup>-1</sup>; Al and Fe in %) from Guanabara Bay.

Site	Al	Fe	Cd	Cr	Mn	Ni	Pb	Zn
Island do Governador (BG 08) <sup>a</sup>	1.83	2.07	0.315	23.0	146.4	8.05	5.71	34.2
Sector East (BG 14) <sup>a</sup>	3.63	3.22	0.545	32.8	294.2	10.8	7.74	50.6
Sector NO (BG 28) <sup>a</sup>	3.98	3.32	0.600	37.2	234.6	12.3	7.80	54.1

<sup>a</sup> Monteiro et al. (2012).**Table 4**  
*I*<sub>geo</sub> classes of contamination.

Classes	Value	Description
0	<0	Background levels
1	0–1	Unpolluted
2	1–2	Unpolluted to moderately polluted
3	2–3	Moderately polluted
4	3–4	Moderately to strongly polluted
5	4–5	Strongly polluted
6	>5	Very strongly polluted

BG14 core, from the eastern sector (22°48'26.22"S, 43°6'5.69"W) dated back 1390 cal yr BP.

Similar to the metal enrichment factor, an index of geoaccumulation (*I*<sub>geo</sub>) can be used as a reference to estimate the extent of metal accumulation. This index was originally defined by Müller (1969) as a criterion to evaluate the intensity of heavy metal pollution and is defined as follows:

$$I_{\text{geo}} = \log_2 \left( \frac{C_n}{1.5B_n} \right)$$

where  $C_n$  is the sedimentary concentration of a measured metal, and  $B_n$  represents the baseline value or reference site of a metal. Factor 1.5 is the background matrix correction factor due to lithogenic effects. Here, *I*<sub>geo</sub> was assessed based on the seven descriptive classes for increasing *I*<sub>geo</sub> values proposed by Müller (1969), depicted in Table 4.

## 4. Results and discussion

### 4.1. Sediment characteristics

GB is a microtidal estuarine environment that can be divided into three zones: an external zone affected by wave action and tidal currents, an inner zone characterized by very low energy, and a transitional zone characterized by a mix of sediment types (Baptista-Neto et al., 2006). The particle sizes of sediment samples collected in this study were quite homogeneous, with mud fractions (silt + clay) always above 70%. The average grain size ranged from 5.07 to 27.5 μm, corresponding to a fine silt to coarse silt classification. The sorting coefficient of samples ranged from poorly to very poorly sorted (3.05 to 4.87 μm) (Fig. 2). The higher values of clay was found at stations 1 to 9, localized in inner zone of GB characterized by very low energy, and the lower values (Baptista-Neto et al., 2006). It is well-established that grain size, carbonate and organic matter contents are important controlling factors in the concentrations of trace metals in sediments. Fine-grained fractions tend to be more reactive than those of coarser grains due to the higher specific surface area of the former (Forstner and Salomons, 1980). This enrichment is mainly due to surface adsorption and ionic attraction (McCave, 1984; Horowitz and Elrick, 1987). In addition, coatings of organic matter are prevalent in fine-grained sediments, binding a variety of trace elements (Wangersky, 1986) and being a significant role in the destination of metal ions in the environment as it provides adsorption or reaction sites, retaining pollutants in the sediments or forming more toxic organo-metallic complexes (Ribeiro et al., 2013). In addition, in the presence of organic matter, the development of microorganisms may affect the chemical speciation of metal ions and control metal bioavailability and/or toxicity in aquatic systems (Wasserman et al., 2000). The mean TOC percentages (campaign 1: 5.32% ± 0.881%; campaign 2: 5.28% ± 1.11%; and campaign 3: 5.55% ± 0.975%) did not differ statistically between campaigns ( $p < 0.05$ ) (Table 5). The concentrations and distribution trends of TOC in this study are similar to those reported in previous studies for GB (between 3.21% and 7.49%, as reported by Baptista-Neto et al., 2006; Fernandez et al., 2005; Carreira et al., 2002; Monteiro, 2008).

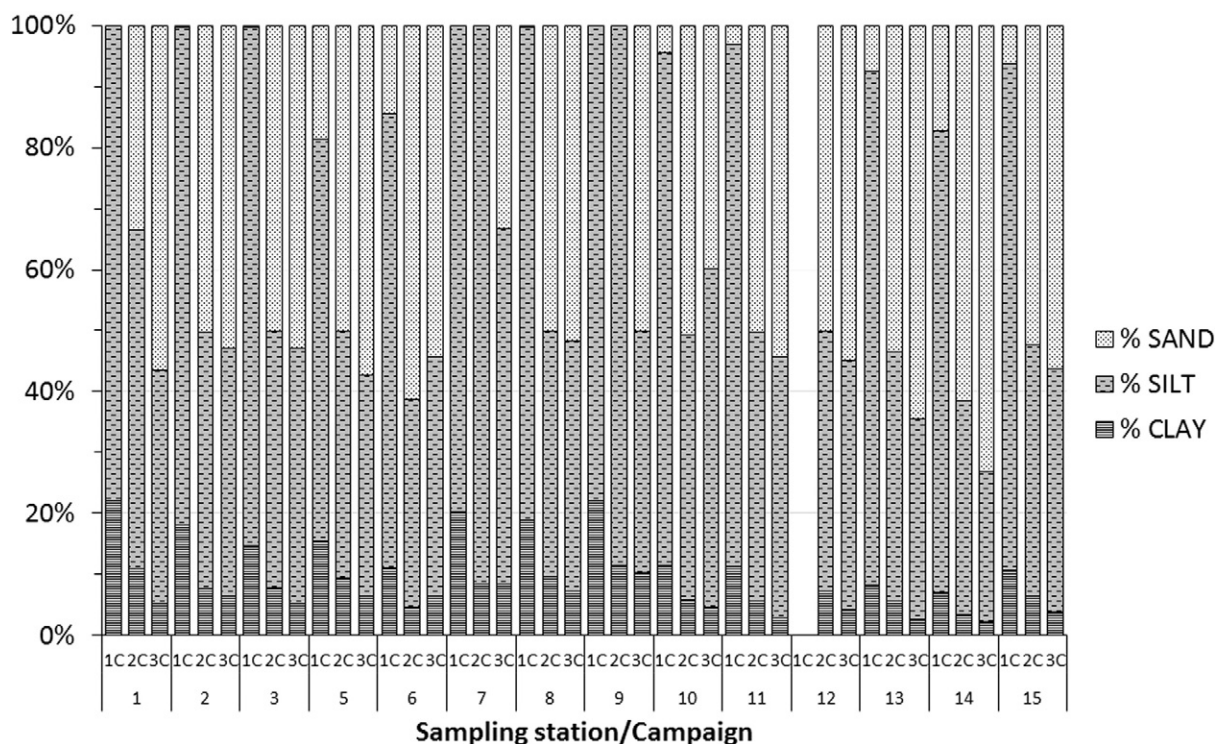


Fig. 2. Grain size fractions in sediments of Guanabara Bay. (1C – campaign 1, 2C – campaign 2, 3C – campaign 3).

4.2. Trace metal distribution

4.2.1. AVS-SEM

Table 5 shows average concentrations and standard deviations of trace metals found in superficial sediments from GB, for each campaign. In general, all metals had similar spatial distribution patterns, with decreasing concentrations from the north to the south of the bay.

In terms of the seasonal distribution of AVS, in general the highest values of AVS were found in rainy season surveys (campaigns 1 and 3), specifically at stations 1 and 13 (campaign 1), and stations 3, 5 and

8 (campaign 3). In the dry season (campaign 2), the highest values of AVS were found at Sector 3 (stations 7, 8 and 9). The lowest AVS concentrations were found at stations 2, 5 and 10 to 15 (campaign 1), stations 5, 7 and 9 (campaign 2) and stations 10 to 12 (campaign 3).

ΣSEM values for Cd, Cu, Ni, Pb and Zn followed the seasonal distribution pattern of other metals, with higher averages during campaign 2 (dry season). In evaluating the spatial distribution of ΣSEM, we found the lowest values for Sector 3, at stations 8 and 9 during campaign 3. Whereas the highest values were found in Sector 2 and at Sector 5, specifically at stations 2 and 14 in campaign 1, stations 2 and 14 in

Table 5 Average concentration of metals in superficial sediments of Guanabara Bay (mean ± standard deviation).

		Campaign 1	Campaign 2	Campaign 3	TEL <sup>a</sup>	PEL <sup>b</sup>	ERL <sup>c</sup>	ERM <sup>d</sup>	Background levels <sup>e</sup>
AVS SEM (μmol g <sup>-1</sup> )	Fe	252.7 ± 98.0	111.8 ± 238.7	182.7 ± 61.9					
	Cd	0.0036 ± 0.0012	0.0020 ± 0.0055	0.0035 ± 0.0015					
	Cu	0.52 ± 0.27	0.33 ± 0.59	0.28 ± 0.19					
	Ni	0.091 ± 0.11	0.02 ± 0.04	0.07 ± 0.07					
	Pb	0.15 ± 0.09	0.11 ± 0.21	0.11 ± 0.09					
	Zn	2.56 ± 0.92	1.30 ± 2.91	1.84 ± 1.12					
	ΣSEM	3.33 ± 1.20	1.67 ± 3.75	2.25 ± 1.34					
	AVS/ΣSEM	86.8 ± 66.9	18.2 ± 29.6	65.1 ± 48.5					
EPA 3051 (μg g <sup>-1</sup> )	Al	18,875 ± 8072	19,521 ± 8502	20,982 ± 8843					31,452.8
	Fe	27,071.2 ± 7567	11,803.6 ± 3289	13,972.4 ± 3604					28,712.0
	Mn	466.4 ± 346.2	416.3 ± 297.3	410.3 ± 247.8					225.1
	Cd	1.00 ± 0.31	0.988 ± 0.20	1.15 ± 0.23	0.68	4.21	1.2	9.6	0.486
	Cr	50.4 ± 36.4	56.0 ± 34.2	56.6 ± 31.7	52.3	160	81	370	31.0
	Ni	11.71 ± 1.74	8.53 ± 2.66	5.45 ± 3.77	15.9	42.8	20.9	51.6	10.4
	Pb	47.4 ± 22.3	38.1 ± 17.7	49.4 ± 25.6	30.24	112	46.7	218	7.08
	Zn	211.3 ± 90.9	204.2 ± 83.0	234.1 ± 104.7	124	271	150	410	46.3
TOC (%)	5.32 ± 0.881	5.28 ± 1.11	5.55 ± 0.975						

TEL, PEL, ERL and ERM values are from Bunchman (2008).

<sup>a</sup> Metal concentrations exceeding TELs.

<sup>b</sup> Concentrations exceeding PELs.

<sup>c</sup> Concentrations exceeding ERLs.

<sup>d</sup> Concentrations exceeding ERMs.

<sup>e</sup> Background levels of metals in sediments from Guanabara Bay (Monteiro et al., 2012).

campaign 2, and stations 14 and 15 in campaign 3. According to the Kruskal-Wallis test, there was no significant difference ( $p < 0.05$ ) between seasons for all elements evaluated in all campaigns.

The formation and preservation of insoluble metal sulfides have been recognized as a key process determining the behavior of metallic elements in coastal sediments under anaerobic conditions. This function of sulfides is often related to the incorporation of metals available in aqueous phase by the solid phase of the sediment through training or adsorption to metal monosulfides, which are included in the mineral phase operably defined as volatile sulfides acid (sulfides acid-volatile - AVS), predominantly consisting of FeS (Chapman et al., 1998). A significant part of this retention mechanism in the form of metal sulfides has been suitable for anaerobic sediments of the GB (Perin et al., 1997; Machado et al., 2004). As part of this mechanism, it is important highlight that metal forming monosulfides more stable than FeS (including Cd, Cu, Ni, Pb and Zn) may replace the Fe of this compound, which results in the incorporation of metal ions into the interstitial water present in the solid phase sediment, affecting the availability of metals to benthic organisms (Di Toro et al., 1992) and for export from the sediments (Teasdale et al., 2003).

Clear trend that the SEM levels were demonstrated did not exceed the AVS levels in GB. The results show consistency on the importance of AVS accumulation for metal retention by sediment from most areas of GB. For all samples, values of  $\Sigma\text{SEM}/\text{AVS}$  ratios were below one, except for a replicate collected at station 7 during campaign 2, indicating that the toxicity of these elements could not be manifested in benthic organisms because the sediment had not exhausted its potential to retain trace metals in the form of AVS (Di Toro et al., 2005).

#### 4.2.2. EPA method 3051A

Table 5 shows average concentrations and standard deviations of trace metals extracted with EPA 3051A method in superficial sediments

from GB, for each campaign. In this study, metal concentrations ranged from: Al: 0.976–4.06%; Cd: 0.478–1.80  $\mu\text{g g}^{-1}$ ; Cr: 24.6–157  $\mu\text{g g}^{-1}$ ; Fe: 0.744–2.12%; Mn: 141–1363  $\mu\text{g g}^{-1}$ ; Ni: 1.11–14.6  $\mu\text{g g}^{-1}$ ; Pb: 14.6–107  $\mu\text{g g}^{-1}$ ; Zn: 89–456  $\mu\text{g g}^{-1}$ . The highest mean levels of Fe and Mn occurred during campaign 1 (wet season), for Cr and Ni they were in campaign 2 (dry season) and for Al, Cd, Pb and Zn they were in campaign 3 (wet season). According to Kruskal-Wallis tests, there were significant differences between campaigns 2 and 3 for Cd, between campaign 1 and both campaigns 2 and 3 for Fe, and between all three campaigns for Ni.

We compared our values with the quality levels described by the National Oceanic and Atmospheric Administration (NOAA): Effects Range-Low (ERL), Effects Range-Median (ERM), Threshold Effect Level (TEL) and Probable Effect Level (PEL). In aquatic toxicity studies, ERL and ERM represent, respectively, the tenth and fiftieth percentile (Lin et al., 2013). TEL represents the concentration threshold below which there are little or no toxic risks to organisms. PEL is the minimum value at which several adverse effects start to occur. All samples showed Cd levels between TEL and PEL limits in the three campaigns, except for station 6 in campaigns 1 and 2. The samples showed levels below TEL for Cr, except for Sector 1 in the three campaigns, in addition to stations 5 and 7 during campaign 2, and stations 6, 7 and 14 during campaign 3, which showed levels above PEL (Fig. 3).

Ni concentrations found in the three campaigns were all below the lower limits of TEL/PEL and ERL/ERM value guidelines. Pb concentrations were below TEL in samples collected at stations 8 and 9 in campaign 1, for stations 3, 6, 7, 8 and 9 in campaign 2 and for stations 3, 7, 8 and 9 in campaign 3 (all other stations had values between TEL and PEL levels). Zn levels were below TEL in stations 8 and 9 in all campaigns, as well as at stations 6 and 7 stations during campaign 2. At stations 2, 14 and 15, Zn values were above PEL for

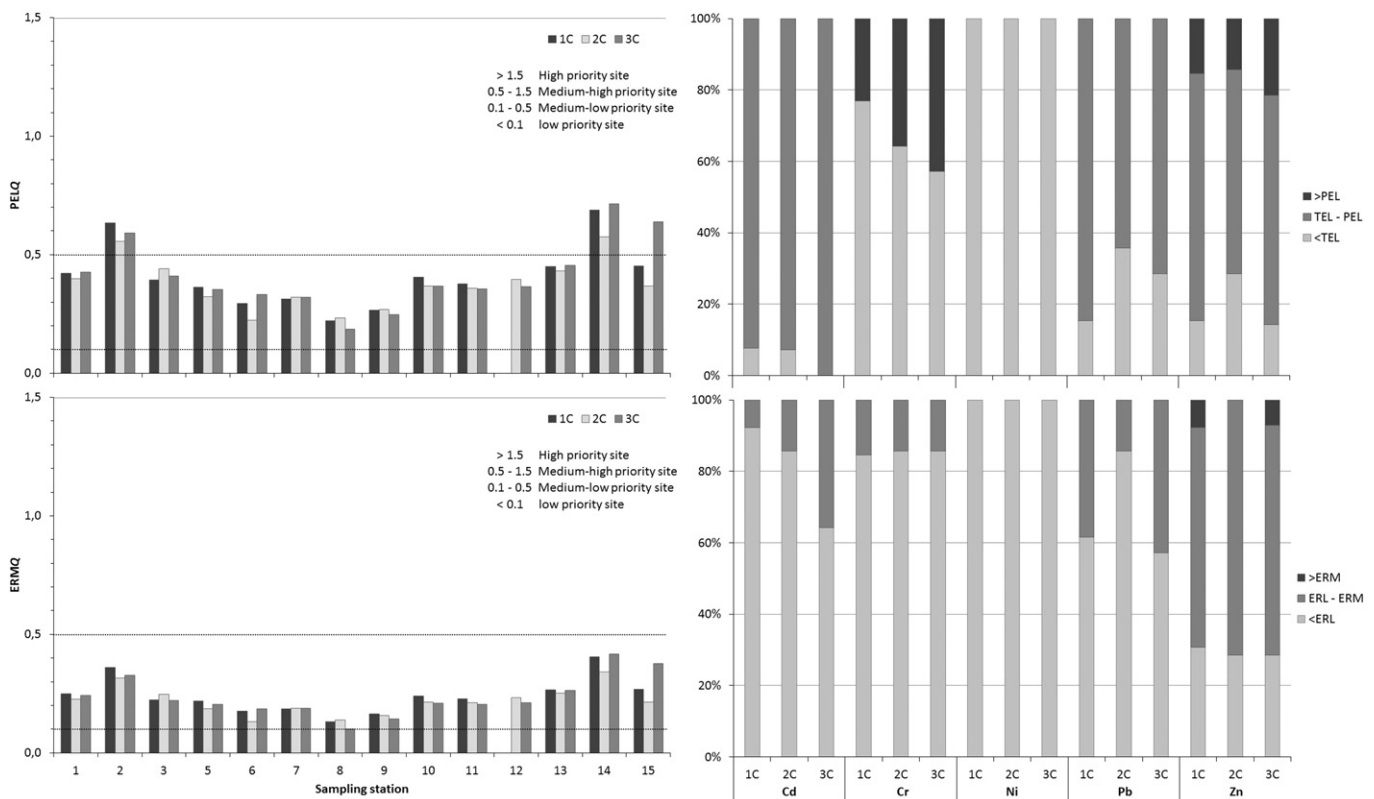


Fig. 3. Distributions of PELQ (a) and ERMQ (c) values for all sampling stations, and distribution of Possible Effect Levels/Threshold Effect Levels (TEL/TEL) (b) and Effects Range Median/Effects Range Low levels (ERM/ERM) (d). (1C – campaign 1, 2C – campaign 2, 3C – campaign 3).

**Table 6**

Metal concentrations in sediments from Guanabara Bay according to different authors. Metal concentrations are given in mg kg<sup>-1</sup> dry wet, except for Al and Fe given in %.

Sites	Al	Fe	Cd	Cr	Mn	Ni	Pb	Zn	Extraction
Guanabara Bay – RJ <sup>a</sup>	0.976–4.06	0.744–3.90	0.478–1.80	24.6–157	141–1363	1.11–15.9	14.6–107	89.0–456	HNO <sub>3</sub>
Guanabara Bay <sup>b</sup>						8.3 ± 1.2	14.9 ± 0.5	70.2 ± 3.9	HNO <sub>3</sub>
Guanabara Bay (BG 08) <sup>c</sup>	0.67–4.2	1–4	0.02–1.8	11.7–55.5	76–696.3	4.3–19.6	2.5–63.4	18.6–216.7	HNO <sub>3</sub>
Guanabara Bay (BG 14) <sup>c</sup>	2.0–5.9	2.6–4.0	0.35–1.13	25.6–46.3	203.3–884.6	7.8–16.4	5.6–36.9	41.3–161.8	
Guanabara Bay (BG 28) <sup>c</sup>	2.3–6.2	2.3–4.5	0.32–1.33	23.4–227.4	163.7–797.3	8.0–17.2	5.1–34.8	35.2–179.1	
Piedade Mangrove - Guanabara Bay <sup>d</sup>	0.56	1.9	0.10	n.a.	169	4.0	13.6	37	HNO <sub>3</sub>
Nova Orleans Mangrove - Guanabara Bay <sup>d</sup>	0.55–0.64	1.6–1.9	0.07–0.09	n.a.	183–360	4.7–6.1	9.1–9.8	31.0–43.2	
Surui Mangrove - Guanabara Bay <sup>d</sup>	0.90–1.01	2.0–2.1	0.07–0.08	n.a.	147–169	5.7	12.8	35.2–39.5	
Guanabara Bay <sup>e</sup>	0.6–9245	n.a.	n.a.	2–41,364	n.a.	1–35,155	2–19,340	5–755,149	HF/HClO <sub>3</sub>
Guapimirim Mangrove Forest - Guanabara Bay <sup>f</sup>	n.a.	n.a.	n.a.	n.a.	273	n.a.	26.0	26.7	HNO <sub>3</sub> /HClO <sub>4</sub>
Ilha do Governador Mangrove Forest - Guanabara Bay <sup>f</sup>	n.a.	n.a.	n.a.	n.a.	150	6.0	130	263	
São Gonçalo Mangrove Forest - Guanabara Bay <sup>f</sup>	n.a.	n.a.	n.a.	n.a.	71.7	8.7	20.0	610	
Duque de Caxias Mangrove Forest - Guanabara Bay <sup>f</sup>	n.a.	n.a.	n.a.	n.a.	80.8	10.3	86.7	53.3	
Jurujuba Sound – GB <sup>g</sup>	n.a.	0.1–2.12	n.a.	10–223	10–414	15–79	5–123	15–337	HNO <sub>3</sub> /HCl
Guanabara Bay <sup>h</sup>	n.a.	0.12–8.38	n.a.	1.9–279	13–1600	5–61	4.7–460	10–1660	HNO <sub>3</sub>
Guanabara Bay <sup>i</sup> (superficial sediments)	n.a.	n.a.	0.02–2.6	3.5–480	n.a.	n.a.	3.6–110	78–707	HNO <sub>3</sub>

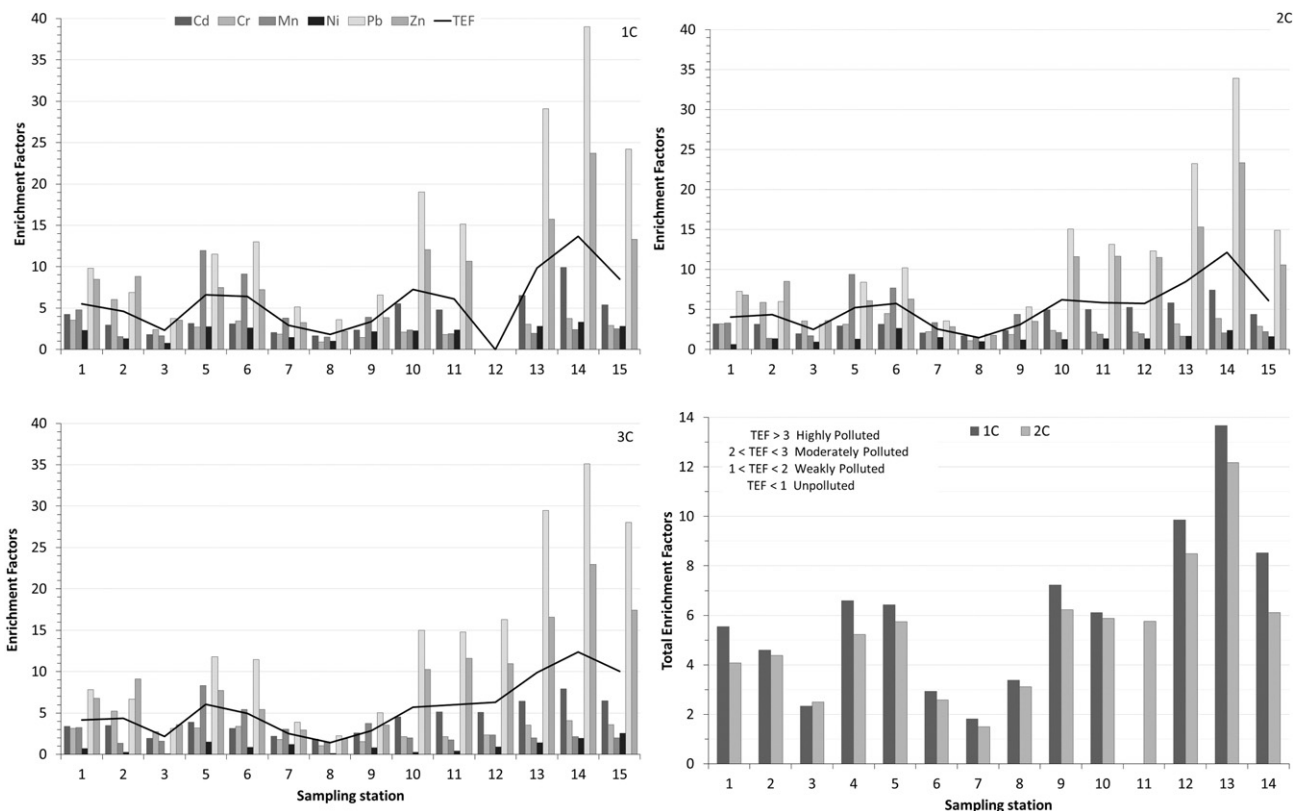
n.a.: not available.

- <sup>a</sup> This study.
- <sup>b</sup> Monteiro et al. (2012).
- <sup>c</sup> Monteiro et al. (2012).
- <sup>d</sup> Farias et al. (2007).
- <sup>e</sup> Baptista-Neto et al. (2006).
- <sup>f</sup> Machado et al. (2002).
- <sup>g</sup> Baptista-Neto et al. (2000).
- <sup>h</sup> Perin et al. (1997).
- <sup>i</sup> Rebello et al. (1986).

all three campaigns, whereas values were between TEL and PEL limits for all other stations.

Cr mainly contaminated Sector 1 (stations 1, 2 and 3), with levels above PEL. Sector 2 (stations 5 and 6) had higher contamination of Pb in campaign 1 with values between TEL/PEL, while Cr levels were above PEL in at least one of the sampling stations in both campaigns 2 and 3. Sector 3 (stations 7, 8 and 9) had rates of Cd in the range between

TEL-PEL during three campaigns, and contents of Cr below TEL in the three campaigns, except for station 7, that were above TEL in campaigns 2 and 3. Stations at Sector 4 (stations 10, 11 and 12) showed Cd, Pb and Zn levels between the TEL/PEL range, and below TEL levels for Cr and Ni in three campaigns. Sector 5 (stations 13, 14 and 15) was contaminated mainly by Zn, with concentrations above PEL in at least one of the sampling stations.



**Fig. 4.** Enrichment Factors (EF) and Total Enrichment Factors (TEF) calculated for sediments of Guanabara Bay (1C - campaign 1; 2C - campaign 2 and 3C - campaign 3).

Regarding mean quotients of PEL values (PELQ), Fig. 3 indicates “medium-high” contamination for the sediments collected from stations 2 and 14 in campaigns 1, 2 and 3 and from station 15 in campaign 3. All other stations were deemed to have “medium-low” contamination.

Comparing the metal concentrations to established ERL and ERM values, environmental impacts in the Sectors 1 and 5 were much greater than for other parts of GB. All values found for Ni were below ERL values. ERL values for Cd were exceeded only in the Sector 1 and at Sector 5—specifically, stations 2 and 14 (campaign 1), 12 and 14 (campaign 2) and in stations 1, 2, 3, 14 and 15 (campaign 3)—indicating a low probability of sediment toxicity, and no values were above the ERM for this metal. ERLs were exceeded for Cr in Sector 1 (stations 2 and 3) during three campaigns. ERL was exceeded for Pb in the GB areas experiencing the greatest shipping traffic; Sector 5 (stations 13, 14 and 15) and Sector 4 (stations 10, 11 and 12) in campaign 1, stations 13 and 14 in campaign 2 and stations 6, 10, 12, 13, 14 and 15 in campaign 3. Values did not exceed ERMs for Cd, Cr, Ni or Pb. However, for Zn, ERL was exceeded at stations 1, 2, 3, 5, 10, 11, 12 and 15 during the three campaigns, station 13 in campaigns 2 and 3, and station 14 in campaign 2. Values of Zn exceeded the ERM level at station 14 during the wet season (campaigns 1 and 3). According to the guide values for ERL/ERM, GB is polluted mainly by Zn, which showed levels ranging between ERL–ERM values in Sectors 1, 2, 4 and 5. Only in the NE zone was contamination levels below ERL for all evaluated metals. Furthermore, ERM mean quotients (ERMQ) indicate overall “low” contamination for GB (Fig. 3). Toxic effects are occasionally observed for metal concentrations exceeding ERL values but not ERM, although it is difficult to accurately predict at what frequency this occurs (McGrath et al., 2002).

Values from different sites and extractions methods are shown in Table 6. Rivers such as the Iguaçú, Sarapuí, Irajá and São João de Meriti situated in Sector 1 (De Souza et al., 1986; Rego et al., 1993; Wasserman et al., 2000) have eutrophic waters from the last decades due to a large sewage discharge, favoring the accumulation of metals in bottom sediments under anaerobic conditions (Perin et al., 1997; Machado et al., 2004). Pereira and Kuch (2005) reported very high metal concentrations for sewage sludge show that the lack of basic sanitation, with consequent discharge of gross sewage, can be an important source of zinc, mercury and copper to the environment. Extreme concentration values were attributed to point sources of contamination, such as the contribution of São João de Meriti river with a considerable decrease away from the river mouth (Wasserman et al., 2000). It is also emphasized as important sources of anthropogenic input the harbor areas, as was properly demonstrated by Baptista-Neto et al. (2005) and Cordeiro et al. (2015), corresponding to the stations 13, 14 and 15, situated in Sector 5.

#### 4.3. Enrichment factor and Igeo analyses

We observed that Ni values were around <1, indicating no anthropogenic enrichment (Fig. 4, Table 7). In contrast, EF values for the others metals most likely due to anthropogenic activities, i.e. Cd, Cr, Mn, Pb and Zn, were >1 (i.e. sediment content at least two times higher than background levels). On the basis of the mean EF values, sediments are enriched in metals in the following order: Pb > Zn > Cd > Mn > Cr > Ni, for the three campaigns.

Metals with EF > 1 can be considered as indicators of anthropogenic metal pollution and can be used to evaluate the degree of pollution of marine surface sediments by computing the Total Enrichment Factor (TEF) for each site by averaging EF values of all (n) indicator metals (in this case, Cd, Cr, Mn, Ni, Pb and Zn; n = 6):

$$TEF = \frac{\sum EF_i}{n}$$

Fig. 4 shows TEF values across sampling sites for the three campaigns and provides an integrated index of local metal pollution. Stations could

**Table 7**

Comparison of qualitative classification of sediments based on different interpretative approaches.

	Station	SEM/AVS	PELQ	ERMQ	TEF	Igeo	ATT*	CTT*
Campaign 1	1	NB	ML	ML	HP	MP	na	na
	2	NB	MH	ML	HP	MP	na	na
	3	NB	ML	ML	WP	UPMP	na	na
	5	NB	ML	ML	HP	MP	na	na
	6	NB	ML	ML	HP	MP	na	na
	7	NB	ML	ML	MP	UPMP	na	na
	8	NB	ML	ML	WP	UPMP	na	na
	9	NB	ML	ML	MP	UPMP	na	na
	10	NB	ML	ML	HP	MP	na	na
	11	NB	ML	ML	HP	MP	na	na
	12	–	–	–	–	–	–	–
	13	NB	ML	ML	HP	MSP	na	na
	14	NB	MH	ML	HP	MSP	na	na
	15	NB	ML	ML	HP	MP	na	na
	Campaign 2	1	NB	ML	ML	HP	MP	T
2		NB	MH	ML	HP	MP	T	SD
3		NB	ML	ML	WP	UPMP	T	NT
5		NB	ML	ML	HP	MP	NT	NT
6		NB	ML	ML	HP	UPMP	NT	NT
7		B	ML	ML	MP	UPMP	T	NT
8		NB	ML	ML	WP	UP	NT	NT
9		NB	ML	ML	MP	UPMP	NT	NT
10		NB	ML	ML	HP	MP	NT	NT
11		NB	ML	ML	HP	MP	NT	NT
12		NB	ML	ML	HP	MP	NT	NT
13		NB	ML	ML	HP	MP	NT	NT
14		NB	MH	ML	HP	MSP	NT	NT
15		NB	ML	ML	HP	MP	NT	SD
Campaign 3		1	NB	ML	ML	HP	MP	T
	2	NB	MH	ML	HP	MP	T	T
	3	NB	ML	ML	WP	MP	T	T
	5	NB	ML	ML	HP	MP	NT	T
	6	NB	ML	ML	HP	MP	T	NT
	7	NB	ML	ML	MP	UPMP	NT	T
	8	NB	ML	MH	WP	UP	T	T
	9	NB	ML	ML	MP	UPMP	NT	T
	10	NB	ML	ML	HP	MP	T	T
	11	NB	ML	ML	HP	MP	T	T
	12	NB	ML	ML	HP	MP	T	NT
	13	NB	ML	ML	HP	MSP	NT	T
	14	NB	MH	ML	HP	MSP	NT	T
	15	NB	MH	ML	HP	MSP	T	T

ATT - acute toxicity test; CTT - chronic toxicity test; B - bioavailable; NB - not bioavailable; ML - medium low; MH - medium high; UP - unpolluted; UPMP - unpolluted to moderately polluted; WP - weakly polluted; MP - moderately polluted; MSP - moderately to strongly polluted; HP - highly polluted; NA - not analyzed; SD - significantly different from the control; T - toxic; NT - not toxic.

\* Qualitative results after the data interpretation, considering the statistical analysis and the NH<sub>3</sub> interference.

be classified as highly polluted (TEF > 3) (stations 1, 2, 5, 6, 10 to 15), moderately polluted (2.0 < TEF < 3.0) (stations 7 and 9), and lower polluted (TEF < 2.0) (stations 3 and 8). The places where there is a pier (Sector 4) or a harbor (Sector 5) were polluted by metals, as well as stations 1 and 2 (Sector 1) that are located near the exit of the Iguaçú and Estrela rivers. These rivers receive industrial effluents, sewage and urban runoff and wastewater input from the Gramacho landfill.

The Igeo results are shown in Fig. 5. Sediment classification ranged from unpolluted (as far as Al, Fe and Ni is concerned) to moderately or strongly polluted (for Pb and Zn). For Al, Fe and Ni, all samples were classified as either background levels (class 0) or unpolluted (class 1). For Cr, station 2 was classified as moderately polluted (class 3), stations 1 and 3 as unpolluted to moderately polluted (class 2), and all other stations were classified as either background levels or unpolluted. Stations from the Sectors 2 and 3 were classified as unpolluted (class 1) for Cd, while the stations at Sectors 4 and 5 were classified as unpolluted to moderately polluted (classes 1–2). The Sectors 1 and 3 were somewhat contaminated with Mn being classified from unpolluted to moderately polluted (classes 1–3), but stations at Sectors 4 and 5 were in classes 0



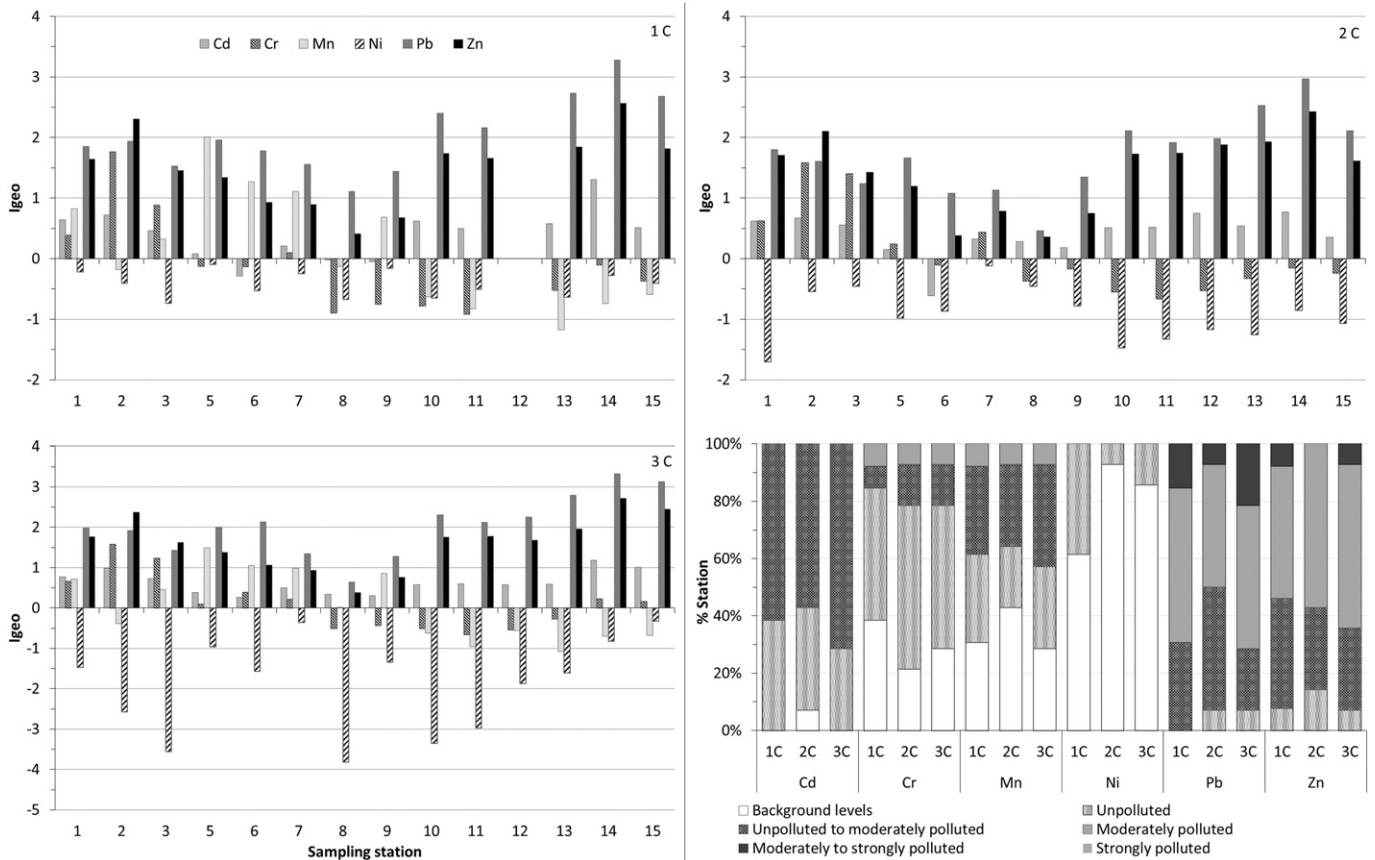


Fig. 5. Index of geoaccumulation ( $I_{geo}$ ) calculated for sediments of Guanabara Bay (1C - campaign 1, 2C - campaign 2 and 3C - campaign 3).

or 1 for this metal. For Zn, stations 3 to 9 were assigned either to class 1 (unpolluted) or 2 (unpolluted to moderately polluted); all other samples were in class 3 (moderately polluted), except for station 14 that was categorized class 4 (moderately to strongly polluted) for campaigns 1 and 3. For Pb, the samples collected in Sectors 1 and 2 were classified as unpolluted to moderately polluted (classes 2 and 3). Sector 3 samples were assigned to class 1 (unpolluted) or class 2 (unpolluted to moderately polluted), those of Sector 4 to class 3 (moderately polluted), and those of Sector 5 to class 3 (moderately polluted) or class 4 (moderately to strongly polluted).

4.3.1. Summary of approaches to assess metal contamination

A summary of sediment classifications based on the different approaches used in this study is presented in Table 7, together with the results of toxicity tests conducted by Maranhó et al. (2009) in samples collected during campaigns 2 and 3 of this study. Those toxicity tests were performed by using the amphipod *Tiburunella viscana* for acute toxicity tests with whole sediments, and embryo-larvae of the sea urchin *Lytechinus variegatus* for chronic toxicity tests with elutriate samples.

Studies have found that sediment characteristics (SEM/AVS) and chemical concentrations (ERL-ERMs) are both valid methods for predicting sediment toxicity (Long and MacDonald, 1998; McGrath et al., 2002). Our attempt in this study to predict sediment impacts using the AVS-SEM method produced results contradictory to those of other methods used in the present work. To predict sediment impacts more accurately, particularly in non-temperate areas for which data was not included in determinations of standard guidelines, evidence from either of these methods should be substantiated through toxicity tests or by other appropriate means (Hinkey and Zaidi, 2007). Appropriate and

accurate sediment quality guidelines (SQGs) should be developed specifically for the unique biogeochemistry of the region in which they will be applied.

There was a discrepancy between the results derived from the  $\Sigma$ SEM/AVS ratio and the acute toxicity test for 3 samples of campaign 2 (see Table 7). In campaign 3, divergent results were also observed for the chronic toxicity test and other methodologies (see Table 7).

Seasonal variation in sediment quality classifications was not apparent according to  $\Sigma$ SEM/AVS, PELQ, ERMQ and TEF approaches. However, according to  $I_{geo}$ , sediments collected during the wet season (campaign 3) had a worse classification in terms of sediment quality. Based on the precautionary principle, for  $I_{geo}$ , we classified a sediment sample according to the worst pollution ranking for each element, i.e. if the sample showed enrichment for a single element, it was ranked based on this worst condition.

Acute and chronic toxicity of GB sediments was evaluated by Maranhó et al., 2009, 2010. Those studies showed that the sediment quality of the bay is low, because sediments are toxic, and that GB sediments are mainly chronically toxic, but acutely toxic ones also occur. The NW zone of the bay exhibits the worse conditions. Moreover, those studies evidenced that ammonia concentrations in GB sediments may vary from rainy to dry seasons, influencing their toxicity and playing an additional role in interactions between the mixtures of contaminants and biota. This toxicity appears to be related to: 1) different contamination sources, which vary between areas of GB; 2) past oil spills, which released large amounts of pollutants in the bay; and 3) to GB hydrodynamics. This explains why legally-protected areas of GB present signs of environmental degradation in terms of chronic toxicity. GB sediments also have the potential to affect the water column since elutriates were toxic.

In summary, stations 2 (Sector 1) and 13, 14 and 15 (Sector 5) were classified as having the worst conditions in at least one of the methodological approaches used, whereas stations 3 (Sector 1) and 7, 8 and 9 (Sector 3) showed the best conditions over the course of three sampling campaigns. Analyses of the predictive powers of each of the geochemical indices showed that TEF is the most sensitive. According to Choueri et al. (2009), sediment quality criteria that are derived from site-specific data better predict toxicity in the environment, among other effects caused by contaminants, and this approach should be applied to sediment management.

## 5. Conclusions

In general, none of the methodologies used here presented seasonal variation in sediment quality. However, the methodologies showed differences in the classification of sediments and the degree of contamination. All methods indicated that stations 2 and 14 were the most affected, (Sectors 1 and 5, respectively), and that the stations of Sector 3 (stations 7, 8 and 9) had the best conditions. The sediments of GB are mainly polluted by Cr, Pb and Zn.

According to AVS/SEM results, metals are not available to the biota, despite toxicity tests showing the opposite. However, it is important to emphasize that ammonia concentrations in sediments may influence toxicity tests, generating false positive results. Thus, in some instances, application of general SQGs approaches may not fully address the local particularities of each environment.

Our combination of diverse risk assessment indices has provided a comprehensive understanding of surface sediment quality in GB. Among the various methods employed, those utilizing background values for the area seem to reflect historical contamination of GB.

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