

METAL AND TRACE ELEMENT ASSESSMENT OF ESTUARY SEDIMENTS FROM SANTOS, BRAZIL, BY NEUTRON ACTIVATION AND ATOMIC ABSORPTION TECHNIQUES

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ABSTRACT

In order to better understanding geochemical and environmental processes and their possible changes due to anthropogenic activities trace metal analyses and their distribution in marine sediments are commonly undertaken. The present study reports result concerning the distribution of some major, trace and rare earth elements in the Santos estuarine marine sediments. Thirteen bottom sediment samples (SV0501 to SV0513) were collected in this estuary, including regions of São Vicente, Santos, Cubatão, Vicente de Carvalho and Santos' Bay, in the summer of 2005. Multielemental analysis was carried out by instrumental neutron activation analysis (INAA). For total mercury determination cold vapor atomic absorption technique (CV AAS) was employed. In both cases methodology validation was performed by certified reference material analyses. The results obtained for multielemental concentrations in the sediment samples were compared with NASC (North American Shale Composite) values. The concentration values obtained for As and metals Cr, Hg and Zn in the sediment samples were compared to Canadian Council of Minister of the Environment (CCME) oriented values (TEL and PEL values). In general, the samples located near the Cubatão region showed higher concentrations for all elements analyzed probably due to the high impact of industrial activities.

1. INTRODUCTION

Sediments represent an important repository of pollutants and a source of contamination for the aquatic food chain. Environmental contaminants sources to coastal system are numerous and may enter the estuarine environment via a number of pathways. Metals may be present in the estuarine system as dissolved species, as free ions or forming organic complexes with humic and fulvic acids. Additionally, many metals associate themselves readily with particulates and thus become absorbed or co-precipitated with carbonates, oxyhydroxides, sulphides and clay minerals. Consequently, sediments accumulate contaminants and may act as long-term stores for metals in the environment [1]. 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 to be answerable for sediments and soils contaminated in this region [2].

The Santos Estuarine system is composed of an intricate pattern of tidal channels and small rivers originating from the adjacent Pre-Cambrian slopes. The region is comprised of two large and complex estuaries known as Santos and São Vicente. 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. The access to the port for large ships is guaranteed by way of periodic dredging of the main shipping lane, which requires a minimum draft of 10 m. This intricate and sensitive ecosystem is highly susceptible to human impact from industrial activities, urban sewage and polluted solid waste disposal. Due to its high vulnerability CETESB (Environmental Control Agency of the São Paulo State) sporadically monitors the contamination levels of waters, sediment and marine organisms.

This estuarine system, located at São Paulo State, Brazil, represents one of the most important examples of environmental degradation in coastal system by water and atmospheric pollution of industrial origin. The coastal regions normally show elevated human occupation, causing a high impact in the fragile ecosystems found there. The largest Brazilian industrial complex is installed in this densely urban region, with the predominant presence of petrochemical, steel, and fertiliser industries [3].

Pollution evaluation impact studies on water, sediment and aquatic organisms made in 1979 and 1981 [4,5] verified the damage of aquatic environment in all locations studied. A list of causes of pollution would include: physical alteration in the habitats by erosion process, channel and mangroves filled up with earth, draining system intervention and degradation by domestic and industrial waste, which are responsible for chemical and microbiological contamination [3].

Despite the great effort for pollution control and improvement of environmental quality, a study in 1988 concluded that the region had been impacted by high concentrations of heavy metals and organic compounds in the water, sediments and aquatic organisms [6-8].

Recently, many studies about the quality of sediments have been undertaken in this region and the results showed that contamination problems concerning heavy metal pollution still exist [9-12].

Instrumental neutron activation analysis (INAA) has been widely applied for soil and sediment analysis [13], allowing the determination of several elements such as Zn, As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, Sb, Se, Ta, Th, U, W, Zr and rare earth elements (REE). For total Hg determination, the cold vapor atomic absorption technique (CV AAS) is largely used for biological, geological and environmental samples [14].

The purpose of this study was to assess the content of heavy metals and other elements in sediment samples from the Santos estuary in the summer of 2005. Multielemental analysis was carried out by instrumental neutron activation analysis (INAA) and total mercury by cold vapor atomic absorption technique (CV AAS).

2. MATERIAL AND METHODS

2.1. Sampling and sample preparation

Thirteen bottom sediment samples (SV0501 to SV0513) were collected in this estuary, including regions of São Vicente, Santos, Cubatão and Vicente de Carvalho, by a steel van Veen sampler in the summer of 2005. The sampling stations are presented in Figure 1. Stations 01 to 06 are located at the Santos estuary, 7 to 10 at the Santos bay and 11 to 13 at the São Vicente estuary. The 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 analysed.

2.2. Total Hg determination

About 500 mg of sediment samples were digested with a mixture of concentrated HNO₃, H₂SO₄ and hydrogen peroxide 30% in Teflon vials. The vials were closed and left overnight at room temperature. The following day, the vials were put into an aluminum block at 90 °C and left there for 3 hours. The samples were allowed to cool at room temperature and the final volume was completed to 50 mL with Milli-Q water. Total mercury determinations were performed using CV AAS, using a FIMS from Perkin Elmer. The analytical procedure used (wet digestion) was that of Horvat [14] with some modifications. Methodology validation for total Hg determination was carried out by means of reference material analyses Marine Sediment (IAEA 433) and Estuarine Sediment (NIST SRM 1646a).

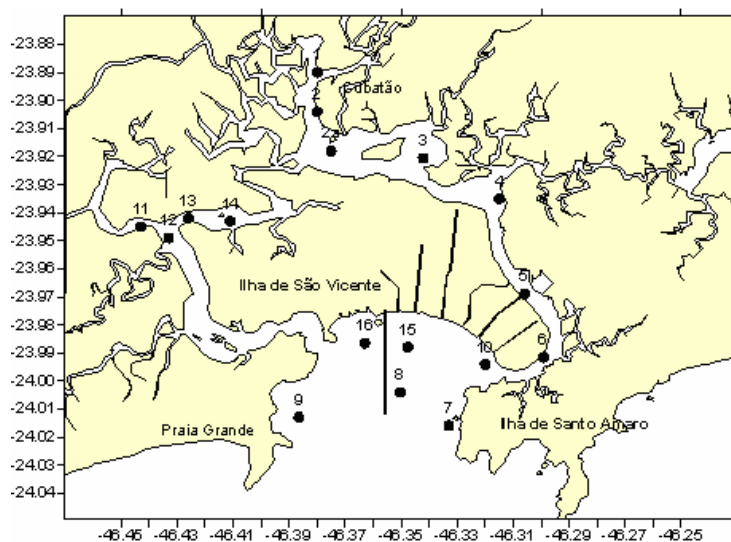


Figure 1 – Sampling station locations

2.3. 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. Sediment samples and reference materials 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 made 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).

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 [15]. 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.

The results obtained for total Hg in Marine Sediment (IAEA 433) and Estuarine Sediment (NIST SRM 1646^a) reference materials, as well as certified and information values are presented in Table 1. Relative standard deviation ranging from 2.0 to 2.3% and relative error of 3.6% were found in the reference material analyses for total Hg determination, showing good precision and accuracy.

Table 1 – Total mercury concentration results ($\mu\text{g kg}^{-1}$) by CV AAS

Reference Material (n =3)	Certified Value	Found Value	RSD (%)	Relative Error (%)
Estuarine Sediment (NIST SRM 1646 ^a)	40	40.2 ± 0.8	2.0	
Marine Sediment (IAEA 433)	168 ± 15	174 ± 4	2.3	3.6

n = number of determinations

Table 2 present the mean, standard deviation, minimum and maximum values (mg kg^{-1}) for the elements analysed by INAA and total Hg content ($\mu\text{g kg}^{-1}$) by CV AAS, for the sediment samples. Also shown is the NASC (North American Shale Composite)[16] and TEL (Threshold Effect Level) and PEL (Probable Effect Level) oriented values from Canadian Council of Minister of the Environment (CCME) [17]. 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.

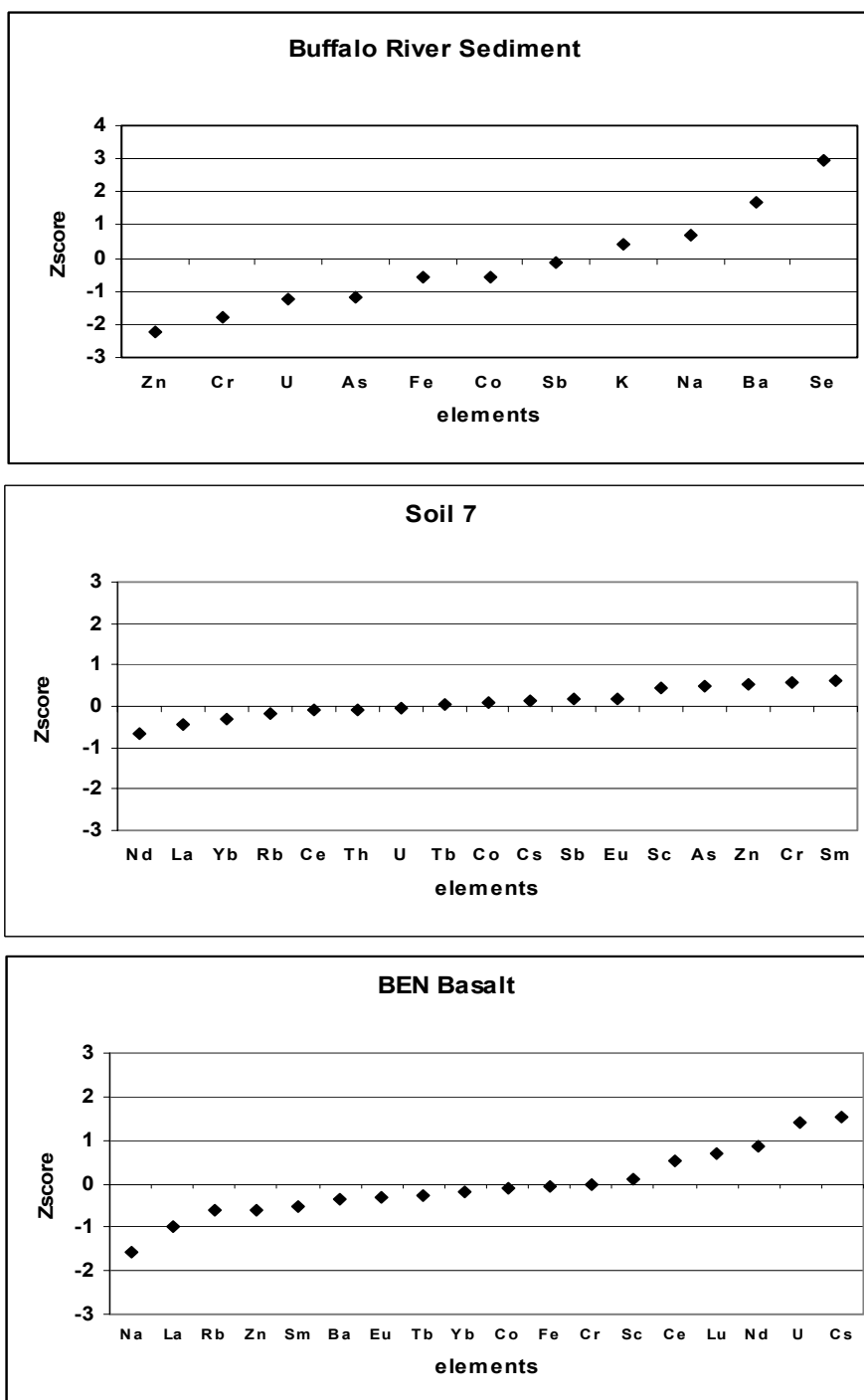


Figure 2 - Control chart (Z-values) for inspection of the normalized concentrations of some elements in the NIST SRM 2704, SOIL-7 and Basalt-BEN reference material samples.

Samples from stations 01 to 06 were labelled as group 1 and are located at the Santos estuary. Samples from stations 7 to 10, named group 2 and are located at the Santos Bay and samples from stations 11 to 13, group 3, located at the São Vicente estuary. As can be seen, the mean concentration values for the three groups are considerably different (Table 2). When the

results obtained for multielemental concentrations were compared with NASC (North American Shale Composite) [16] values there was an enrichment for light REE (La, Ce, Eu, Nd, Sm) and U (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 [18]. For groups 2 and 3 it was not possible to observe this influence. For group 1 it is also possible to verify higher concentration for most elements analysed, especially for the heavy metals Cr, Hg and Zn. These samples are located near the Cubatão region, suffering high impact from industrial activities and harbor influence.

Luiz-Silva et al [12] studied this region, sampled 15 stations distributed through seven rivers where 156 surface sediment samples were collected in 1997 and fine fraction was analyzed (< 63 μm fraction). Mercury levels ranging from 0.10 to 6.77 mg kg^{-1} were observed and concluded that Hg levels in surface sediments from Santos-Cubatão estuary were as high as in past (1980's).

Hortellani et al [10] also studied this region in 1996. Thirty-one surface sediment samples were collected and the sediment fraction < 80 mesh was analyzed. The range of Hg values was between 0.04 to 1.19 mg kg^{-1} , where 90% of samples presented Hg > 0.13 mg kg^{-1} levels (TEL), below which no adverse effects on the biological community has been observed. About 35% of these samples presented concentrations of Hg > 0.70 mg kg^{-1} (PEL), the probable level of occurrence of adverse effects on the biological community.

Siqueira & Braga [19], at the same points of this study, in 2000, observed values of Hg from 0.05 to 0.81 mg kg^{-1} , with a maximum value located near the industrial pole of Cubatão region (SV0501), placed at the end of the dredged artificial channel, in front of a steel plant. It was observed high concentrations near the garbage disposal, nowadays inactive and also around the exit of the submarine emissary of waste, at Santos' Bay. The Al presented similar behavior and a range from 1.6 to 6.4%. The authors calculated Hg enrichment factors >8 in the region using Al and Li as normalizers. These results confirming important sediment metal influence to the local biota without a big difference considering the observed data in the 80-90 decades.

Abessa et al [9] 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} ; Hg, from 0.05 to 0.17 mg kg^{-1} . For the sake of comparison the results obtained in this study for these elements in the stations 7 to 10 (Santos Bay, group 2) varied from 22 to 79 mg kg^{-1} for Zn, from 14 to 47 mg kg^{-1} for Cr and from 0.02 to 0.06 mg kg^{-1} for Hg.

In this study the concentration values obtained for As and metals Cr, Hg and Zn in the sediment samples were compared to TEL and PEL values. Group 1 sample values (st 1 to 6) for As, Cr and Zn exceeded TEL values (As – 7.24, Cr – 52.30, Zn – 124 mg kg^{-1}) for most samples. For Hg, the values found for samples from group 1 were the highest ones but did not exceed the TEL value (0.13 mg kg^{-1}). For group 2 samples only the concentration values for As exceeded the TEL value (7.24 mg kg^{-1}) in all stations (7 to 10). For metals Cr, Hg and Zn

all the results were below TEL values. For group 3 samples, all concentration values for As, Cr, Hg and Zn were far below TEL values.

Table 2 –Results obtained for the elements analyzed by NAA (mg kg⁻¹) and CV AAS (µg kg⁻¹): mean, standard deviation, minimum, maximum, NASC, TEL and PEL values

	Group 1 (st 1 to 6)				Group 2 (st 7 to 10)				Group 3 (st 11 to 13)				NASC [16]	TEL[17]	PEL[17]
	Mean	std	Min	max	mean	std	min	max	mean	Std	min	max			
As	10.3	5.0	3.8	18.0	8.8	1.2	7.4	10.3	2.9	2.5	0.4	5.4		7.24	41.6
Ba	388	94	283	524	401	47	338	443	146	70	79	218	636		
Br	76	21	53	103	52	21	22	70	22	10	12	32			
Ce	95	47	24	167	43	18	20	64	19	11	7	26	73		
Co	8.8	3.0	3.1	11.7	5.9	2.3	3.1	8.5	2.0	1.5	0.5	3.4	26		
Cr	59	23	19	89	34	14	14	47	17	11	5	24	125	52.3	160
Cs	4.7	1.6	1.5	5.9	2.8	1.3	1.1	4.3	1.0	0.8	0.2	1.8	5.2		
Eu	1.35	0.62	0.41	2.30	0.84	0.24	0.52	1.10	0.31	0.18	0.10	0.46	1.24		
Fe (%)	3.3	1.2	1.1	4.8	2.1	0.6	1.4	2.9	0.8	0.6	0.1	1.4			
Hf	4.7	2.2	1.7	7.5	3.3	1.3	1.4	4.2	4.6	1.3	3.6	6.0	6.3		
Hg (µg kg ⁻¹)	375	223	48	682	42	18	18	58	38	18	18	52		130	696
La	42	21	10	74	18	8	8	27	8	5	3	11	32		
Lu	0.25	0.10	0.08	0.38	0.16	0.07	0.07	0.24	0.09	0.03	0.05	0.11	0.48		
Na	14135	3099	10565	17749	12345	3087	8458	15350	4023	1664	2351	5678			
Nd	37	17	9	54	17	3	13	21	10	4	5	12	33		
Rb	94	39	38	149	59	16	39	73	17	12	5	30	125		
Sb	0.57	0.27	0.21	0.87	0.31	0.07	0.21	0.37	0.22	0.13	0.08	0.35			
Sc	9.5	3.4	2.9	12.3	5.5	2.6	2.0	8.2	2.2	1.5	0.6	3.6	15		
Sm	7.0	3.5	1.6	12.0	3.2	1.4	1.5	4.8	1.4	0.8	0.5	1.9	5.7		
Ta	1.1	0.6	0.3	2.1	0.5	0.3	0.0	0.8	0.3	0.1	0.2	0.4	1.1		
Tb	0.71	0.37	0.11	1.22	0.44	0.20	0.16	0.61	0.21	0.11	0.09	0.29	0.85		
Th	11	4	3	16	6	2	3	8	3	2	1	4	12		
U	3.3	1.8	1.0	6.2	1.6	0.9	0.5	2.5	1.7	0.9	0.6	2.3	2.7		
Yb	1.8	0.6	0.6	2.4	1.1	0.4	0.6	1.6	0.7	0.3	0.3	0.9	3.1		
Zn	118	45	31	147	51	24	22	79	20	13	8	34		124	271

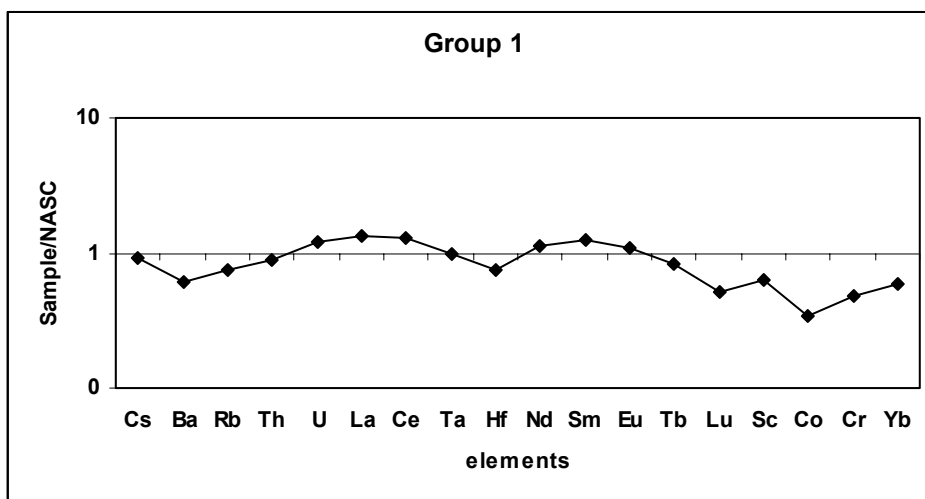


Figure 3 - Normalized elements (NASC) for the sediment samples

3. CONCLUSIONS

Instrumental Neutron Activation Analysis and CV AAS analytical techniques 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, Hg 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. Furthermore these samples 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 and showed higher As, Cr, Sb, Sc and Zn concentrations.

For samples from group 2, located at the Santos Bay and near the SSOS, the only concentration that exceeded the TEL value (7.24 mg kg^{-1}) was As. For the other analysed elements the concentration values were below NASC values.

Samples from group 3 located at São Vicente estuary, presented the lowest concentrations for all analysed elements. For As and metals, all concentration values were far below TEL 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.

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REFERENCES

1. K.L. Spencer. "Distribution and partitioning of heavy metals in estuarine sediment cores and implications for the use of sediment quality standards". *Hydrology and Earth System Sciences*, **6(6)**, pp.989-998 (2002).
2. F.G. Cunha. Contaminação humana e ambiental por chumbo no Vale do Ribeira nos Estados de São Paulo e Paraná. Tese de doutorado, Departamento de Geologia e Recursos Naturais, UNICAMP (2003).
3. CETESB – Sistema Estuarino de Santos São Vicente, Relatório Técnico, São Paulo/SP, Brasil, 219p, (2001).
4. CETESB – Poluição das Águas no Estuário e Baía de Santos. Relatório Técnico CETESB, volume 1, 71p, (1979).
5. CETESB – Metais pesados na Baía de Santos e Estuários de Santos e São Vicente. Relatório Técnico CETESB, 231p, (1981).
6. CETESB – Contaminantes na Bacia do rio Cubatão e seus reflexos na biota aquática. Relatório Técnico CETESB., 81p. mais anexos, (1990).
7. G.G.J. Eysink, M.C. Lamparelli, C. Vargas-Boldrini, M.C. Martins. *Contaminants in the Cubatão Riverbasin and its Estuary (SP, Brazil), relating to the Aquatic Biota. Part I. Heavy Metals, Arsenic and Cyanide*. 11th Biennial International Estuarine Research Conference – San Francisco, USA. Session: Inputs and Cycling of Natural and Contaminant Materials in Estuaries, November (1991).
8. C. Vargas-Boldrini, G.G.J. Eysink, M.C. Lamparelli, M.C. Martins. *Contaminants in the Cubatão River basin and its Estuary (SP, Brazil), relating to the Aquatic Biota. Part 2. Organic Compounds*. 11th Biennial International Estuarine Research Conference - San Francisco USA. Session: Inputs and Cycling of Natural and Contaminant Materials in Estuaries, November (1991).
9. D.M.S. Abessa, R.S.Carr, B.R.F. Rachid, E.C.P.M. Sousa, M.A. Hortelani, M.A.; J.E.S. Sarkis. Influence of a Brazilian sewage outfall on the toxicity and contamination of adjacent sediments. *Mar. Poll. Bull.* **50**, pp.875-885 (2005).
10. M.A.Hortellani, J.E.S. Sarkis, J. Bonetti, C. Bonetti. Evaluation of Mercury Contamination in Sediments from Santos-São Vicente Estuarine System, São Paulo state, Brazil. *J.Braz.Chem. Soc.* **16(6a)**, pp.1140-1149 (2005).
11. W. Luiz-Silva, R.H.R.Matos, G.C. Kristosch, W. Machado. Variabilidade espacial e sazonal da concentração de elementos-traço em sedimentos do sistema estuarino de Santos-Cubatão (SP). *Química Nova*, **29(2)**, pp. 256-263 (2006).
12. W. Luiz-Silva, R.H.R. Matos, G.C. Kristosch. Geoquímica e Índice de Geoacumulação de Mercúrio em Sedimentos de Superfície do estuário de Santos-Cubatão (SP). *Química Nova*, **25(2)**, pp.753-756 (2002).
13. D.I.T. Fávoro, S.R. Damatto, E.G. Moreira, B.P. Mazzilli, F. Campagnoli. Chemical Characterization and Recent Sedimentation Rates in Sediment Cores from Rio Grande reservoir, São Paulo, Brazil. *Journal of Radioanalytical and Nuclear Chemistry*, **273(2)**, pp.451-463 (2007).
14. M. Horvat. "Mercury Analysis and Speciation". In **Environmental Samples in Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances**, p. 1-31, W. Baeyens et al (eds), (1996).
15. P. BODE. Instrumental and Organizational Aspects of a Neutron Activation Analysis Laboratory. Interfaculty Reactor Institut. Delft University of Technology. Delft. The Netherlands, p. 147, (1996).
16. S.R.Taylor & S.M. Mc Lennan. **The continental crust: its composition and evolution**. Blackwell Scientific, Palo Alto, Ca., p. 25-27, (1985)
17. CCME - Canadian Environmental Quality Guidelines - Summary Tables- <http://www.ec.gc.ca/ceqg-rcqe/English/ceqg/sediment/default.cfm>, June, (2007)
18. S.M.B. Oliveira, P.S.C. Silva, B.P. Mazzilli, D.I.T. Favaro, C.R. Sauiea. Rare earth elements as tracers of sediment contamination by phosphogypsum in the Santos estuary, southern Brazil. *Applied Geochemistry*, **22(4)**, pp.837-850 (2007).
19. G. W. Siqueira & E. S. Braga. Estudo dos teores de Hg na fração fina do sedimento: uma visão ambiental com aplicação de normalizantes geoquímicos para as regiões estuarinas de Santos/São Vicente e Baía de Santos. *Anais do VIII Congresso Brasileiro de Geoquímica e I Simpósio de Geoquímica dos Países do Mercosul*, 21-16 de outubro de 2001, Curitiba.7p.