

SANTOS ESTUARINE SEDIMENTS, BRAZIL - METAL AND TRACE ELEMENT ASSESSMENT BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

The Santos estuary system is an intricate pattern of tidal channels and small rivers originating from the adjacent Pre-Cambrian slopes. These two major estuaries share a common area in the upper portion of the region which interacts with each other. The largest harbor in Latin America is located at the eastern outlet of the Santos estuary. This intricate and sensitive ecosystem is highly susceptible to human impact from industrial activities, urban sewage and polluted solid wastes disposal. Due to its high vulnerability CETESB (Environmental Control Agency of the São Paulo State) sporadically monitors the contamination levels of water, sediment and marine organisms in this region. The present study reports results concerning the distribution of some major, trace and rare earth elements in the Santos estuarine marine sediments. Thirty two bottom sediment samples (SS0601 to SS0616 (summer) and SW0601 to SW0616 (winter) were collected in this estuary, including regions of Sao Vicente, Santos, Cubatao and Vicente de Carvalho, by a vanVeen sampler in the summer and winter of 2006. Multielemental analysis was carried out by instrumental neutron activation analysis (INAA). The concentration values obtained for As and metals Cr and Zn in the sediment samples were compared to Canadian Council of Minister of the Environment (CCME) oriented values (TEL and PEL values) and are adopted by CETESB.

1. INTRODUCTION

Sediments are mineral and organic particle layers found in the lower areas of natural body waters such as lakes, rivers and oceans. In sediments, the mineral proportion in relation to the organic matter is variable depending on place and natural, biological and anthropogenic activities. Sediments thus have a high importance since they represent the areas where deposits of many chemical products, especially organic composites and heavy metals can be transferred to organisms, affecting the food chain [1].

The natural processes of sediment formation can be affected by anthropogenic activities. The sediments analysis presents important information concerning the environment. The chemical characterization of sediments is necessary to understand the natural process and anthropic influence [2].

Metal contamination impacts the coastal environment through atmospheric precipitation, fluvial income and direct effluent disposal. Fluvial income is the main carrier of continental metals to coastal zones, especially through suspended particulate materials which, in turn, contaminate sediments and soils in this region. [3] As a rule, coastal regions present intense human occupation and high pressure on the ecosystem. The estuarine systems of Santos and Sao Vicente are the most important examples of environmental degradation of coastal regions in Brazil. In this region there is the largest harbor of Latin America, the Santos harbor and the most important industrial complex in Brazil, Cubatao [4].

Despite the great effort for pollution control and environmental quality improvement, a study in 1988 concluded that the Santos region suffered from the impact of high concentrations of heavy metals and organic compounds in the water, sediments and aquatic organisms [5]. Recently, many studies about the quality of sediments in this region showed that contamination problems concerning heavy metal pollution still exist [6-11].

Instrumental neutron activation analysis (INAA) has been widely applied for soil and sediment analysis in environmental studies all over the world, including at LAN from IPEN/CNEN-SP [12-15]. So much so, that this study assessed the content of heavy metals and other elements in bottom sediment samples from the Santos estuary in two periods of 2006, summer and winter. Multielemental analysis was carried out by instrumental neutron activation analysis (INAA). This study was initiated in 2005 and previous results have already been published [16]

2. MATERIAL AND METHODS

2.1. Sampling and sample preparation

Thirty two bottom sediment samples (SS0601 to SS0616 (summer) and SW0601 to SW0616 (winter)) were collected in the Santos estuary, including regions of Sao Vicente, Santos, Cubatao and Vicente de Carvalho, by a vanVeen sampler in the summer and winter of 2006. Samples were previously dried at 50°C in a ventilated oven, passed through a 2 mm sieve and then homogenized before analysis. The total fraction (< 2 mm) was then analyzed. Sampling stations are presented in Figure 1.

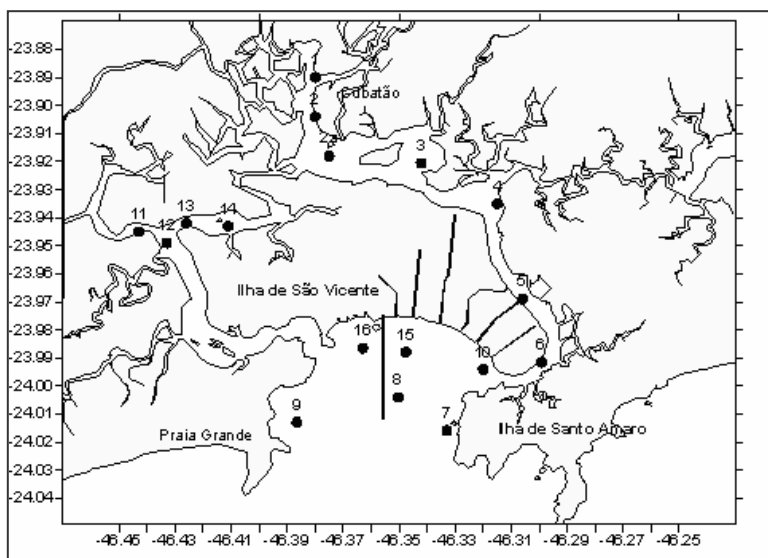


Figure 1 – Santos estuary sampling station locations

2.2. Instrumental Neutron Activation Analysis – multielemental determination

For the multielemental analysis, approximately 200 mg of sediment (duplicate samples) and about 150 mg of reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Single and multi-element synthetic standards were prepared by pipetting convenient aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman No.41 filter paper. Sediment samples, reference materials and synthetic standards were irradiated for 16 hours, under a thermal neutron flux of 10^{12} n cm⁻² s⁻¹ in the IEA-R1 nuclear reactor at IPEN. Two series of counting were made: the first, after one week decay and the second, after 15-20 days. Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ⁵⁷Co and ⁶⁰Co, respectively.

The elements analyzed by using this methodology were As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U, Zn and the rare earths Ce, Eu, La, Lu, Nd, Sm, Tb and Yb. The analysis of the data was done by using in-house gamma ray software, VISPECT program to identify the gamma-ray peaks and by an ESPECTRO program to calculate the concentrations. The uncertainties of the results were calculated by errors propagation. The methodology validation was verified by measuring the reference materials Buffalo River Sediment (NIST SRM 2704), Soil 7 (IAEA) and BEN (Basalt –IWG-GIT). Details of the analytical methodology is described at Larizzatti et al [13].

3. RESULTS AND DISCUSSION

The results obtained by INAA for Buffalo River Sediment, Soil 7 and BEN-Basalt reference materials analyses are presented in Figure 2. The Z value calculation was according to Bode [17]. If $|Z| < 3$ the individual result of the control sample (reference material) lies on the 99% confidence interval of the target value. All Z-score values were in this interval range ($|Z| < 3$), indicating a good precision and accuracy of the INAA technique. These data are showed in the Figure 2. The obtained values for the reference materials were in this interval range ($|Z| < 3$), indicating a good precision and accuracy of the INAA technique.

Table 1 presents the mean, standard deviation, minimum and maximum values (mg kg⁻¹) for the elements analyzed by INAA for the sediment samples collected in the summer of 2006. Samples collected in the winter of 2006 are presented in Table 2. Both tables also show the NASC (North American Shale Composite) values [18]. Samples from stations 01 to 06 were labeled as group 1 and are located at the Santos estuary extending into the upper portion of the estuarine system, near the industrial pole of Cubatão. Samples from stations 7 to 10, 15, 16, named group 2 are located at the Santos bay where the depuration processes tend to be more accentuated due to the circulation of chemical compounds, and samples from stations 11 to 14 named as group 3, located at the São Vicente estuary extending to the Casqueiro region, an area characterized by extensive mangrove vegetation and with urban development presenting poor sanitary processing.

When the results obtained for multielemental concentrations (Tables 1 and 2) were compared with NASC (North American Shale Composite) [18] values it could be observed that there was enrichment for light REE (La, Ce, Eu, Nd, Sm) and U in group 1, in summer and winter (Figure 3). This is probably due to the influence of fertilizer plants that have been operating along the margins of some rivers producing a large volume of phosphogypsum, a by-product

of the production of phosphoric acid, which is disposed of in nearby storage areas, as piles on the margins of the rivers. This was already observed in the previous study for samples collected in 2005 [16]. For groups 2 and 3 it was not possible to observe this influence. For group 1 it is also possible to verify higher concentrations for most elements analysed, especially for the metals Cr, Fe, Rb, Sb and Zn. These samples are located near the Cubatão region, suffering high impact from industrial activities and harbor influence.

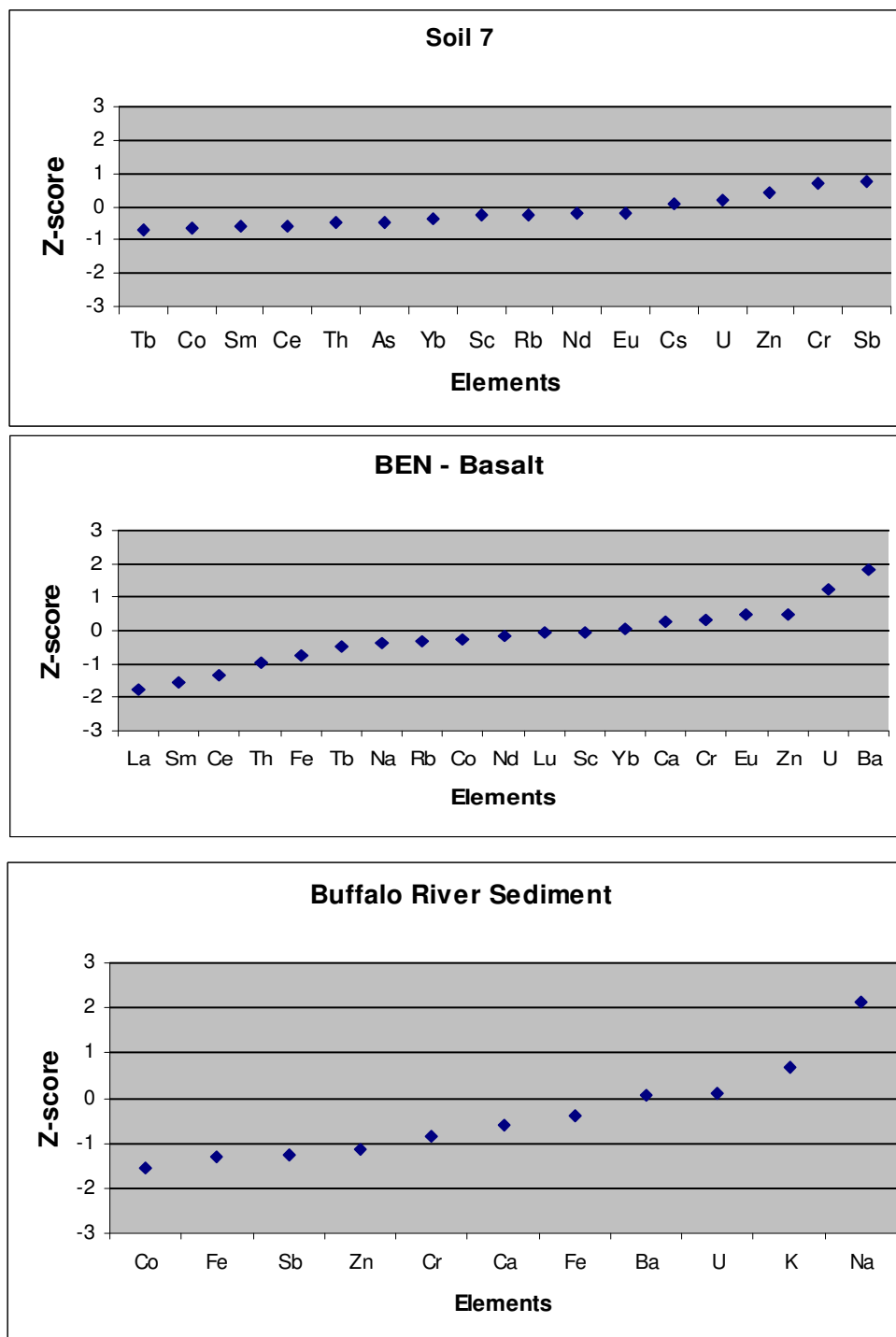


Figure 2. Control chart (Z-values) for inspection of the normalized concentrations of certified elements in the SOIL-7, Basalt-BEN and Buffalo River Sediment reference material samples.

Table 1 –Results obtained for the elements analyzed by NAA (mg kg⁻¹) for samples collected in summer (2006): mean, standard deviation, minimum and maximum and NASC values

	Group 1 (St 01 to 06)				Group 2 (St 07 to 10, 15, 16)				Group 3 (St 11 to 14)				NASC [18]	
	mean	std	min	max	mean	std	min	max	mean	std	min	max		
As	9.6	2.7	6.4	14.0	8.1	3.3	2.5	12.0	9.7	2.8	6.9	13.1	636	
Ba	153	168	N.D.	320	442.8	55.2	365.6	505.2	293	38	244	337		
Br	131	52	69	212	75.0	44.8	23.0	135.9	148	98	69	285		
Ca(%)	1.7	0.6	1.3	2.8	1.3	0.6	0.6	2.0	3.4	4.5	1.0	10.1		
Ce	98.3	64.6	35.1	187.4	33.7	7.9	23.0	45.1	68.8	30.2	38.1	101.0		73
Co	8.7	2.6	4.7	11.5	4.9	1.3	3.4	6.9	6.6	2.5	4.2	9.0		26
Cr	56	18	25	73	25.0	7.7	13.9	36.0	48	22	28	71		125
Cs	5.0	1.7	2.2	6.8	2.0	0.8	1.0	3.2	4.0	2.0	2.0	5.8		5.2
Eu	1.5	0.9	0.5	2.8	0.6	0.1	0.5	0.8	0.9	0.4	0.6	1.4		1.2
Fe(%)	3.5	1.4	1.6	5.5	1.9	0.4	1.5	2.4	2.8	1.3	1.6	4.2		
Hf	-	-	-	-	2.7	0.9	1.2	4.0	3.7	1.3	2.2	5.3		6.3
K(%)	0.5	0.6	N.D.	1.2	1.1	0.9	N.D.	2.1	0.6	0.4	N.D.	1.0		
La	43.0	26.8	15.6	81.6	15.5	4.0	10.2	21.3	27.7	11.7	15.1	40.6	32	
Lu	0.1	0.1	N.D.	0.2	0.1	N.D.	0.1	0.2	0.3	0.1	0.1	0.4	0.5	
Na (%)	2.02	0.53	1.21	2.74	1.3	0.4	0.9	2.0	1.78	1.20	0.92	3.50		
Nd	59.9	55.7	20.8	166.7	11.6	6.6	N.D.	20.4	26.3	17.7	10.9	47.7	33	
Rb	82.7	26.1	56.1	124.7	67.5	12.2	48.1	80.9	59.6	28.3	33.9	91.9	125	
Sb	0.6	0.2	0.3	0.9	0.2	0.2	N.D.	0.5	0.5	0.2	0.3	0.6		
Sc	9.6	3.2	4.5	13.1	4.2	1.6	2.2	6.4	8.4	3.7	4.8	12.3	15	
Sm	6.6	3.8	2.4	12.0	2.2	1.2	N.D.	3.3	4.5	2.0	2.4	6.8	5.7	
Ta	-	-	-	-	0.3	0.3	N.D.	0.8	0.7	0.5	0.3	1.1	1.1	
Tb	0.6	0.4	0.2	1.3	0.3	0.2	N.D.	0.5	0.6	0.4	0.2	1.0	0.9	
Th	10.5	4.6	4.2	16.6	4.3	1.1	2.8	5.9	8.8	3.7	5.0	12.7	12	
U	3.2	2.2	1.1	7.1	1.2	0.2	1.0	1.4	3.5	0.8	2.4	4.3	2.7	
Yb	1.8	0.8	0.8	2.7	0.9	0.3	0.5	1.3	1.4	0.5	0.8	2.0	3.1	
Zn	113	44	48	173	41.4	25.1	N.D.	66.8	109	57	57	176		

*N.D. – Not detected – Values lower than Quantification Limits

The results obtained for the elements As, Cr and Zn for all samples in the present study are shown in Table 3, as are the results of the TEL (threshold effect level) and PEL (probable effect level) oriented values from Canadian Council of Minister of the Environment (CCME) [19]. These are the limits established by Canadian legislation and adopted by the Environmental Control Agency of Sao Paulo state (CETESB). TEL is the limit below which no adverse effects on the biological community is observed and PEL, the probable level of occurrence of adverse effects on the biological community.

Comparing the results obtained for As in all sampling points in winter, with the exception of the samples SW0607 and SW0608, all samples presented concentration values higher than TEL oriented value (5.9 mg kg⁻¹). For samples collected in summer, only the sample SS0610 presented concentration value lower than TEL. Concerning PEL, only sample SW0602 exceeded the PEL value (17 mg kg⁻¹).

For Cr, the samples SW0601 to SW0605, SW0611 to SW0614 presented concentration values higher than the TEL value (37.3 mg kg⁻¹). For samples collected in summer, except for sample SS0612, the same samples presented concentration values higher than TEL. None of the samples exceeded the PEL value (90 mg kg⁻¹).

Regarding Zn, samples SW0601, SW0603, SW0604, SW0605 and SW0614 collected in the winter and samples SS0601, SS0602, SS0604, SS0613 and SS0614 collected in summer

presented concentration values higher than the TEL value (123 mg kg⁻¹). None of the samples collected in summer and winter, surpassed the PEL value (315 mg kg⁻¹).

These variations can be explained by the insertion of those pollutants in different seasons by anthropogenic pathways or by natural marine process removal.

Comparing the results obtained in the present study with the previous one for samples collected in 2005 [16], the mean concentration values for all elements analyzed were very similar for groups 1 and 2. Group 3 (st 11 to 14) in this study had a new site, station 14, a highly polluted point, which in the previous study was not considered (st.11 to 13). Because of this, the mean concentration values for group 3 in the present study were much higher than that of 2005.

Table 2 –Results obtained for the elements analyzed by NAA (mg kg⁻¹) to samples collected in winter (2006): mean, standard deviation, minimum and maximum, and NASC values

	Group 1 (St 01 to 06)				Group 2 (St 07 to 10, 15, 16)				Group 3 (St 11 to 14)				NASC [18]
	mean	Std	Min	max	mean	std	min	max	mean	std	min	max	
As	10.3	5.6	1.6	18.5	7.4	2.2	5.2	11.4	11.6	3.9	7.2	16.7	636
Ba	415	196	201	681	482	72	401	601	331	156	212	544	
Br	155	40	84	199	47	25	22	74	155	54	105	232	
Ca(%)	1.7	0.7	1.2	3.0	1.0	0.4	0.6	1.5	2.3	0.9	1.2	3.3	73
Ce	118.8	82.1	46.4	257.2	32.8	8.5	19.5	44.0	69.0	27.5	44.8	103.2	
Co	9.3	1.8	7.0	11.2	4.1	0.8	2.8	5.2	7.3	2.2	5.4	10.2	
Cr	59	16	35	77	21	7	13	30	52	15	37	69	125
Cs	4.7	0.9	3.7	5.8	1.8	0.6	1.1	2.7	4.5	1.6	3.2	6.6	5.2
Eu	1.7	1.2	0.7	3.7	0.6	0.1	0.4	0.8	1.1	0.4	0.7	1.6	1.2
Fe(%)	3.7	1.2	2.2	5.7	1.7	0.3	1.3	2.1	3.0	1.1	2.1	4.5	6.3
Hf	4.1	1.2	2.9	5.5	2.4	1.2	1.1	4.5	3.0	0.5	2.3	3.4	
K(%)	0.9	0.6	N.D.	1.6	2.1	1.8	N.D.	5.0	1.0	0.8	N.D.	1.9	
La	46.5	29.3	2N.D.	93.3	14.5	4.7	8.7	21.6	31.4	12.1	20.5	46.2	32
Lu	0.3	0.1	0.2	0.4	0.1	N.D.	0.1	0.2	0.3	0.1	0.2	0.4	0.5
Na (%)	2.07	0.45	1.46	2.51	1.17	0.23	0.78	1.45	1.99	0.82	1.28	3.11	33
Nd	45.4	23.0	21.0	80.1	13.8	3.5	8.6	18.4	28.9	11.3	19.2	44.1	
Rb	84.7	25.8	55.4	128.5	60.9	9.3	46.3	72.5	60.8	21.5	42.2	88.2	
Sb	0.6	0.1	0.4	0.8	1.1	1.9	0.2	4.9	0.6	0.3	0.4	1.2	15
Sc	10.4	2.7	6.5	13.2	3.6	1.4	2.0	5.5	9.1	3.1	6.5	13.0	
Sm	8.0	10.7	N.D.	29.5	2.7	0.4	2.3	3.1	1.8	2.1	N.D.	3.7	
Ta	0.5	0.8	N.D.	2.2	0.2	0.2	N.D.	0.4	0.8	0.3	0.5	1.1	1.1
Tb	1.1	1.7	N.D.	4.4	0.1	0.1	N.D.	0.2	0.7	0.1	0.6	0.9	0.9
Th	10.8	4.0	6.3	18.0	4.3	1.9	2.3	7.6	9.1	3.5	6.0	13.6	12
U	3.0	1.4	1.9	4.8	1.1	0.5	0.6	2.0	3.2	0.7	2.4	3.9	2.7
Yb	2.1	0.9	1.1	3.7	0.8	0.2	0.6	1.2	1.4	0.4	1.0	1.7	3.1
Zn	107	65	N.D.	177	36	14	21	53	108	59	63	190	

* N.D. – Not detected – Values lower than Quantification Limits

Table 3 – Values of Arsenic, Chromium and Zinc (mg kg⁻¹) in samples collected in winter (SW) and summer (SS) (2006), TEL and PEL values [19]

	As	s.d.	Cr	s.d.	Zn	s.d.		As	s.d.	Cr	s.d.	Zn	s.d.
SW0601	1.6	0.3	76.6	2.1	177.1	7.5	SS0601	11.4	0.2	69.1	1.1	173.5	2.4
SW0602	18.5	0.5	67.9	2.5	N.D.	N.D.	SS0602	8.5	0.3	72.8	4.3	141.8	2.3
SW0603	8.1	0.3	45.0	1.3	130.9	10.1	SS0603	8.0	0.3	63.5	0.9	89.2	1.6
SW0604	12.4	0.4	68.1	1.2	129.1	9.2	SS0604	14.0	0.3	61.5	0.7	127.8	4.3
SW0605	12.0	0.5	59.4	2.8	145.4	6.1	SS0605	9.2	0.2	46.8	0.5	95.5	3.0
SW0606	9.1	0.3	35.2	1.6	58.4	3.5	SS0606	6.4	0.1	24.9	0.3	48.0	1.2
SW0607	5.2	0.3	29.4	1.4	52.9	3.6	SS0607	7.7	0.2	23.4	0.9	47.0	2.0
SW0608	5.5	0.2	20.5	0.6	33.6	1.1	SS0608	12.0	1.9	36.0	1.6	66.8	2.0
SW0609	7.7	0.2	13.2	0.5	20.9	0.6	SS0609	10.2	0.2	13.9	0.5	24.7	0.9
SW0610	7.0	0.4	30.5	1.1	50.0	1.3	SS0610	2.5	0.1	28.1	1.0	47.4	1.7
SW0611	11.2	0.4	37.1	1.3	67.1	2.4	SS0611	8.0	0.2	27.7	0.7	66.0	3.3
SW0612	7.2	0.3	40.8	0.7	62.9	2.5	SS0612	6.9	0.2	31.5	0.9	57.4	2.1
SW0613	11.2	0.7	61.8	1.0	111.9	4.2	SS0613	10.8	0.3	63.6	1.7	138.8	5.2
SW0614	16.7	0.7	68.5	3.5	190.4	6.6	SS0614	13.1	0.6	70.9	2.6	175.8	6.6
SW0615	7.4	0.3	16.3	0.9	21.7	1.0	SS0615	6.7	0.2	20.0	0.8	N.D.	N.D.
SW0616	11.4	0.4	18.6	1.0	34.8	1.3	SS0616	9.3	0.3	28.5	1.1	62.8	3.8
TEL	5.9		37.3		123		TEL	5.9		37.3		123	
PEL	17		90		315		PEL	17		90		315	

*N.D. – Not detected ; s.d. – standard deviation

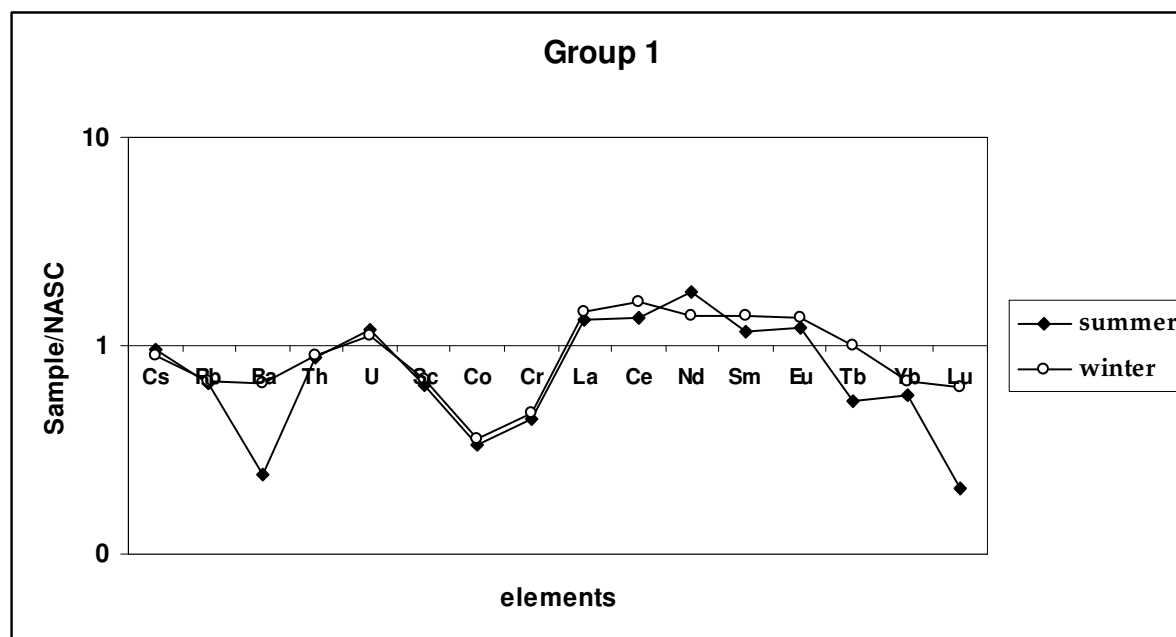


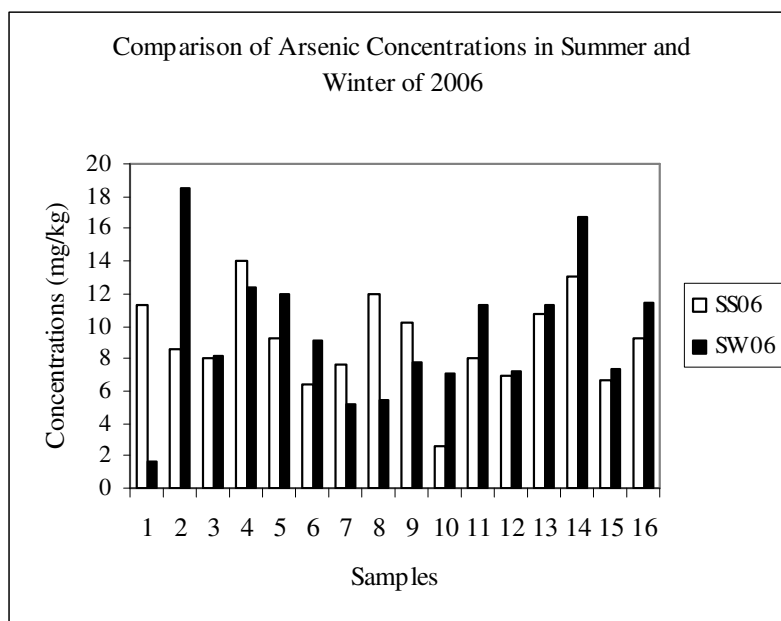
Figure 3 – Normalized elements (NASC) for the sediment samples (2006)

Machado et al. [20] studied the history of contamination and the sources of 38 elements in sediments of the Santos-Cubatao estuarine system. The composition of the 260 cm core of the Morrao River was analyzed by ICP-MS and data evaluation was performed by means of enrichment factors, principal component analysis (PCA), correlation matrices and geochemical signatures. The purpose of this study was to contribute with base levels (background) of metals concentration in sediment before the contamination of the site by anthropogenic sources.

Silva et al. [21] evaluated the distribution of some radionuclides and elements in Cubatao river sediments. Cluster analysis was applied to radioactive and stable elements such as manganese, calcium, lead, iron, copper, magnesium, lithium, aluminum, nickel, radium, uranium, thorium and mercury. By means of this statistical analysis, three groups were identified: the first group accounts for manganese and iron oxy-hydroxide elements. The second group accounts for the granulometric characteristics of the sediments and the elements that are generally associated to silt and clay fractions. The third group was formed by radioactive elements and mercury.

Abessa et al [6] studied the influence of the submarine sewage outfall (SSOS) in the Santos bay on the toxicity and contamination of adjacent sediments. They concluded that at the disposal site, sediment tended to be finer, organically richer and exhibited higher levels of surfactants and metals, sometimes exceeding the TEL values. The values found for the samples collected during the summer of 2000 were: Zn, from 43 to 66 mg kg⁻¹; Cr, from 5.5 to 38 mg kg⁻¹. For the sake of comparison the results obtained in this study (sampling in 2006) for these elements in the stations 7 to 10, 15, 16 (Santos Bay, group 2) presented a mean concentration value of 41 ± 25 mg kg⁻¹ for Zn (< 3 to 67 mg kg⁻¹) and 48 ± 22 mg kg⁻¹ (14 to 36 mg kg⁻¹), for Cr. When compared the results were quite similar.

Figure 4 presents the comparison of As, Cr and Zn concentrations in summer and winter of 2006. It can be observed that the relationship of winter and summer vary sharply in some cases as in samples 01, 02 and 08 to parameter As, samples 06 and 08 to parameter Cr and samples 02, 08 and 15 for Zn.



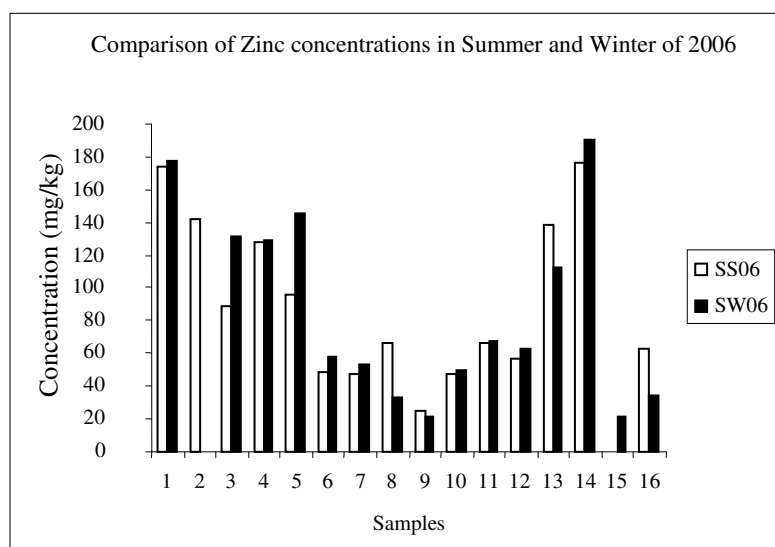
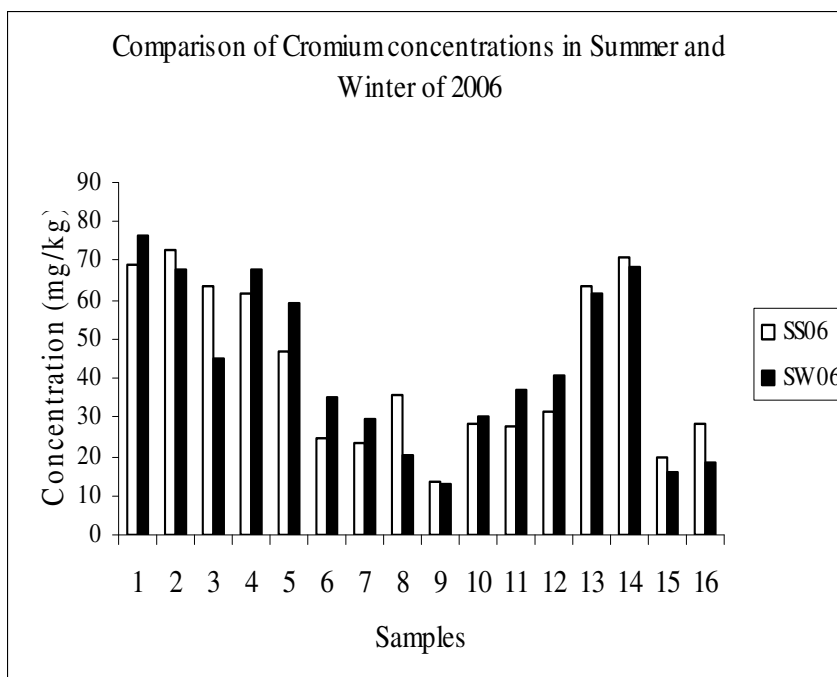


Figure 4 – Comparison of As, Cr and Zn values for samples collected in winter and summer (2006)

4. CONCLUSIONS

Instrumental neutron activation analysis used to determine metals and trace elements presented appropriate sensitivity for sediment monitoring, showing good precision and accuracy.

When the concentration values for As and metals Cr and Zn in the sediment samples were compared to TEL values from Canadian legislation and adopted by CETESB, it was possible to conclude that samples from group 1 (Santos estuary) presented the highest values exceeding the TEL for As, Cr and Zn. Regarding PEL values only station 2 (winter) exceeded for As (17 mg kg^{-1}). Furthermore, samples from this group showed light REE and

U enrichment probably due to the influence of fertilizer plants that have been operating along the margins of some rivers producing a large volume of phosphogypsum. These sample stations are located near the Cubatão region, an area under strong impact caused by industrial activities. Station 4 also receives the influence of the Santos harbor.

For samples from group 2, located at the Santos bay and near the SSOS, the only concentration that exceeded the TEL value (5.9 mg kg^{-1}) was As in some stations. For the other analyzed elements the concentration values were below NASC values. These group located at Santos bay receives more influence from local hydrodynamic and where the depuration processes tend to be more accentuated due to the circulation of chemical compounds.

Samples from group 3 located at São Vicente estuary, exceeded the TEL values for As in all sampling points, in summer and winter. In winter, also results for Cr exceeded the limit in all stations. For Zn only station 14 exceeded the TEL value. For samples collected in summer the values found for Cr and Zn exceeded the TEL values only in the stations 13 and 14. None of the stations from this group surpassed the PEL value. For the other analyzed elements the concentration values were below NASC values.

Comparing the results obtained in this study with other studies in the Santos-São Vicente estuary system the sediment quality appears to be improving and in general, the concentration levels observed for metals is decreasing. This is probably due to the great effort for pollution control established by CETESB for the region.

ACKNOWLEDGMENTS

The authors wish to thank FAPESP for financial support (Process n° 05/50769).

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