



Baseline

Metal distribution in sediment cores from São Paulo State Coast, Brazil

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ARTICLE INFO

Keywords:

Baixada Santista
Sediment
Metals
Total fraction
INAA

ABSTRACT

Ten sediment core samples with lengths ranging from 35 to 100 cm were collected in the Baixada Santista region and analyzed to determine As, Br, Co, Cr, Cs, Fe, Rb, Sb, Ta, Th, U, Zn and rare earths (Sc, Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) level concentrations using instrumental neutron activation analysis (INAA). The studied region is located in the southeastern coast of São Paulo State and is comprised of a densely urbanized area, the largest industrial complex of the country, with a predominance of petrochemical and fertilizer plants. It is also home to Brazil's most important and busiest port. The conclusions found that the As, La, Sm, Ne, Ce, Eu, Hf, Ta, Th, and U elements have a high background level in the region and that Fe and Zn were the main indicators of anthropogenic contribution in the sediments.

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The coast of São Paulo is comprised of a 622 km-long sedimentary basin divided into the North coast, the South coast and the metropolitan area known as the “Baixada Santista.” The cities of São Vicente, Brazil's founding city, and Santos, which shelters the country's most important and busiest port, together with Praia Grande, Mongaguá, Cubatão, Guarujá, Itanhaém, Bertioga and Peruibe are part of the “Baixada Santista.” This region, which covers an area of 2372 km² is one of the most populated and industrialized regions of São Paulo state (IBGE, 2007). Due to its proximity to the city of São Paulo, the cities of the “Baixada Santista” have become a getaway destination and are even considered a virtual suburb of the city.

The anthropogenic activities of the cities of Santos, São Vicente and Cubatão have affected this region's aquatic ecosystem since the early fifties due to uncontrolled urbanization, port and industrial activities and the inflow of river water contaminated with fertilizers and agricultural pesticides; hence, its mangrove area has been seriously impacted (CETESB, 2001; Silva et al., 2003; Siqueira, 2003).

Another important environmental concern is the contamination of the sediment that is dredged in the port of Santos. In 2004, a regulation was created (Resolution No. 344/04 dated 25/03/04) establishing critical limits of metals concentration in the dredged material for further disposal. This regulation is reviewed from time to time, however the critical limits currently applied are based on the international experience since the geochemical background for the region is not known due to the intense human activity since the

early twentieth century. Therefore it is essential to establish the regional basal level of the element concentrations to support this regulation.

Based on this, a project was established in 2007 with the objective of studying the metal distribution in sediment cores of the main cities of the Baixada Santista: Cubatão, São Vicente, Santos and Bertioga. The latter is a city whose coastal area has not yet been so heavily impacted (Silva, 2004). In this project, core samples, with depths varying from 35 to 100 cm were collected and analyzed to verify the content of As, Br, Co, Cr, Cs, Fe, Rb, Sb, Ta, Th, U, Zn and rare earths (Sc, Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) using instrumental neutron activation analysis (INAA).

In May and July 2007, 10 sediment core samples were collected: three in São Vicente, three in Bertioga, two in the Santos Bay and two in Cubatão, all with a gravity core sampler. The location of the sampling points is shown in Fig. 1 and their coordinates are given in Table 1.

The RO and CS cores were collected in Cubatão, where severe anthropogenic impact has been observed over the last decades due to the industrialization process which began in the early sixties. The region's main industries included steel, fertilizer and oil production. In this region, less energetic conditions favor the deposition of fine sediment grain size.

The BO, VI and PO cores were collected in the São Vicente Channel and tributary rivers. In the region of the BO core collection, less energetic conditions of sediment transport enabled the deposition of fine grain size particles while, in points VI and PO, the sediments collected were coarser. The main source of organic matter deposition is of terrigenous origin and due to the deposition of metals from urban sewage discharges. Industrial contribution is also significant.

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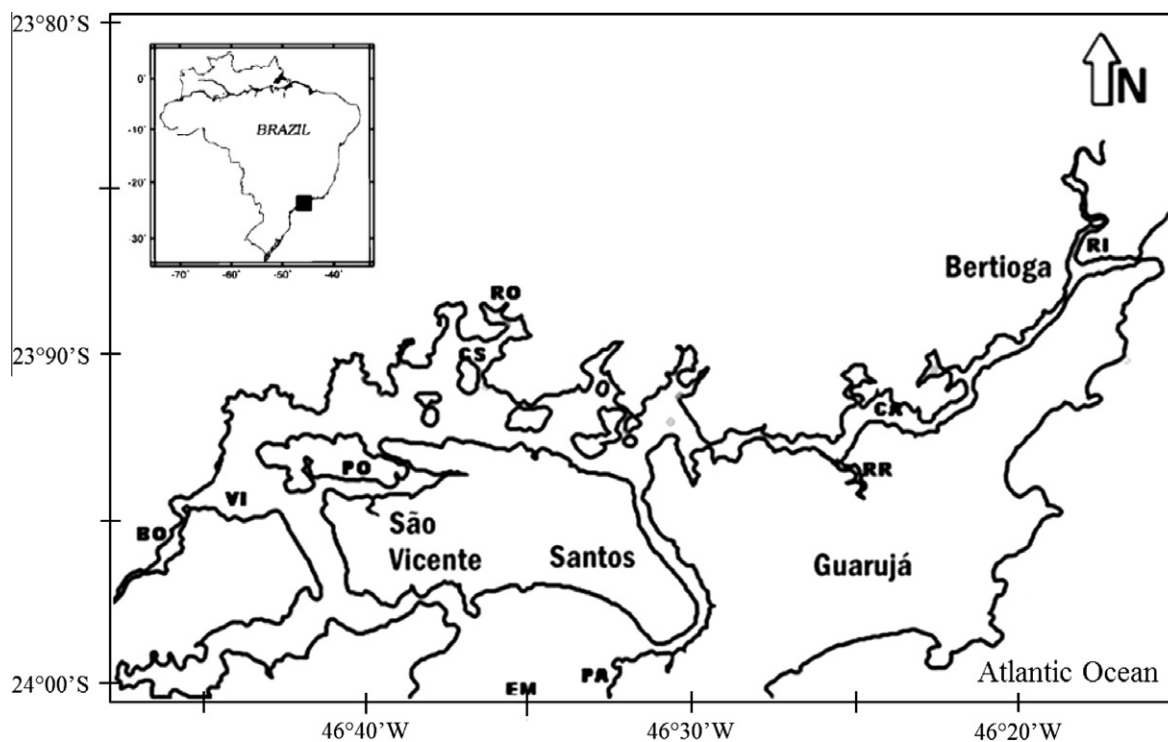


Fig. 1. Location of the sampling points in the “Baixada Santista”, São Paulo State, Brazil.

Table 1

Location of the sampling points in coordinates and physical-chemistry parameters of the sediment and overlying water.

	S	W	Sampling point – location				pH ^a	pH ^b		
RO	23° 52' 75.3"	46° 21' 40.2"	Onças River – Cubatão				7.7	7.4		
CS	23° 53' 13.6"	46° 22' 14.8"	Cosipa Channel – Cubatão				7.2	7.4		
BO	23° 55' 93.7"	46° 27' 52.5"	Boturoca River – São Vicente				7.0	7.1		
VI	23° 57' 14.4"	46° 25' 48.3"	São Vicente River – São Vicente				7.4	nd		
PO	23° 55' 00.6"	46° 25' 12.0"	Pompeba River – São Vicente				7.4	nd		
RI	23° 51' 61.8"	46° 09' 45.9"	Itapanhaú River – Bertioga				8.0	8.1		
RR	23° 52' 63.8"	46° 11' 86.3"	Iriri River – Bertioga				7.9	8.3		
CA	23° 55' 20.7"	46° 14' 28.8"	Candinho River – Bertioga				7.5	7.4		
EM	24° 00' 20.7"	46° 20' 98.8"	Submarine Emissary – Santos Bay				7.8	7.8		
PA	24° 52' 64.0"	46° 19' 49.6"	Palmas Island – Santos Bay				8.5	nd		
	Conductivity ^a (mS cm ⁻¹)	Conductivity ^b (mS cm ⁻¹)	Salinity ^a (mg L ⁻¹)	Salinity ^b (mg L ⁻¹)	DO ^a (mg L ⁻¹)	DO ^b (mg L ⁻¹)	T ^a (°C)	T ^b (°C)	pH sed.	Depth ^c (m)
RO	17.5	32.5	3.5	20.5	2.0	nd	23.8	24.1	7.2	2.8
CS	21.5	27.5	13	16.7	4.4	2.7	23.3	23.6	7.2	2.3
BO	25.2	25.3	15.4	15.6	2.4	2.6	22.6	22.7	6.9	2.2
VI	32.9	nd	20.4	nd	3.7	nd	22.8	nd	6.9	0.6
PO	31.6	nd	31.6	nd	3.3	nd	22.7	nd	7.4	1.0
RI	51.5	51.5	33.6	33.6	6.8	6.7	22.6	22.6	6.5	1.5
RR	46.1	48.3	29.6	31.2	nd	nd	21.7	22.0	7.0	2.0
CA	38.9	38.9	24.6	24.5	nd	nd	20.9	20.9	7.0	2.5
EM	51.0	52.0	33.5	34.2	6.6	6.9	21.5	21.7	7.5	11.0
PA	nd	nd	nd	nd	nd	nd	nd	nd	7.4	10.0

nd = not determined.

^a Measured at surface water.

^b Measured at 1 m depth.

^c Water column depth.

The CA, RI and RR cores were collected in Bertioga, which is connected to the Santos estuary on the south and to the open sea on the north. According to Miranda et al. (1998) the north mouth is a secondary connection between the ocean and the Santos estuary. The Bertioga Channel is 1 km wide and is directly influenced by tides, which cause the deposition of suspended material. The Bertioga Channel also has social and economic importance since it neighbors the port of Santos and the Cubatão complex. In addition, the channel is used for recreational activities and fishing.

In the Santos Basin, cores were collected at the EM point near the underwater sewer discharge pipe and at the PA point near Palmas Island. The sewer outfall pipe drains the sewage of Santos and the neighboring cities into the open sea. This point is mainly affected by domestic contributions and has relatively low energetic conditions for sediment deposition.

At the time of the sampling the following parameters were determined for sediment surface and overlying water: pH of the sediment and water, conductivity, dissolved oxygen (DO) and

salinity. In the laboratory, the sediment cores were sliced at every 2 cm. The sediment samples were oven dried at 60 °C to reach constant weight and then were pulverized in a glass mortar until they reached a size of less than 0.075 mm without mineralogical separation and were then homogenized for the elemental analysis of INAA.

Elements As, Br, Co, Cr, Cs, Fe, Hf, Rb, Sb, Ta, Th, U, Zn and rare earths (Sc, Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) were determined using instrumental neutron activation analysis. Approximately 150 mg of sediment samples and reference materials Buffalo River Sediment (SRM 8704 – NIST) and Soil 7 (IAEA) were accurately weighed and sealed in pre-cleaned double polyethylene bags for irradiation. Sediment samples and reference materials were irradiated for 16 h in a thermal neutron flux of $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ in the IEA-R1 nuclear research reactor at IPEN. Two series of counts were made: the first, after a one week decay period and the second after 15–20 days.

The counting time was 1.5 h for each sample and reference materials. Gamma spectrometry was performed using a coaxial Be-layer HPGe detector with a 22% relative efficiency, resolution of 2.09 keV at 1.33 MeV of ^{60}Co photopeak and associated electronic devices. The spectra were acquired using the Spectrum Master multichannel analyzer and for the analysis, Winner Gamma software was used.

The methodology validation related to precision and accuracy was performed by measuring the Buffalo River Sediment and Soil 7 reference materials. The Z value was calculated according to Bode (1996). If $|Z| < 3$, the individual result of the control sample (reference material) lies in the 99% confidence interval of the target value.

For the grain size analysis of the sediments, approximately 5 g of each sample was passed through sieves of 600, 250, 63 and 20 μm (30, 60, 230 and 635 mesh, respectively) which enabled the samples to be separated into coarse, medium and fine sand, silt and clay.

Table 1 shows the results obtained for the pH of the sediment and water at the surface and at 1 m depth, conductivity, dissolved oxygen (DO) and salinity, as well as, the identification of the sampling location. According to these measurements the RO, CS, BO

and VI sampling points are within a mesohaline environment ($5.0\text{--}18.0 \text{ pg g}^{-1}$) with neutral pH. The PO, RI, RR, CA, EM and PA cores are polyhaline ($18.0\text{--}30.0 \text{ pg g}^{-1}$) within euhaline environments with a slightly alkaline pH and a higher quantity of dissolved ions.

Figs. 2a and 2b, respectively. All Z-score values were in the interval ($|Z| < 3$), indicating good precision and accuracy of the INAA technique.

Table 2 shows the mean, standard deviation, and the range of concentration for the results obtained by INAA. The variability and homogeneity of the elements concentration in the sediment column can be assessed by variation coefficient (VC) calculation (Chapelle, 1995; Sainz and Ruiz, 2006; Kisi et al., 2009). Small VC values can indicate homogeneity in the elemental concentration distribution with depth. This variability can occur as a result of many natural processes such as difference in the grain size distribution, changes in the sediment source and weathering processes, variation in the organic matter content, sedimentation rate or anthropogenic contributions. In the case of natural processes causing the variation in the total amount of element concentration this information can be accessed by multivariate statistical methods of analysis (Stanimirova et al., 1999; Einax and Soldt, 1999; Loska and Wiechula, 2003; Casado-Martínez et al., 2006) which also enables to distinguish outliers as for example man made contributions, as will be discussed later. Hence, as a first approach a VC analysis can be conducted to verify the extent of the homogeneity or heterogeneity of the sediment column being analyzed to postulate hypothesis about the causes of variability in the total elemental concentration. To classify small or high variability Gil et al. (2011) adopted a limit of 25% for the variation coefficient. In this paper it will be used a limit of 30% that is the value accepted by USEPA (2001) for the dispersion in the replicates for sediment analysis. Therefore, a slight variation of under 30% in the CV values for the element concentrations in sediment core indicates homogeneity while VC values above 30% indicates high variability caused by granulometric variation inside the core sample (our first hypothesis to be tested since this study has been conducted by analyzing the total fraction of the sediment).

The elemental concentration of all analyzed elements in the BO core presented a VC below 30%. In the RO, CS, RR, EM and PA cores, only a few elements had a coefficient variation of over 30%: Hf, Sb, Ta and U in the RO core; As, Br, Co, Sb and U in the CS core; Hf and Sb in the RR core; As, Br, Rb, Ta and Zn in the EM core and Zn in the PA core. In the VI, PO, RI and CA cores, almost all elements showed variation coefficients of above 30%. In cores VI and RI, this large variation can be explained by the high granulometric changes throughout the core.

As stated above, the variability of trace metals in sediment may be due to natural or anthropogenic causes. Metals originating from the same source generally group together, mainly in silt and clay fractions and enrichment, if it occurs, can be observed by using a normalization procedure that offsets the variability in mineralogy and grain size (Kim et al., 1998; Batista Neto et al., 2000; Aloupi and Angelidis, 2001). This method consists of establishing a correlation between the ratio of the element concentration and the conservative element concentration and the ratio of the element concentration in the sample and the conservative element concentration in shale (Turekian and Wedepohl, 1961), in the main values of the upper crust (Taylor and McLennan, 1981; 1985) or in the mean values of the bottom layers analyzed in the deepest core (Danielsson et al., 1999; Li et al., 2000). The elements of natural origin that are structurally combined with one or more mineral phases are considered conservative. The main assumption for the application of a geochemical normalization for conservative elements is the existence of a linear relationship between the normalizer and other metals (Aloupi and Angelidis, 2001) and its concentration should not be anthropogenically altered (Ackerman, 1980; Idris, 2008). Several elements were used for this purpose: Al (Hirst, 1962; Bruland et al., 1974; Sharma et al., 1994; Carral et al., 1995), Li (Loring, 1990; Siqueira and Braga, 2001), Cs (Ackerman, 1980), Fe (Piper, 1971; Blomqvist et al., 1992; Herut et al., 1993),

Table 2 Mean values, standard deviation and range of concentrations in $\mu\text{g}\cdot\text{g}^{-1}$ except were indicated %.

	RO		CS		BO		VI		PO		RI		RR		CA		EM		PA		
	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	
As	12 \pm 1	9.0–14	10 \pm 4	9.0–14	13.1 \pm 2.0	9.6–16	10 \pm 5	9.6–16	2.6–22	5 \pm 2	1.4–9.3	5 \pm 2	1.1–8.5	13 \pm 3	7.3–20.5	10 \pm 3	5.2–15	9 \pm 2	5.3–11		
Br	59 \pm 4	46–66	125 \pm 60	77–339	nd	nd	100 \pm 75	82–103	43–294	33 \pm 13	19–63	44 \pm 16	23–74	149 \pm 14	129–179	97 \pm 32	38–154	104 \pm 24	60–129		
Ce	104 \pm 11	85–136	110 \pm 20	76–146	91 \pm 5	82–103	55 \pm 13	36 \pm 10	30–77	36 \pm 10	21–58	44 \pm 16	23–74	153 \pm 102	68–373	49 \pm 10	29–65	70 \pm 13	42–91		
Co	11 \pm 0.6	9.5–12	14 \pm 5	7.8–30	9.9 \pm 0.6	9–11	6 \pm 2	3.7–9.2	3.7–9.2	3 \pm 1	1.6–5.6	5 \pm 1	1.3–6.4	12 \pm 6	6–24.3	7 \pm 1	4.3–9.5	10 \pm 2	6.6–12		
Cr	66 \pm 6	56.1–74	69 \pm 14	53–113	63 \pm 4	54–69	40 \pm 11	24–58	25 \pm 11	9–49	9–49	24 \pm 6	7–33	78 \pm 44	39–162	48 \pm 9	28–56	49 \pm 11	28–64		
Cs	76 \pm 0.6	6.1–8.5	7 \pm 1	5.6–9.4	6.3 \pm 0.7	5.2–7.6	4 \pm 1	2.2–5.8	1.7 \pm 0.6	0.8–3	0.8–3	3.0 \pm 0.9	1.0–4.3	8 \pm 4	4.0–17	3.2 \pm 0.6	2.2–4.5	5 \pm 1	2.7–6.3		
Eu	1.5 \pm 0.1	1.2–1.7	1.5 \pm 0.2	1.2–1.9	1.4 \pm 0.1	1.3–1.6	0.9 \pm 0.2	0.5–1.3	0.4 \pm 0.2	0.2–0.8	0.2–0.8	0.8 \pm 0.2	0.4–1.2	2 \pm 1	1.1–4.1	0.8 \pm 0.3	0.5–1.3	1.2 \pm 0.1	0.9–1.3		
Fe (%)	5 \pm 1	3.7–8.4	4.1 \pm 0.5	3.6–4.2	3.9 \pm 0.2	3.6–4.2	3 \pm 1	1.4–5.0	1.4 \pm 0.5	0.6–2.5	0.6–2.5	1.7 \pm 0.5	0.5–2.3	5 \pm 3	2.5–12	2.4 \pm 0.4	1.4–3.1	3.1 \pm 0.6	2.1–3.8		
Hf	8 \pm 3	4.5–12	6 \pm 1	2.8–10	4.5 \pm 0.3	4–5	4 \pm 1	2.5–5.7	3.5 \pm 0.9	2.2–5.2	3 \pm 1	2.5–8.0	7 \pm 2	6 \pm 3	3–13	3.5 \pm 0.8	1.5–4.8	4.1 \pm 0.7	3.5–5.2		
La	46 \pm 4	40–56	45 \pm 11	23–69	43 \pm 3	39–52	37 \pm 28	14–104	16 \pm 5	9–25	9–25	26 \pm 11	15–46	60 \pm 4	33–51	26 \pm 4	18–31	34 \pm 6	21–40		
Lu	0.38 \pm 0.03	0.3–0.4	0.35 \pm 0.04	0.3–0.4	nd	nd	0.2 \pm 0.1	0.1–0.3	0.1 \pm 0.3	0.1–0.3	0.1–0.3	nd	nd	0.3 \pm 0.1	0.4 \pm 0.1	0.2 \pm 0.1	0.1–0.3	0.3 \pm 0.1	0.2–0.3		
Nb	47 \pm 5	37–53	47 \pm 7	35–59	43 \pm 5	32–58	32 \pm 31	6–91	15 \pm 4	9–24	9–24	55 \pm 4	nd	53 \pm 4	8–25	24 \pm 11	9–41	28 \pm 7	16–37		
Nd	122 \pm 16	97–143	136 \pm 33	92–180	94 \pm 8	83–108	65 \pm 12	47–83	31 \pm 8	17–43	94 \pm 29	44–143	44–143	74 \pm 13	115 \pm 64	51–256	61 \pm 16	87 \pm 8	77–96		
Sr	0.7 \pm 0.2	0.5–1	0.7 \pm 0.2	0.4–1.3	0.5 \pm 0.1	0.5–0.7	0.5 \pm 0.4	0.1–1.6	0.3 \pm 0.1	0.1–1.1	0.1–1.1	0.3 \pm 0.1	0.1–0.4	0.6 \pm 0.2	0.3–0.9	0.5 \pm 0.1	0.3–0.7	0.5 \pm 0.1	0.3–0.6		
Sb	13 \pm 2	10–16	13 \pm 2	11.5–14	12.8 \pm 0.6	11.5–14	9 \pm 2	6.0–14	3.8 \pm 1.0	2.0–5.6	5 \pm 1	2.2–7	1.1 \pm 3	11 \pm 3	15 \pm 8	8.4–32	6 \pm 2	4–9.2	9 \pm 2		
Sm	7.9 \pm 0.7	6.8–9.5	8 \pm 2	4.1–11.4	7.1 \pm 0.4	6.5–8.2	6.0 \pm 4	2.4–17	3.0 \pm 0.8	1.8–4.4	4 \pm 2	2.3–7.6	9.3 \pm 0.5	7.4 \pm 0.8	6.0–9.2	4 \pm 1	2.9–6.5	6 \pm 1	3.1–7.2		
Ta	1.5 \pm 0.3	1.1–2.4	1.2 \pm 0.2	0.8–1.6	nd	nd	0.6 \pm 0.2	0.3–1.0	0.5 \pm 0.2	0.1–0.8	nd	nd	nd	1.4 \pm 0.3	0.8–2	0.7 \pm 0.3	0.2–1.3	0.9 \pm 0.1	0.6–1.0		
Tb	0.9 \pm 0.3	0.6–1.5	0.9 \pm 0.2	0.5–1.2	nd	nd	0.8 \pm 0.5	0.3–2.2	0.3 \pm 0.1	0.1–0.6	nd	1.3 \pm 0.5	nd	2.2	0.5–7.1	0.4 \pm 0.1	0.3–0.5	0.5 \pm 0.2	0.1–0.6		
Th	17 \pm 2	14–22	16 \pm 3	10–20	13.0 \pm 0.8	12–15	7.5 \pm 2	4.4–11	4.5 \pm 1.4	1.3–6.9	6 \pm 1	2.5–7.6	17 \pm 2	18 \pm 11	8.3–38	6 \pm 1	4.0–7.8	11 \pm 2	6.8–13.4		
U	8 \pm 2	4.6–10	6 \pm 2	2.0–10	7.7 \pm 1.2	6.3–10	5.0 \pm 4	1.4–17	3.7 \pm 0.7	2.3–5.0	1.7 \pm 0.5	0.9–2.4	6 \pm 1	3.4–7.4	5.4–21	1.2 \pm 0.3	0.7–1.7	3.8 \pm 0.6	3.1–4.6		
Yb	2.3 \pm 0.3	1.5–3	2.4 \pm 0.4	1.8–3.1	2.2 \pm 0.4	1.6–3.1	1.6 \pm 0.4	0.9–2.4	1.0 \pm 0.3	0.6–1.7	1.2 \pm 0.4	0.7–2	3.2 \pm 0.6	2.0–4.2	1.9–7	1.4 \pm 0.3	0.8–1.6	2.1 \pm 0.3	1.5–2.6		
Zn	120 \pm 15	90–146	114 \pm 23	77–168	95 \pm 21	72–139	62 \pm 13	43–85	43 \pm 26	18–103	44 \pm 12	29–75	80 \pm 20	39–99	127 \pm 82	61–343	67 \pm 20	31–98	107 \pm 34	52–162	

nd = not determined.

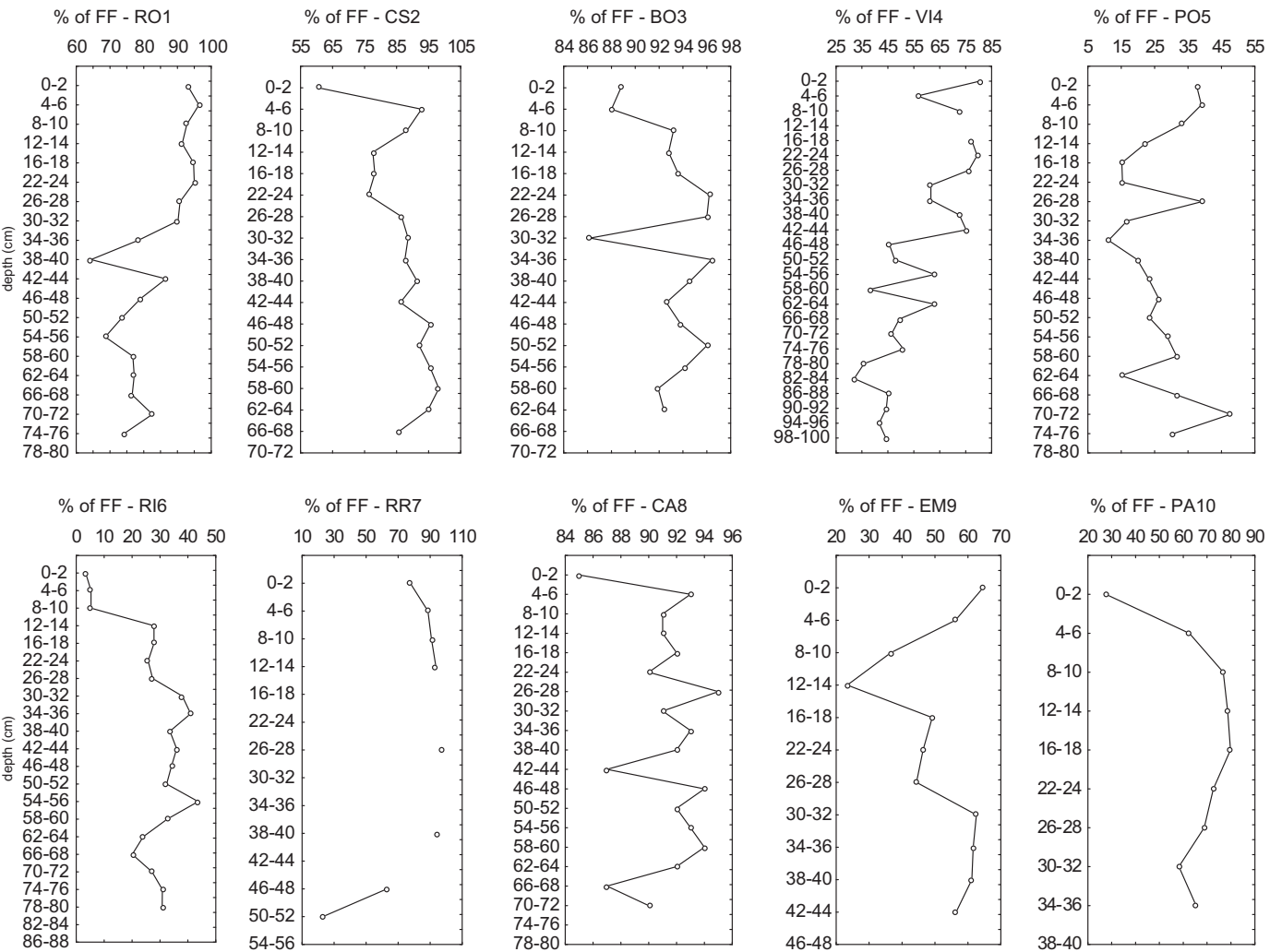


Fig. 3. Granulometric distribution of FF – fine fraction (silt + clay) in the cores collected for this study.

Table 3
Suggested reference values for the sediment of "Baixada Santista" considering the granulometric distribution as follow: 90% FF, sediment whose fine fraction content reaches up to 90% of fine fraction (silt plus clay) and 70% clay, sediments whose clay content reaches up to 70% of clay.

As	Ce	Co	Cr	Cs	Eu	Fe (%)	Hf	La	Lu	Nd	Rb	Sb	Sc	Sm	Ta	Tb	Th	U	Yb	Zn
90% FF	12.0	105.4	9.3	57.0	5.5	1.5	3.8	48.5	0.4	37.6	82.0	0.6	12.0	8.0	1.1	1.0	13.6	8.0	2.7	87.0
70% Clay	6.3	35.7	3.8	23.0	2.5	0.6	1.4	16.7	0.2	16.5	66.0	0.3	4.4	2.9	0.4	0.2	5.2	2.8	1.0	36.5

Sc (Ackerman, 1980; Grousset et al., 1995; Silva et al., 2002), and organic carbon (Horowitz, 1991). In this study Sc was used as a normalizer (Silva, 2004) and the NASC values (North American

Shale Composite) were used to calculate the enrichment factor (EF). The element Sc was chosen because it is easy and precisely determined by the analytical technique employed in this research

(INAA). It is a conservative element and there is no evidence for anthropogenic contribution for its concentration in the region as occurs with Al and Fe (Luiz-Silva et al., 2008), due to the presence of steel industry in the vicinity of the sampling points.

The EF was calculated for the elemental concentration in the ten cores analyzed using NASC (North American Shale Composite) values and Sc as a normalizer (Silva, 2004) according to the following equation:

$$EF = [C_{n(\text{sample})}/C_{Sc(\text{sample})}]/[C_{n(\text{shale})}/C_{Sc(\text{shale})}]$$

According to Zhang and Liu (2002), if $0.5 < EF < 1.5$, the elemental concentration is probably due entirely to crustal or natural weathering origin; values above 1.5 indicate anthropogenic contribution. The higher the EF value the more severe is the anthropogenic contribution.

The EF calculated for the RO and CS cores (from the Cubatão region) presented values above 1.5 for the following elements: light rare earth (LRE – La, Ce, Nd, Sm), Th, U, Zn and Hf. In both cases, the EF values were higher in the deepest layers for these elements. The RO core also showed an EF higher than 1.5 for Ta.

In the cores collected in the São Vicente region, the BO core showed an $EF > 1.5$ only for La, Nd and U at all depths and Zn in the upper 10 cm. The Cs element registered higher values of EF in the lower 40 cm. In the VI core, $EF > 1.5$ was observed for LRE and Cs, Fe and U in the upper 60 cm; and from this depth down, the EF values were characteristic of natural weathering. The PO core showed enrichment for LRE, Hf, and U at all analyzed depths and for Tb, Ta, Th and Zn in the first 40 cm. As mentioned above, the elemental concentrations in the BO core are almost constant without variations of over 30% while in the VI and PO cores all the elements had variation coefficients above this value. Similar results were observed in the cores collected in the Bertioiga region

(RI, RR and CA) and in the Santos Bay (EM and PA) where the elements that had EF values above 1.5 were the same as those in the cores from Cubatão and São Vicente: LRE, Hf, Th, U. For these cores, it is also worthwhile noting that the following elements had an EF value of over 1.5: Zn in the RI core, Ta in the RR core, Zn in the CA core, Fe and Zn in the EM and PA cores.

These results indicate that the variation in granulometric content is not enough to justify the observed EF values of the LRE, Hf, Th and U elements in each core. According to Reimann and Caritat (2005), the comparison of such ratios with ratios in the crust is bound to give EFs different from unity (and in some cases much larger than unity). In the present study these elements showed high values of EF in virtually all depths, in almost all the core samples, indicating that in the sediment source the ratio $[C_n/C_{Sc}]$ must be naturally higher than the $[C_n/C_{Sc}]$ ratio in NASC.

One possible explanation for the high EF values of these elements could be the presence of enriched minerals in the source of the sediment, as will be discussed later, and possibly associated to other processes such as fractionation of elements due to weathering, pedogenesis, erosion and transport (Reimann et al., 2001).

The results observed for the elements Fe and Zn on the other hand must be due to anthropogenic contributions, insofar as these elements presented high EF values mainly in the surficial layers with a tendency of stabilizing near or under 1.5 in the deeper layers as can be seen in Fig. 4.

Although the enrichment factor calculation procedure aims to offset the differences in the mineralogy and granulometric distribution, its application is not straightforward when sediment granulometry varies considerably with depth, especially when the concentrations are being measured in the total fraction.

Another approach to verify contamination in sediment is to compare the measured values in samples with guided values. In

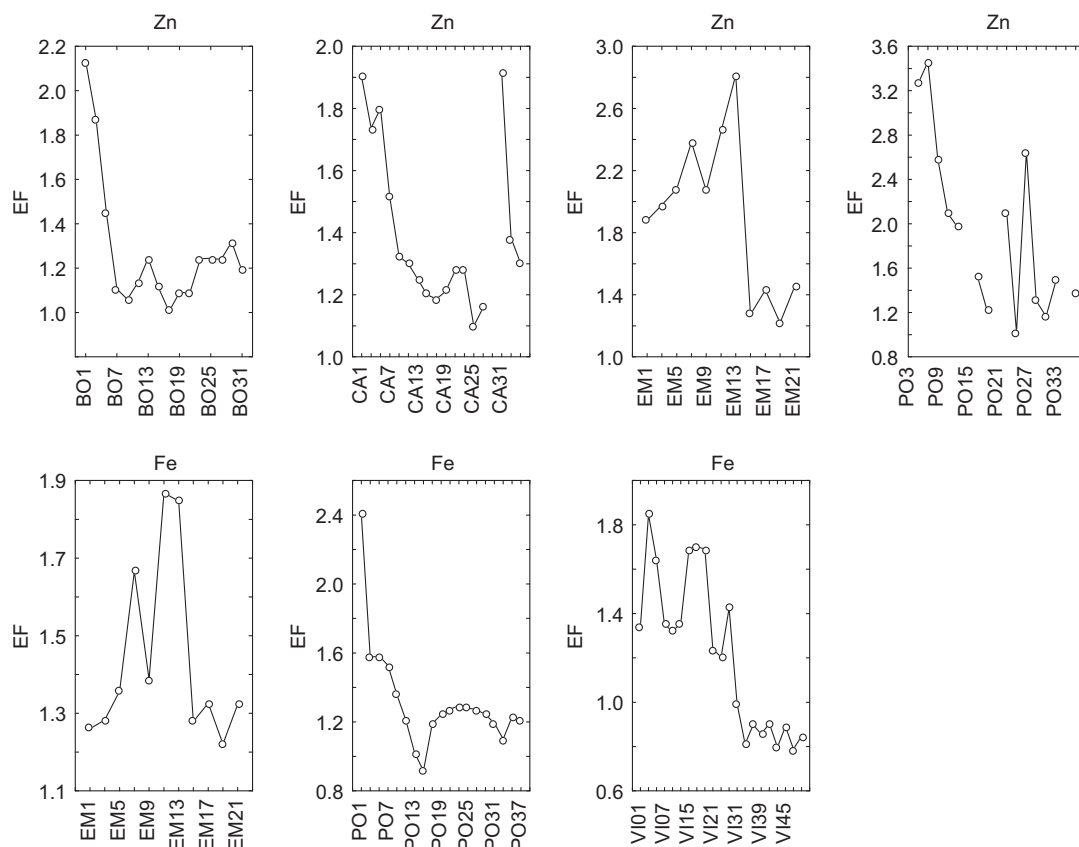


Fig. 4. Enrichment factor for Fe and Zn distribution with depth.

Brazil there are no legal values for sediment quality, as such the results obtained were compared with guided TEL and PEL values from the Environmental Agency of Canada (Environment Canada, 1999) and FDEP (1994). TEL, Threshold Effects Level, represents the concentration below which adverse effects are expected to occur only rarely and PEL, Probable Effects Level, represents the concentration above which adverse effects are frequently expected. These reference parameters were used in spite of the fact that they were obtained by performing ecotoxicological experiments that consider the available concentration of the elements in the sedi-

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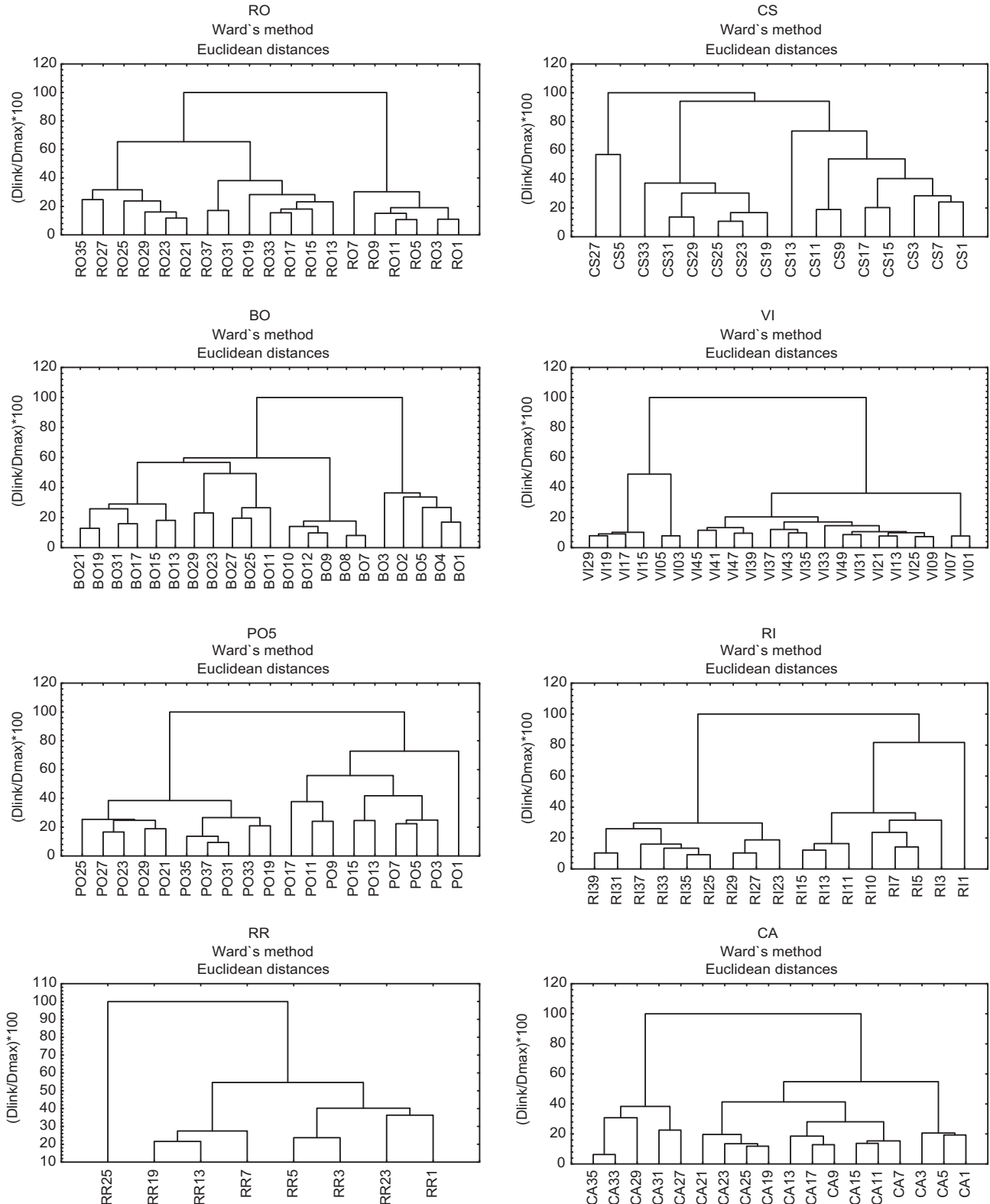


Fig. 5. Dendrograms obtained for the normalized concentrations in relation to Sc in samples.

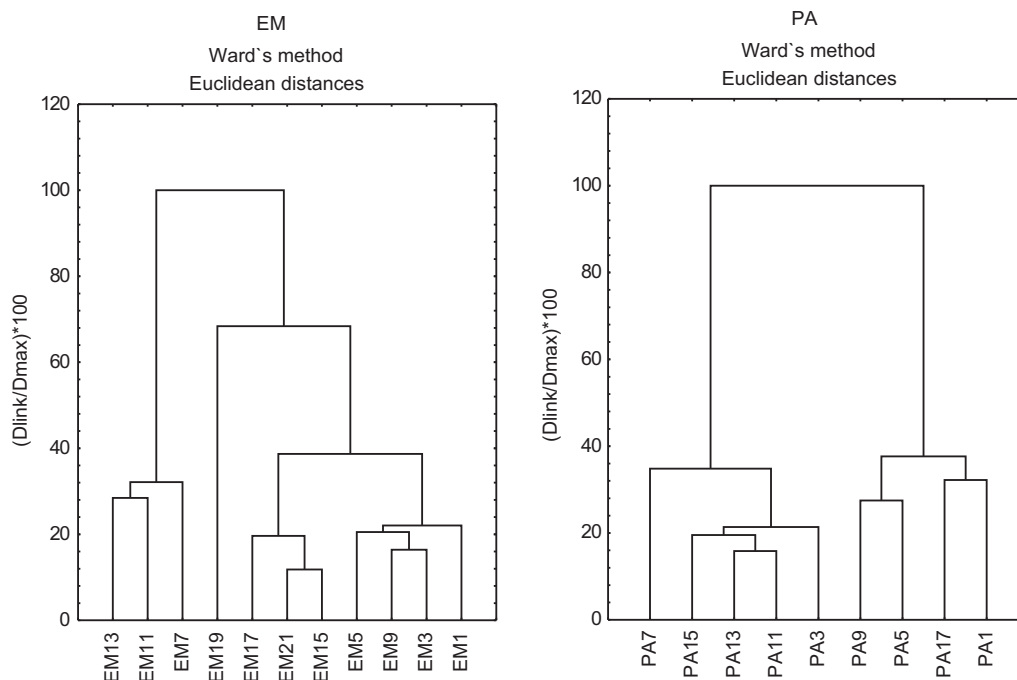


Fig. 5 (continued)

ments and not only the total concentration. That is, the occurrence of adverse biological effects cannot be precisely predicted from concentration data alone. The likelihood of adverse biological effects occurring in response to a certain element exposure at a particular site depends on the sensitivity of individual species and endpoints examined, as well as a variety of physicochemical (e.g., pH and redox potential), geochemical (e.g., particle size, organic matter content, and metal oxide and sulphide contents), and biological (e.g., feeding behavior and uptake rates) factors that affect the bioavailability of this element (Environment Canada 1999).

The only element under the TEL values in all the PO and RI core samples was As. In the VI core, only the surface samples had values above TEL and in the RR core, all samples except the last one, were above the TEL value. The Cr element showed results similar to As, being under the TEL only in PO, RI and PA. Only few samples had a Zn concentration above the TEL value: all the slices of the RO and CS cores and in the BO core in the upper 10 cm. None of the values of the samples analyzed were close to the PEL threshold.

According to Resolution No. 344/04 dated 03/25/2004 (CONAMA, 2009) for dredged management purposes sediments are classified in Level 1 and Level 2 corresponding to TEL and PEL, respectively. Of all elements analyzed only As, Cr and Zn have threshold limits within the Brazilian law sediment with values (in $\mu\text{g g}^{-1}$): As = 30; Cr = 150 and Zn = 350 for Level 2. None of these values were exceeded in all the samples analyzed. Another approach for geochemical data analysis is the geochemical normalization factor (NF), defined by the following equation:

$$\text{NF} = C_n / C_{\text{normalizer}}$$

According to Rath et al. (2009) this normalization is useful in environmental studies concerning the determination of human contribution in metal enrichment in aquatic sediments. If the source of the sediment is the same for the analyzed elements, the NF must be constant or vary slightly. Cluster analysis can identify similarities in samples of a group by variance analysis and provide information about expected or unexpected clusters including

the presence of outliers (Idris, 2008). These two analyses were combined, the NF was calculated using Sc as the normalizer and results were used in cluster analysis to create the dendrograms.

According to the results presented in Fig. 5, the RO, CS, BO, PO, RI, and CA cores were divided into two distinct groups composed of surface samples and deeper samples. In the RO and CS cores, as mentioned above, higher concentrations of LRE, Hf, Ta, Th and U elements and EF values were found in the deeper samples, whereas all other element concentrations decreased with depth. This seems to indicate a change in the sediment composition based on depth which could reflect anthropogenic contributions of industrial complex located in the region. Also in the CS core, two outlier samples were identified: one at 10 cm (CS5) of depth and the other at 54 cm (CS27). For the BO core, the group formed by the surface samples (upper 14 cm) can be attributed to variations in the Zn concentration. This result confirms those obtained in the CV analysis and the EF values indicate that sediments below 14 cm originated from natural weathering. For the PO core, the surface group samples included all the samples up to 34 cm (PO17). From this depth on, the concentrations of all elements, except As, were lower than of the surface samples. The main elements responsible for the observed variability in this core were Co, Cr, Fe and Zn according to the NF. This set of elements is generally characteristic of man-made contributions. For the RI core, the group of surface samples was comprised of the upper 46 cm. From this depth down, lower concentrations with less variation were found. In the CA core, the group of deeper samples starts at the depth of 54 cm (CA27). These samples are characterized by an increase in the concentration of all elements. These high concentrations also indicate, as in the case of the RO and CS cores, a change in sediment composition.

For the RR, VI, EM and PA cores, it was not possible to observe the formation of two distinct groups as occurred with the cores mentioned above. The RR core seemed to form a homogeneous group in accordance with the results of the VC analysis. Only one sample was separated as an outlier, sample RR 25, whose concentrations were lower than those of all the analyzed elements and characterized by a sudden change in granulometry since it was almost entirely sand. In the VI core, all elements showed the same

tendency to decrease their concentration with depth and from 20 cm down the variation were considerably low. The samples that were separated in this dendrogram were characterized by high values of normalization factor in accordance with the EF analysis. In the EM and PA cores, the samples were not clearly separated, possibly due to the fact that this location is more affected by human activity, such as sewage outflow and Santos Port, as indicated by the high EF for Fe and Zn.

Generally, high enrichment factor values were obtained for light rare earth elements (La, Nd, Sm and Eu), Hf, Ta, Th and U along the cores, indicating that the region possesses relatively elevated background for these elements. This hypothesis is corroborated by a study of Pereira et al. (2008), which states that the accessory minerals that comprise the granitic bed, the main source of lithogenic sediments of the Baixada Santista, are rich in these elements. Luiz-Silva et al. (2008) analyzed sediments from the Cubatão region in a deeper core than the one obtained in this study and they found background concentrations of $2.8 \mu\text{g g}^{-1}$ for Hf; $1.5 \mu\text{g g}^{-1}$ for Ta; $15.8 \mu\text{g g}^{-1}$ for Th and $5.3 \mu\text{g g}^{-1}$ for U. Considering these values instead of the NASC values, the EF was recalculated. The interval varied from 0.89 to 22, for Hf, and from 0.3 to 6.1, for U, which indicates contamination. The enrichment factor for Ta and Th was always below 1 in almost all samples using this approach.

For As, the background value found by Luiz-Silva et al. (2008) was $14.6 \mu\text{g g}^{-1}$. Only the VI core in São Vicente and the CA core in Bertioga presented concentrations of As above this value, which confirms that the concentration of this element is also relatively high in this region.

Another element that presented EF above 1.5 was Zn, when considering the value established by Luiz-Silva et al. (2008) as the background value for the region, $92.5 \mu\text{g g}^{-1}$. For this element, a high EF was found mainly in the upper layers of cores BO, PO, RI, CA and EM and throughout the RO, CS and PA cores. According to Jackson (1991), Zn is one of the elements with strong anthropogenic origin and its high concentration values (higher than 1.5 reference value) indicate contamination by human activity.

Based on the above discussion and the results of the multivariate analysis applied to the amount of analyzed elements in the bottom layers of the BO, PO, RI, and CA cores and the entire profiles of the RR and VI cores, the mean values can be considered as concentration reference values for the region studied (Table 3). The distribution of the granulometric fractions in these cores showed that the sediments can be characterized as predominantly fine fraction (approximately 90% or more) and predominantly sandy (approximately 70% or more). Based on this it was reasonable to propose a set of reference values for sediments with up to 90% of fine fraction and a set of values for sediment samples with up to 70% of sand for the “Baixada Santista”. These two proposed set of values are shown in Table 3.

Ten core samples were analyzed in the Baixada Santista region, located in São Paulo's coast: Cubatão, São Vicente, Bertioga and Santos Bay, with the objective of determining the concentration distribution levels of As, Br, Ce, Cs, Co, Cr, Eu, Fe, Hf, La, Lu, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Yb and Zn elements. A normalization of the geochemical data was applied to the obtained results and then treated by multivariate statistical analysis with the purpose of determining reference values for the elements analyzed in the sediments of the studied region, considering the total fraction. This data may be used to assess the status and trends in the environmental quality of the sediment from “Baixada Santista”. This information is also valuable for the decision making process needed for the dredging and final disposal of the sediment. The enrichment factor calculated showed an enrichment of various elements i.e. LRE (La, Ce, Sm, Nd and Eu), Hf, Ta and U which confirms a high background for these elements. In the case of Zn, an anthropogenic contribution was also observed. The combined use of enrichment

factors, normalization factors and cluster analysis enabled the bottom layers of the BO, PO, RI, and CA cores and the entire profiles of the RR and VI cores to be considered as concentration reference values for the studied elements for the region. This study was conducted in the total fraction of the sediment and it was noted that the content of sand, silt and clay, although not the only but rather one of the main natural processes that affect the concentrations, is the main factor to determine reference values for the amount of elements considered in this study. For disposal of dredged material one must consider the distribution of the granulometric fractions according to the values presented in Table 3.

Contributors

Paulo S.C. Silva: samples collection, neutron activation analysis measurement, calculations and article preparation.

Sandra R. Damatto: samples collection, samples preparation, neutron activation analysis measurement and calculations.

Caio Maldonado: sample preparations for neutron activation analysis and calculations.

Deboráh I.T. Fávoro: neutron activation analysis measurement and article preparation.

Barbara P. Mazzilli: coordination of the Project and article preparation.

Acknowledgments

The authors thank FAPESP for financial support in this project, under Contract No. 2006/05686-4, to CNPq for Grant No. 300835/95-7 and to CETESB for collaboration in the core sampling.

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