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Contamination of port zone sediments by metals from Large Marine Ecosystems of Brazil

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ABSTRACT

Sediment contamination by metals poses risks to coastal ecosystems and is considered to be problematic to dredging operations. In Brazil, there are differences in sedimentology along the Large Marine Ecosystems in relation to the metal distributions. We aimed to assess the extent of Al, Fe, Hg, Cd, Cr, Cu, Ni, Pb and Zn contamination in sediments from port zones in northeast (Mucuripe and Pecém) and southeast (Santos) Brazil through geochemical analyses and sediment quality ratings. The metal concentrations found in these port zones were higher than those observed in the continental shelf or the background values in both regions. In the northeast, metals were associated with carbonate, while in Santos, they were associated with mud. Geochemical analyses showed enrichments in Hg, Cd, Cu, Ni and Zn, and a simple application of international sediment quality guidelines failed to predict their impacts, whereas the use of site-specific values that were derived by geochemical and ecotoxicological approaches seemed to be more appropriate in the management of the dredged sediments.

1. Introduction

Port terminals and harbor areas play important roles in the economy worldwide through the transport and storage of traded goods. However, their operating activities have been recognized to be extremely harmful to marine and coastal environments. The berths, docks and storage warehouses of ports are often installed in highly important ecological areas, such as bays and mangroves. Consequently, the installation of ports has been attributed to several negative environmental impacts on the coastal zone, such as (1) the construction of jetties, which can change sediment transport, (2) pollution due to the generation of waste; the discharge of contaminants, such as sewage and wastewater, petroleum and its derivatives; and compounds that are released by antifouling paints, and (3) the introduction of exotic species to the community through ballast water (NRC, 1997). Port activities are often associated with aquatic pollution and the spreading of contaminants along the different environmental compartments, such as the water, sediment and biota (Riba et al., 2005; Pereira et al., 2007). Moreover, special attention must be given to sediments, which frequently present with higher concentrations of contaminants compared with the water column, and may constitute not only a sink but also a secondary source of contaminants to the water column and biota (Burton, 1992).

Despite being a consequence of port operation, aquatic pollution represents a problem in port management; in particular, sediment contamination restricts dredging operations and the disposal of dredged material. The impacts that are associated with dredging may be immediate and affect two regions: the dredged areas themselves, by the removal and resuspension of sediment and recontamination due to overflow, and the disposal sites that receive the dredged material. Such disposal may cover natural benthic communities and transfer contaminants to the disposal sites (USEPA, 1991). Some countries, such as the United States and Canada, have developed enforcements and criteria to characterize and classify the contaminated sediments (EPA, 1991; CCME, 1995). Among them, the development and application of Sediment Quality Guidelines (SQGs) have been particularly important to facilitate decision-making aimed at protecting or remediating the aquatic environments.

In Brazil, the Federal Resolution CONAMA 344/04 (Brazil, 2004) is a normative enforcement that addresses the management of dredged sediments and the environmental permits that are required for such operations; this resolution also includes some SQGs, which are based on international values. It states that sediments

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must be analyzed and results compared with the respective SQGs, considering two levels (1 and 2) to determine three quality categories for each contaminant. Concentrations below level 1 indicate good quality; concentrations above level 2 indicate sediments are polluted and are most likely to affect the biota and finally, concentrations between levels 1 and 2 indicate the potential for adverse effects.

Among the contaminants that are associated with harbor areas, metals have been reported to be of major concern due to their potential toxicities and tendencies to bioaccumulate along the food chain. Once deposited in the sediments, metals can be adsorbed by fine particles and form complexes with carbonates ($CaCO_3$), iron and manganese oxides (FeOOH and Mn-OOH), organic carbon (CO) and sulfides (S^{2-}). These complexes are important geochemical carriers, regulating partition, mobility, bioavailability and thus, metal toxicity, according to environmental conditions (DiToro et al., 1991; Chapman et al., 1999; Riba et al., 2003; DelValls and Conradi, 2000).

Lacerda and Marins (2005) suggested that the first step to understanding metal dynamics and monitoring their concentrations is to know the origin, transport and geochemical information of the sediments that are found along the continental and coastal shelves. Adopting the Large Marine Ecosystems (LME) concept and typology, the Brazilian coast can be divided into three large regions, including the north (extremely northern Brazil, Amazon coast), east (actual northeastern Brazil) and south (including southeastern and southern Brazil), based on similarities in bathymetric, hydrological, hydrographic, sedimentology and productivity. The north and south portions are controlled mainly by a coastal topography and a continental input of material, while the east portion is an oligotrophic environment that is dominated by boundaries of ocean currents that possess high diversity and low productivity (Ekau and Knoppers, 1999; Marins et al., 2004). Additionally, according to Lacerda and Marins (2005), there are differences in sedimentology between the inner and outer shelves in the Brazilian northeast and southeast regions (east and south LMEs, respectively), with a predominance of clastic materials in the southeast compared with the northeast, which is richer in carbonates.

In this context, the aim of the present study was to assess the distribution of major and trace metal levels in the port zone sediments from two different LMEs in Brazil: the east LME, including Mucuripe and Pecém harbors, both of which are located in the state of Ceará (NE Brazil), and the south LME, including Santos harbor, which is located in São Paulo state (SE Brazil). Moreover, this study also intended to assess the sediment quality in these three ports by applying geochemical indices and comparisons with sediment quality values and correlating them with the properties of the different sedimentary facies.

2. Materials and methods

2.1. Study areas

Mucuripe harbor is located within Mucuripe Bay, in Fortaleza, Ceará, and its infrastructure comprises the access channel, anchorage areas and evolution basins and a long jetty (1900 m long). Pecém harbor is located in a port-industrial complex at Ponta do Pecém, which is the municipal district of Sao Gonçalo do Amarante and is located approximately 60 km west of Fortaleza. Pecém is an offshore terminal that is considered to be technologically advanced because of its construction 2000 m away from the shoreline and connection to the land by a bridge; thus, the coastal currents are not completely affected and sediment transport occurs between its pillars.

The Brazilian northeast coastal region is marked by a tropical wet climate (Aw) due to the intertropical convergence zone (ITCZ). There is a predominance of trade winds in E–W direction, which influences the sediment transport in this direction (Jimenez and Maia, 1999; Nogueira et al., 2005). The composition of the coast of Ceará shows two distinctive characteristics: organogenic and terrigenous facies. Organogenic substrates are derived from calcareous algae and contribute to some 75–95% of calcium carbonate deposition with organic matter concentrations ranging from 23.6% to 46%. The outer shelf sediments (40 m isobath) are covered by gravel, while the sediments from the inner shelf (below the 20 m isobath) are predominantly composed of sand with biodetritic gravel and low levels of mud (below 2.5%). Sediments from terrigenous facies are characterized by siliciclastic material, including quartz sand, feldspar, heavy minerals (smectite, kaolinite and illite) and clay (Freire et al., 2004).

Located in the Santos Estuarine System (SES) in the southeast region, Santos harbor is the major port of Latin America and the main hub for cargo and goods in Brazil. Currently, the port activities and the Cubatão industrial complex, mainly through effluent discharges, are the main sources of contaminants to the SES, accounting for more than 90% of the known toxins that are released into the environment (Lamparelli et al., 2001; Abessa et al., 2008).

The climate in the SES can be classified as hot, humid and tropical (Swa) with doldrums with no wind during 51.8% of the period and winds blowing from the southeast with a decreasing scale from the south the remainder of the time (Siqueira et al., 2006). In the Santos Estuarine System, the deposition of sediment in the estuary results from the influences of continental and marine hydrodynamic processes (Fúlfaro and Ponçano, 1976; Fukumoto et al., 2004). The former includes a wide net of freshwater drainage and erosion by the rivers crossing the region and is characterized by the presence of granites, migmatites, quartz and alkaline rocks as a terrigenous facies. The marine input, on the other hand, is controlled by tidal currents and continental shelf erosion, with sediment transport that is reworked by currents that are parallel to the coast. The particle size composition of the sediment deposits ranges gradually from silt to sand, where the presence of mangroves function as a sedimentary material retainer.

2.2. Sediment sampling and handling

In Mucuripe harbor, sediment sampling was carried out in August 2007 in 10 stations with different sedimentation conditions and bathymetry that were spaced between 500 and 1000 m from one to the next (Fig. 1): M1 and M2 were located in front of the commercial docks beside the docking of ships and also received industrial discharge from the PETROBRAS oil refinery (Brazilian oil company); M3, M4 and M5 were situated close to fishing and tanker piers, where oil from the refinery was unloaded; M6 and M7 were placed at the access channel; and M8, M9 and M10 were in unsheltered areas, upstream from the port. In Pecém harbor, the collection was carried out in January 2008 in 5 distinct stations that were spaced by 500 to 750 m. (Fig. 1). P1 and P2 were located close to docking piers 1 and 2, respectively, where steel products, bulk liquids, liquefied gases and general cargo were shipped and received; P3 was located at the access channel; and P4 and P5 were in unsheltered areas, of which P4 was located close to a zone of waves and current diffraction, and P5 was influenced by the sediment transport that occurred through the port bridge pillars. In Santos harbor, the sediment was sampled in November 2007 from five stations (Fig. 1): S1, which was positioned at the Santos Channel mouth; S2, which was at the Container Terminal; S3, which was located at Diana Island towards the area of an expected port

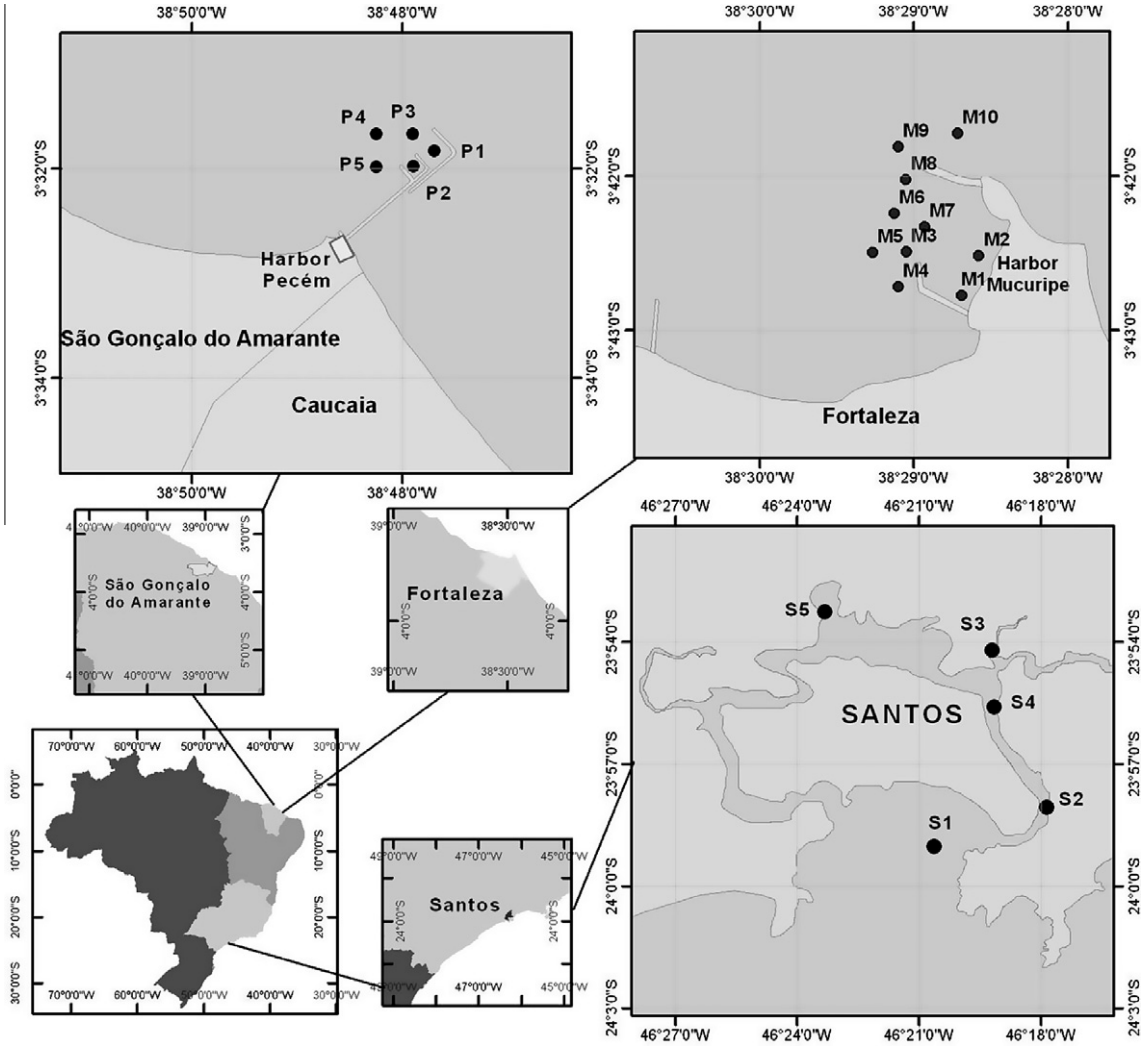

Fig. 1. Stations of sediment sampling in Mucuripe, Pecém and Santos harbors.

expansion; S4, which was situated at Alemoa Terminal; and S5, which was at the Piaçaguera channel.

Samples were collected using a *Van Veen* grab, and during sediment sampling, the depth of each station was determined. Following collection, the samples were dried at 40 °C, separated into 50 g aliquots and packed in plastic containers at room temperature until analyses. Samples were analyzed for levels of major (Al, Fe) and trace elements (Hg, Cd, Cr, Cu, Ni, Pb and Zn) in addition their concentrations of carbonates and organic matter and sediment properties.

3. Analytical techniques

3.1. Sediment properties

Particle size distribution was measured by the wet sieving method for total mud (silt + clay) separation followed by dry sieving to separate the gravel and sand fractions according to Suguio (1973). The estimations of carbonate concentrations in the sediments ($CaCO_3$) were conducted following digestion in HCl and gravimetry (Gross, 1971), while organic matter concentrations (OM) were determined by adapting the method of combustion in a muffle and gravimetry (Luczak et al., 1997). Values that were determined in all methods are expressed as percentages.

3.2. Major and trace elements

For each sample, a known quantity (0.5 g) of sediment was digested in a high-pressure microwave system (CEM Corporation, model MDS—2000). Metals were extracted using an acid solution that contained 9 ml of HNO_3 and 3 ml of HCl, according to the recommendations of EPA 3051A (USEPA, 1996). Al, Fe, Cd, Cr, Cu, Ni, Pb and Zn concentrations were measured using the flame mode of a Fast Sequential Atomic Absorption Spectroscope Varian, model Spectr-AAS-220-FS, with deuterium lamp background corrections for Pb, Ni and Hg. The Hg concentration was measured by cold vapor generation. The spectrometer was coupled to a typical FIA (Flow Analysis Injection) manifold with a manual injection valve that injected 500 μL of digested sample into a flow of Milli-Q water (10 mL min^{-1}) (Hortellani et al., 2008).

This method was validated by analyzing two Standard Reference Materials SRM 2704 (the Buffalo River Sediment and SRM-1646a Estuarine Sediment) in three replicates (Appendix A). These reference materials were certificated for the total extraction of metals, and this method was not intended to completely decompose the sample; it was rather aimed at providing a near total digestion of the samples to obtain the elements that are associated with the adsorbed, exchangeable, oxidizable and reduced geochemical fractions. That being said, these elements, regardless of their bonding strength, can be considered to be anthropogenic in

origin, with the exception of those from the residual fraction, which are associated with the crystalline structures of minerals and thus are considered to be of natural origins (Sastre et al., 2002).

3.3. Enrichment factor and Index of geoaccumulation analysis

After the concentrations of the metals were obtained, an index of geoaccumulation (I_{geo}) was applied to evaluate and classify the sediment quality of these different areas. This index was originally defined by Muller (1979) as a criterion to evaluate the intensity of heavy metal pollution and is defined as the following:

$$I_{geo} = \log 2(Cn/1.5^{*}Bn)$$

where Cn refers to the sedimentary concentration of a measured metal n, Bn represents the baseline value or reference site of a metal n, and the factor 1.5 corresponds to possible variations from the baseline due to lithological processes.

Hence, for quality classifications, I_{geo} results are applied to a qualitative scale of pollution intensity (Table 1) and, according to this scale, samples with I_{geo} values of above 1 possess early signs of pollution. Based on the precautionary principle, for this index, a sediment sample was classified considering the worst pollution ranking for each element; i.e., if the sample showed enrichment for a single element, it would be ranked based on this worse condition.

In addition to I_{geo}, normalization has been widely used to detect anomalous concentrations of metals in sediments. To achieve this, grain size, corrections with inert mineral, comparisons with conservative elements and background levels are the most employed normalizers (Rubio et al., 2000; Aloupi and Angelidis, 2001; Adamo et al., 2005; Hortellani et al., 2008). Due to the lack of studies focusing on the geochemical backgrounds of major and trace metals for the coast of Ceará (East portion), in this study, an absolute metal concentration that was obtained by Aguiar et al. (2007) for total sediment digestion from the continental shelf of Ceará was adopted for all of the elements with the exception of Hg, for which the background value was proposed by Marins et al. (2004). For the Santos harbor (south portion), the baseline values were proposed by Luiz-Silva et al. (2006) by the near-total digestion of sediments from the Santos Estuarine System, including Cd, which was also used to interpret the results for the Ceará harbor areas. Thus, these baseline levels were used as a background reference for normalizing metal concentrations as proposed by Adamo et al. (2005). The enrichment factor (EF) for each element was also calculated as follows:

$$EF = (C_{sed} - C_{back})/C_{back} \quad (1)$$

where C_{sed} is the concentration of a given metal in each sample, and C_{back} is the background or reference value. If the EF is higher than one, it may be indicative of an anthropogenic source and used for assessing the degree of pollution by computing a total enrichment factor (R) for each station, averaging the EF values of all of the metals. Samples with values that were below the QL were calculated using their own QL:

Table 1
Scale of pollution intensity for Geoaccumulation index values (I_{geo}).

I_{geo}	Class	Pollution intensity
>5	6	Very strongly polluted
4–5	5	Strongly polluted
3–4	4	Moderately to strongly polluted
2–3	3	Moderately polluted
1–2	2	Unpolluted to moderately polluted
0–1	1	Unpolluted
<0	0	Background levels

$$R = \left(\sum EF\right)/n \quad (2)$$

Using these calculations, a classification of the examined sites was conducted using the following criteria: highly polluted ($R > 3$), moderately polluted ($2.0 < R < 3.0$), weakly polluted ($1.0 < R < 2.0$) and unpolluted ($R < 1$) (Adamo et al., 2005).

4. Results and discussion

4.1. Sediment properties

Grain size, carbonates and organic matter distributions are shown in Table 2. The sediments from Mucuripe harbor were classified as sandy for most samples, except for station M10, where the predominant fraction was gravel. In Pecém harbor, sediments were also classified as sandy. According to Marques et al. (2008), most of the outer shelf sediments are predominately composed of gravel, while in the inner shelf, sands account for the higher occurrences, although some gravel can be found, and the concentration of mud is below 2.5%.

The carbonate levels in the eastern areas were high, ranging from 5.74% to 34.96% in Mucuripe and 24.78% to 36.96% in Pecém. For these areas, the organic matter concentrations ranged from 0.13% to 16.22% (Mucuripe) and 2.49% to 14.87% (Pecém). Such values corroborate with the terrigenous facies that are characteristic of the region, where the carbonate fraction is biogenic with levels ranging from 0.2 to 95% and organic matter concentrations ranging from 0.76% to 38.9% (Freire et al., 2004; Lacerda and Marins, 2005; Marques et al., 2008; Nascimento et al., 2010). The distribution of fine particles in high levels at the deeper stations in the sheltered areas can be associated with the hydrodynamic effects of sediment transport that are induced by the jetties, creating areas of deposition in both ports.

In Santos harbor, sediments showed a predominance of fine sands for all sites with increasing amounts of mud towards the inner estuary (from S2 to S5). Carbonate concentrations ranged from 7.54% to 12.46%, and organic matter levels ranged from 5.35% to 13.88%. In contrast with the east LME, finer particle sizes occurred in the Santos estuary, which gradually ranged from mud to sand, which is where the presence of mangroves functioned as a sedimentary material retainer, and the sewage outfall from Santos promoted the input of material to the Bay, explaining the high levels of

Table 2
Sediment properties from Mucuripe, Pecém and Santos harbors.

Stations	Depth (m)	Gravel (%)	Sand (%)	Mud (%)	$CaCO_3$ (%)	OM (%)
M1	7.4	0.00	75.97	24.03	18.28	5.61
M2	15.0	0.00	92.14	7.86	30.26	12.72
M3	15.4	0.00	77.26	22.74	25.05	5.99
M4	14.7	0.00	97.58	2.42	34.96	16.22
M5	10.7	0.16	84.44	15.56	15.72	3.28
M6	14.6	0.00	83.26	16.74	26.60	8.64
M7	9.6	0.00	94.55	5.45	22.19	12.23
M8	9.6	0.00	99.41	0.59	9.41	0.96
M9	11.9	0.00	99.92	0.08	5.74	0.57
M10	12.6	40.82	59.18	0.00	8.58	0.13
P1	16.7	0.00	95.58	4.42	36.96	14.87
P2	16.4	0.00	89.06	10.94	33.76	12.23
P3	17.5	0.00	91.83	8.17	28.90	14.69
P4	17.2	0.00	85.70	14.30	26.50	7.71
P5	15.1	0.00	93.11	6.89	24.78	2.49
S1	15.0	0.00	88.63	11.37	10.96	9.91
S2	14.0	0.24	93.59	6.17	7.99	5.35
S3	2.0	0.00	91.49	8.51	10.16	12.22
S4	3.0	0.00	93.40	6.60	12.46	13.88
S5	4.0	0.00	82.59	17.41	7.54	11.41

mud, carbonates and organic matter in S1. Fukumoto et al. (2004) identified two sectors for Santos Bay: (a) the east and center of the bay, which is characterized by higher amounts of fine sediments corresponding with higher amounts of organic matter, where sedimentation is related either to the interaction between the circulation and estuarine flows or the influence of the dynamics that occur after the installation of sewage outfall systems, and (b) the west, north and south boundaries of the bay, comprising areas near the coastline and the external portion, where the sediments are sandy and of marine origin, and the deposition of organic matter is less significant.

4.2. Spatial distribution of major and trace metals

Major and trace element concentrations are presented in Table 3. In the Mucuripe harbor, there was an enrichment of up to one order of magnitude in the sheltered stations (M1–M7) compared with the unsheltered ones (M8, M9 and M10) in Cr, Cu, Ni and Zn. Low concentrations of Hg, which neared the detection limit, were observed. Although Cd was detected in only half of the stations, the levels were above the baseline for the Santos harbor region. A similar pattern was found in Pecém, where average levels were relatively higher than those found in Mucuripe. Cd was detected only in P1 and P2 and Pb only in P1. At the Santos harbor, the pattern of distribution suggested that metal concentrations rose towards the inner estuary. In this region, there was a significant increase in Hg and Zn levels compared with the local baseline, while for the other elements, this increase was relatively higher. Cd levels were below the detection limit.

Natural concentrations of major and trace elements are strongly influenced by the nature of the inorganic matter that results from physical and chemical weathering. This inorganic matter is essentially formed from a limited number of silicate minerals, such as quartz, feldspar, mica and clay minerals, with smaller contributions from metal oxides and sulfides that make up the material that is transported by the masses of water in the coastal zone (Carvalho et al., 2002). Nevertheless, the input of contaminants by anthropogenic sources also promotes changes in this distribution pattern. Industrial, hospital, urban and domestic wastes, which may contain products such as paint, pesticides, pharmaceuticals, photographic chemicals, detergents, personal care products, waste oil, batteries and plastics, are among the main anthropogenic sources of contamination (Petrovic et al., 2003; Marins et al., 2004).

According to Casado-Martínez et al. (2006), metals are some of the main contaminants in harbor sediments and dredged material. Table 4 presents a compilation of Hg, Cd, Cr, Cu, Ni, Pb and Zn concentrations from the total and near-total digestion of sediments in different port zones worldwide, including Brazil. Although there are regional particularities in sediment composition in the different LMEs along the coastal zone, it is clear that enriched elements, such as Cr, Cu, Ni and especially Zn, even occurring at the same order of magnitude and specifically in the east harbors of the areas of this study, are similar to those found in contaminated regions and other port areas. In the case of Zn, several studies demonstrate the toxicity of sediments that are contaminated by Zn-enriched complex mixtures (Liu et al., 1999; Dave and Nilsson, 1999; Anderson et al., 2007; Choueri et al., 2009a). Fishes and benthic organisms

Table 3
Major and trace elements in $\mu g\, g^{-1}$ (dry weight) from Mucuripe, Pecém and Santos harbors. AL and Fe expressed in%.

Stations	Al	Fe	Hg	Cd	Cr	Cu	Ni	Pb	Zn
M1	2.90	1.94	0.04	0.90	38.00	13.82	16.54	2.59	469.33
M2	2.42	2.39	<0.03	0.85	38.10	15.46	19.89	6.69	535.82
M3	2.49	1.85	0.03	1.41	32.32	11.20	16.66	3.58	399.58
M4	3.13	2.47	0.04	0.64	50.13	16.76	21.49	2.60	583.51
M5	0.87	0.80	<0.03	<0.60	13.45	3.71	6.949	<2.00	199.46
M6	3.36	1.99	0.04	0.60	41.48	12.13	17.78	2.54	420.90
M7	1.70	1.66	0.03	<0.60	26.89	9.77	15.24	2.06	365.65
M8	0.30	0.29	<0.03	<0.60	5.23	0.49	7.20	<2.00	62.64
M9	0.16	0.13	<0.03	<0.60	3.33	<0.7	<2.00	<2.00	25.03
M10	0.20	0.28	<0.03	<0.60	5.16	1.01	5.29	<2.00	41.98
Mean	1.75	1.38	0.04	0.88	25.41	8.48	14.11	3.34	310.39
SD	1.23	0.87	0.01	0.33	16.39	6.12	6.04	1.71	200.26
P1	4.46	2.78	0.04	0.60	63.13	18.77	24.71	3.55	639.95
P2	3.56	2.38	0.03	1.28	48.55	16.93	22.20	<2.00	569.04
P3	4.09	2.70	0.04	<0.60	56.24	15.78	23.81	<2.00	583.05
P4	1.56	1.49	0.03	<0.60	25.65	8.62	11.48	<2.00	312.49
P5	0.83	1.10	<0.03	<0.60	17.68	5.49	11.72	<2.00	215.03
Mean	2.90	2.09	0.04	0.94	42.25	13.12	18.79	NC	463.91
SD	1.61	0.75	0.01	0.48	19.69	5.74	6.62	NC	187.82
S1	1.62	2.15	0.04	<0.60	28.17	9.01	10.88	9.09	509.08
S2	1.99	1.91	0.15	<0.60	26.31	15.04	11.42	15.6	621.24
S3	3.01	2.14	0.18	<0.60	29.82	12.02	11.10	7.57	810.93
S4	2.89	2.56	0.28	<0.60	34.26	17.56	15.18	16.7	917.43
S5	3.78	3.23	0.64	<0.60	42.74	27.28	22.28	12.76	1077.33
Mean	2.66	2.40	0.26	NC	32.26	16.18	14.17	12.34	787.20
SD	0.86	0.52	0.23	NC	6.56	6.98	4.86	3.97	227.26
BST	2.12	2.90	0.12	0.11	31.00	14.00	14.00	15	51.00
BCE	1.13	2.80	0.012	–	11.40	2.01	11.70	19.7	24.10
Brazilian SQGs[a]		Level 1	0.15	1.2	81.00	34.00	20.90	46.7	150.00
		Level 2	0.71	9.6	370.00	270.00	51.60	218	410.00
Site-specific SQV for SES[b]		T	0.08	–	27.85	–	5.90	10.3	37.90
		P	0.32	0.75	48.80	6.55	21.20	19.2	61.70

BST-baseline for a Santos Estuarine System (Luiz-Silva et al., 2006).
BCE-baseline for Ceará coast (Marins et al., 2004; Aguiar et al., 2007).
Nc–not calculated.
[a] Brazilian SQGs for dredging activities.
[b] Site-specific SQVs for Santos Estuarine System proposed by Choueri et al. (2009b).

Table 4
Trace metals distribution in μg g^{-1} from different Ports and harbor areas.

Location	Hg	Cd	Cr	Cu	Ni	Pb	Zn	Author
Victoria harbor	–	2.61–3.33	57.5–601.2	45–3789.5	23.6–177.1	47.4–138.1	97.9–610.4	A
Port of Rotterdam	<0.2–0.8	<0.5–1.8	–	<5–40	<5–20	<10–60	15–190	B
Montevideo harbor	0.6–1.3	<1.0–1.6	79–253	59–135	26–34	44–128	174–491	C
Port of Barcelona	–	4–1.4	45–95	70–195	18–27	85–130	180–300	D
Port of Ceuta	–	–	13–381	5–865	8–671	10–516	29–695	E
Santos Estuarine System	<0.03–0.92	<0.50–1.49	<5.0–97.5	–	1.3–44.2	<2.0–204.8	6.0–312.0	F
Vitoria Estuarine System	0.03–0.82	–	35–280	5–660	6–245	5–292	27–812	G
Paranaguá Estuarine System	–	<0.001	14.50–58.00	<0.04–16.20	6.65–21.90	<0.30–29.75	26.95–80.50	H
Santos harbor	0.04–0.64	<0.60	26.31–42.74	9.01–27.28	10.88–22.28	7.57–16.7	509.08–1077.33	I
Mucuripe harbor	<0.03–0.04	<0.60–1.41	3.33–50.13	<0–16.76	<2.00–21.49	<2.00–3.58	25.03–583.51	I
Pecém harbor	<0.03–0.04	<0.60–1.28	17.68–63.13	5.49–18.77	11.48–24.71	<2.00–3.55	215.03–639.95	I

A – Wong et al. (1995); B – Van den Hurk et al. (1997); C – Muniz et al. (2004); D – Guevara-Riba et al. (2004); E – Guerra-García and García-Gómez (2005); F– Hortellani et al. (2008); G – Jesus et al. (2004); H – Choueri et al. (2009a); I – This study.

are sensitive to this element, which may bioaccumulate (Pierson, 1981; Hassler and Wilkinson, 2003; Riba et al., 2004) and be transferred by the food web, thus representing a risk to human health (Doğam-Sağlamtimur and Kumbur, 2010).

Bezerra et al. (2007) emphasized that coastal hydrodynamic aspects were not evaluated for Mucuripe harbor and generated impacts that were observed approximately 20 km west of Fortaleza with the erosion of adjacent beaches. The construction of a jetty resulted in a change in sediment transport, which occurred naturally in the east–west direction and in the sheltered areas. The current diffraction induced by the jetty caused siltation of the bottom (Maia et al., 1998), which may have intervened in matter dispersion and deposition. In Pecém harbor, during the installation of the jetty, there was a temporary interruption of sediment transport, causing heavy sedimentation in the southeast and erosion on the northwest end of the structure with shoreline reduction. After the termination of construction, sediment transport was restored and conditions returned to baseline with coastline stability. Considering the similarities in jetty arrangement and direction of currents, it is possible that a deposition process similar to that which occurred in Mucuripe also took place in Pecém, which would explain the presence of high levels of metals in the sheltered stations of both ports. However, further studies must be conducted, including current modeling and sediment transport, to elucidate this question.

On the other hand, in Santos harbor, as previously described, the sedimentation process is different and shows two distinct areas: the first is the result of a unidirectional flow due to river drainage, and the second is under tide influence. Therefore, in the inner estuary, transport and deposition are influenced by the interaction of these two processes, resulting in a zone of low energy transport (Tessler et al., 2006). In the bay, sediment composition is dominated by sedimentary facies that are associated with two main hydrodynamic factors: eddies, causing the deposition of marine-originated matter with high $CaCO_3$ concentrations, and the outfalls, the flows of which act as hydraulic barriers resulting in the matter transport pattern that occurs along the bay (Fukumoto et al., 2004).

Therefore, to best understand the metal distribution that is associated with the sedimentation patterns Table 5 was constructed, which contains the Pearson's correlations of the analyzed elements and the sediment properties. For the east LME harbors (Mucuripe and Pecém), Al, Fe, Cr, Cu, Ni and Zn showed significant correlations with $CaCO_3$ and OM concentrations, and mud presented with positive correlations to the majority of the elements with the exception of Pb. According to Aguiar et al. (2007), in the east LME continental shelf between the Ceará and Rio Grande do Norte states, the presence of terrigenous sediments and matter that is transported by local rivers has influenced the metal deposition in the inner shelf; it is likely that the transport process in combination with the deposition area that is generated by the jetties in both harbors explain the correlations found herein. In the south LME, however, sediments from Santos harbor did not show correlations of any element with $CaCO_3$ concentrations. Nevertheless, Fe, Hg, Cr and Ni correlated well with mud concentrations, whereas Al, Fe, Cr and Zn correlated positively with organic matter. In this case, there is a clear association of metal distribution with the pattern of deposition that is described above because the stations with larger amounts of mud and organic matter are in the upper estuary around areas with industrial and irregular urban occupation (including a major steel plant).

Table 5
Comparison of Pearson's correlation coefficient between major and trace metals and sediment properties from Mucuripe and Pecém (East portion) and Santos (South portion) harbors.

	East			South		
	$CaCO_3$	Mud	OM	$CaCO_3$	Mud	OM
Al	0.84[a]	0.33	0.85[a]	−0.25	0.51	0.58
Fe	0.92[a]	0.31	0.92[a]	−0.22	0.78	0.52
Hg	0.45	0.17	0.53[b]	−0.47	0.70	0.33
Cd	0.26	0.54[b]	0.11	NC	NC	NC
Cr	0.90[a]	0.25	0.90[a]	−0.25	0.76	0.53
Cu	0.91[a]	0.31	0.91[a]	−0.51	0.61	0.20
Ni	0.91[a]	0.24	0.91[a]	−0.39	0.75	0.34
Pb	0.37	0.11	0.35	−0.02	−0.29	−0.15
Zn	0.91[a]	0.31	0.92[a]	−0.17	0.46	0.60

Nc–not calculated.
[a] Correlation is significant at the 0.01 level (2-tailed).
[b] Correlation is significant at the 0.05 level (2-tailed).

Correlations between major and trace metals that are found in the east and south portions of the harbors are presented in Table 6. For Mucuripe and Pecém, significant correlations suggest that Al, Fe, Hg, Cr, Cu, Ni and Zn share the same origin, which was expected because areas of deposition were identified in each harbor. Freire et al. (2004), in a geochemistry study of sediments from the outer and continental shelves from the coast of Ceará, suggested the presence of two groups of metals with different sources. The first, which occurred near the coast, included Al, Si, K, Ti, Fe and Mn and was derived from continental Precambrian feldspar granites, while the second group was mainly of marine origin and included Ca, Mg, Sr, P, Cr and Ni in association with $CaCO_3$. Nevertheless, according to the authors, Cr and Ni were most likely included due to primary productivity; this process involves the sequestration of metals and their biomineralization by coralline algae in the area surrounding the continental shelf.

Table 6
Pearson's coefficient of major and trace metals from Mucuripe and Pecém (East portion) and Santos (South portion) harbors.

		Al	Fe	Hg	Cd	Cr	Cu	Ni	Pb
East	Fe	0.95[a]							
	Hg	0.73[a]	0.62[b]						
	Cd	0.30	0.30	−0.20					
	Cr	0.99[a]	0.98[a]	0.71[a]	0.24				
	Cu	0.95[a]	0.99[a]	0.62[b]	0.35	0.97[a]			
	Ni	0.95[a]	0.98[a]	0.62[b]	0.32	0.97[a]	0.98[a]		
	Pb	0.28	0.43	0.01	0.28	0.32	0.43	0.39	
	Zn	0.95[a]	0.99[a]	0.62[b]	0.33	0.98[a]	0.99[a]	0.99[a]	0.42
South	Fe	0.81							
	Hg	0.89[b]	0.93[b]						
	Cr	0.87	0.99[b]	0.957[b]	NC				
	Cu	0.81	0.88[b]	0.98[a]	NC	0.90[b]			
	Ni	0.81	0.97[a]	0.98[a]	NC	0.98[a]	0.96[a]		
	Pb	0.07	0.18	0.27	NC	0.18	0.45	0.31	
	Zn	0.98[a]	0.86	0.910[b]	NC	0.90[b]	0.86	0.86	0.26

Nc–not calculated.
[a] Correlation is significant at the 0.01 level (2-tailed).
[b] Correlation is significant at the 0.05 level (2-tailed).

A similar pattern was also found by Aguiar et al. (2007), who investigated the metal distribution of the western sediments from the Ceará continental shelf using a multivariate analysis and also identified two groups, one that was formed by Fe, Al, Mn, Cr, and Zn of a continental origin and another that was composed of $CaCO_3$, MO, Ni, Pb, Ba and Cu and was influenced by marine deposition.

In contrast to the northeast region harbors, Santos harbor is located in an estuarine system, and like the sedimentation pattern discussed above, its origin and source of metals can be associated with human occupation. Hortellani et al. (2008) used dissimilarity analyses to studying contamination by metallic elements in the Santos Estuarine System and found an association of element concentrations that occurred in two groups: the first included Al, Fe, Ni, Co and Cr and showed the highest levels at the Piaçaguera channel, which is a site that is impacted by the influence of Cubatão's industrial complex; the second group was composed of Zn, Hg, Pb and Cd and was under the influence of industrial and port activities and in close proximity to solid waste landfills. Tessler et al. (2006) assessed the metal sedimentation rates the region of the estuary using the ^{137}Cs and ^{210}Pb radionuclides from the sediment cores and found significant enrichments in Cr, Cu, Pb and Zn in the upper estuary and bay since the 1950's, which is a period of intense occupation in this region.

4.3. Enrichment factor and Index of geoaccumulation analysis

Based on the I_{geo} results (Appendix B), harbor zones from the east portion (Mucuripe and Pecém) showed the following pattern of classification: Fe and Pb in class 1 (unpolluted), Ni in class 2 (unpolluted to moderately polluted), Hg and Cr in class 3 (moderately polluted), Cu in class 4 (moderately to strongly polluted) and Zn in class 6 (strongly to very strongly polluted). For Al, in Mucuripe, all of the stations were placed into class 2, while the Pecém stations were included in classes 3. For Santos harbor, Fe, Cr and Pb were placed into class 1, Al, Cr and Ni into class 2, Cd and Hg into class 3 and Zn into class 5 (Fig. 2).

The *EF* values for the harbor areas from the east portion showed a similar pattern, occurring in the following order: Zn > Cd > Cu > Hg > Cr > Al > Ni > Fe > Pb. However, in Santos harbor, the pattern of enrichment was similar, considering the fact that all of the stations showed Cd levels below the QL, and thus, the order was: Zn > Cd > Hg > Cu > Cr > Al > Ni > Fe > Pb. The integration of *EF* (*R*) resulted in a classification of stations ranging from highly polluted to unpolluted: M4 > M2 > M1 > M3 > M6 > M7 > M5 > M8 > M10 > M9 for Mucuripe Harbor, P1 > P2 > P3 > P4 > P5 for Pecém harbor and S5 > S4 > S3 > S2 > S1 for Santos harbor. These results clearly demonstrate the influence of proximity to contaminant sources on the enrichment of metals (Appendix C).

4.4. Comparison with sediment quality guidelines

Because the concerned areas are subject to dredging activities and sediment removal, in addition to the fact that the metal levels have shown enrichment in relation to the baseline, the present results were compared with the SQGs that are recommended by the Brazilian federal legislation (resolution CONAMA 344/04) and with specific SQVs that were derived for the Santos Estuarine System (Choueri et al., 2009b). Such comparisons involved the use of the sediment quality guideline quotients (SQGQ) approach (Fairey et al., 2001), considering both the probable effect levels, which in this specific case were CONAMA 344 level 2 values, and the P levels that were established by site-specific SQVs (SQVQ). According to the abovementioned authors, the criterion for sample ranking was:

Minimal contamination: SQGQ and SQVQ value between 0 and 0.1
Moderate contamination: SQGQ and SQVQ value between 0.1 and 0.25
Strong contamination: SQGQ and SQVQ value greater than 0.25

Thus, Mucuripe harbor exceeded level 1 values for Cd, Ni and Zn and level 2 values for Zn. The same was found for sediments from Pecém harbor; stations showed above level 1 values for Cd and Ni and level 2 values for Zn. At Santos harbor, Ni and Cd were above level 1, while Zn was above level 2 for all stations. For the site-specific SQV, the threshold and probable values (*T* and *P*) were relative to levels 1 and 2. The comparison for Mucuripe harbor showed that Cr and Ni exceeded *T*. Similar results were observed in Pecém, with Cr and Ni above *T*, and for Santos harbor, Hg, Cr, Ni and Pb also exceeded *T*. At Mucuripe, Cd, Cu and Zn were below level 1 and above *P*. At Pecém, Cd, Cr and Cu, Ni and Zn all exceeded the *P* values. Similarly, for Santos harbor, Hg, Cd, Cu, Ni and Zn all exceeded *P*.

When compared with the site-specific SQV, it is possible to see a failure in impact prediction using the Brazilian criterion. Abessa et al. (2006) showed that, for the Santos Estuarine System, over 75% of the sediment samples, in which levels of contamination were above level 1 according to the Resolution No. 344/04, were considered to be acutely toxic. Data such as these reaffirm the need for supplementary studies with special focus on the coverage of these values in Brazil, where there seems to be a trend of even

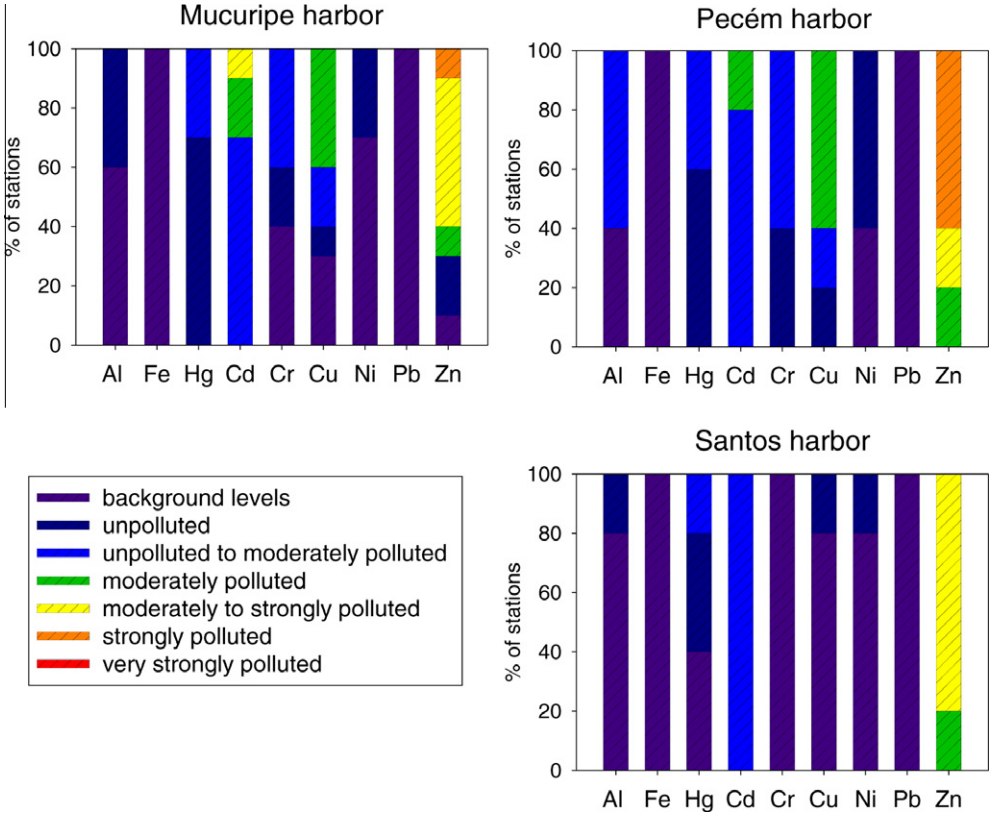

Fig. 2. I_{geo} index calculated from Mucuripe, Pecém and Santos harbors.

lower SQG values that are close to the baseline values that are observed in Table 7.

4.5. Summary of approaches to assess metal contamination

A summary of the sediment classifications that are based on the different approaches and criteria that are used in this study is presented in Table 8. The analyses of the predictive powers of each approach among the geochemical indices showed that I_{geo} is more sensitive than *EF*. The comparisons of SQGs and local SQVs showed that use of site-specific values is more appropriate than the application of the values that were set in Resolution No. 344/04, which were derived from international criteria that do not reflect the realistic conditions of Brazilian environments.

Thus, when combining different approaches (geochemical indices and SQGs comparisons) for determining impacts due to pollution, the need to use methods that take into account regional values becomes clear. According to Choueri et al. (2009b), the sediment quality criteria that are derived from site-specific data are better able predict toxicity in the environment, among other

Table 7
Comparison of exceedences between Brazilian SQGs for dredging activities and site-specific SQVs for Santos Estuarine System.

Stations	CONAMA 344/05			Choueri et al. (2009b)		
	⩾Level 1	⩾Level 2	SQGQ	⩾T	⩾P	SQVQ
M1	–	Zn	0.25	Cr and Ni	Cd, Cu and Zn	1.82
M2	–	Zn	0.29	Cr and Ni	Cd, Cu and Zn	2.05
M3	Cd and Zn	–	0.23	Cr and Ni	Cd, Cu and Zn	1.69
M4	Ni	Zn	0.31	–	Cr, Cu, Ni and Zn	2.17
M5	Zn	–	0.11	Ni	Zn	0.77
M6	–	Zn	0.24	Cr and Ni	Cu and Zn	1.63
M7	Zn	–	0.20	Ni	Cu and Zn	1.38
M8	–	–	0.06	Ni	–	0.36
M9	–	–	0.03	–	–	0.22
M10	–	–	0.05	Zn	–	0.31
P1	Ni	Zn	0.35	–	Cr, Cu, Ni and Zn	2.40
P2	Cd and Ni	Zn	0.31	Cr	Cd, Cu, Ni and Zn	2.25
P3	Ni	Zn	0.32	–	Cr, Cu, Ni and Zn	2.17
P4	Zn	–	0.17	Ni	Cu and Zn	1.21
P5	Zn	–	0.13	Ni	Zn	0.89
S1	–	Zn	0.25	Cr and Ni	Cu and Zn	1.73
S2	Hg	Zn	0.32	Hg, Ni and Pb	Cu and Zn	2.22
S3	Hg	Zn	0.38	Hg, Cr, and Ni	Cu and Zn	2.55
S4	Hg	Zn	0.46	Hg, Cr, and Ni	Cu and Zn	3.07
S5	Hg and Ni	Zn	0.61	Cr and Pb	Hg, Cu, Ni and Zn	3.86

Table 8
Comparison of qualitative classification of sediments based on different interpretative approaches.

Stations	Geochemical approach		SQGs	
	I_{geo}	*EF* (*R*)	SQVQ	SQGQ
M1	Moderately to strongly	Highly polluted	Strong	Moderate
M2	Moderately to strongly	Highly polluted	Strong	Strong
M3	Moderately to strongly	Highly polluted	Strong	Moderate
M4	Strongly polluted	Highly polluted	Strong	Strong
M5	Moderately polluted	Low polluted	Strong	Moderate
M6	Moderately to strongly	Highly polluted	Strong	Moderate
M7	Mmoderately to strongly	Moderately polluted	Strong	Moderate
M8	Unpolluted to moderately polluted	Unpolluted	Strong	Minimal
M9	Unpolluted to moderately polluted	Unpolluted	Moderate	Minimal
M10	Unpolluted to moderately polluted	Unpolluted	Strong	Minimal
P1	Strongly polluted	Highly polluted	Strong	Strong
P2	Strongly polluted	Highly polluted	Strong	Strong
P3	Strongly polluted	Highly polluted	Strong	Strong
P4	Moderately to strongly	Moderately polluted	Strong	Moderate
P5	Moderately polluted	Low polluted	Strong	Moderate
S1	Moderately polluted	Low polluted	Strong	Moderate
S2	Moderately to strongly	Low polluted	Strong	Strong
S3	Moderately to strongly	Moderately polluted	Strong	Strong
S4	Moderately to strongly	Moderately polluted	Strong	Strong
S5	Moderately to strongly	Highly polluted	Strong	Strong

effects caused by contaminants, and this approach should be applied to sediment management, not only in Brazil, due to its variation in the composition of sediments along the coast, but all over the world.

According to the Brazilian government's current policy for port management, there is a "National Plan of Dredging," which predicts the dredging and expansion of major ports, including the Santos and Mucuripe harbors. Due to the demands that are imposed by the economic growth of the country, greater attention must be paid to sediment contamination because areas of ecological relevance are now positioned to become disposal sites of large volumes of dredged material, putting significant ecosystems of the Brazilian coast at risk.

5. Conclusions

Based on our results, sediments from Mucuripe, Pecém and Santos harbors show distributions of major and trace metals that exceed reference values. Due to differences in the sedimentological facies, for Mucuripe and Pecém, major and trace metals exhibit deposition patterns that are associated with carbonates and organic matter due to the urbanization and industrial and harbor activities that occur in these areas. For Santos harbor, the pattern of deposition was associated with mud and proximity to the sources, which increased towards the inner estuary.

All of the studied areas showed the enrichment of metals, such as Hg, Cd, Cu, Ni and Zn, and the application of I_{geo} and *EF* explained their contamination levels. The simple application of international SQGs alone, given the failure of impact prediction compared with other criteria, was not considered to be the best approach for ranking and, consequently, for the management of dredged sediments. The integrated application of specific values that were derived for each region based on geochemical and ecotoxicological approaches and on enrichment and geochemical indices appears to be a more appropriate way to deal with this issue.

Contributions

Lucas M. Buruaem: sample collection, sediment properties and atomic absorbance spectrometry analyses, calculations and article preparation.

Marcos A. Hortellani: sample preparation, atomic absorbance spectrometry analyses, calculations and article preparation.

Jorge E.S. Sarkis: atomic absorbance spectrometry analyses and calculations.

Leticia V. Costa-Lotufo: article preparation and the discussion of results.

Denis M. S. Abessa: coordination of the project, data analysis and discussion and article preparation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.marpolbul.2012.01.017.

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