2007 International Nuclear Atlantic Conference - INAC 2007
Santos, SP, Brazil, September 30 to October 5, 2007
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-02-1

PRINCIPAL COMPONENT ANALYSIS APPLIED TO ASSESS METALS AND ARSENIC SOURCES IN SEPETIBA BAY, RIO DE JANEIRO.

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ABSTRACT

Sepetiba bay, located about 60 km west of the metropolitan region of Rio de Janeiro city, has undergone notable development in the last decades, with the establishment of about 400 industrial plants in its basin, basically metallurgical. These industries release their industrial waste either straight into the bay or through local rivers. The Sepetiba harbor also brought up a lot of industrial investment in that area. This urban and industrial expansion caused several environmental impacts, mainly due to the presence of metals, metalloids (such as As) and other potentially toxic substances present in the effluents discharged into the bay. In this work, Neutron Activation Analysis (NAA), Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and Inductively Coupled Plasma – Optical Emission Spectrometry (ICP OES) were used to determine As, Cd, Cu, Ni, Pb and Zn concentration in sediment samples from Sepetiba bay. The results obtained were treated by using Factor Analysis with Extraction Principal Components. This statistic method has been commonly used in geochemical studies to identify sources of several elements in environmental samples, separating the anthropic contributions from the natural ones. According to eigenvalues, 2 principal components explain 71% of the total variance. The factor loadings indicated that Cu, Pb and Ni presented good correlation to sediment grain sizes and organic carbon and were associated to first factor (F1), while As, Cd and Zn were associated to second factor (F2). The results suggest that these elements have different sources.

1. INTRODUCTION

Over the last few decades the expansion of urban centers has caused continuously modifying in the physical, chemical and biological environmental aspects. As a result, millions of people around the world are exposed to unnatural and unhealthy substances and elements such as As, Cd, Cu, Ni, Pb and Zn.

Natural sources of, generally, related to physical and chemical weathering of rocks of catchments area of rivers. On the other hand, they are stable and persistent environmental contaminants. Thus, they tend to accumulate in soils and sediments, and are known to cause adverse effects on environment and human health. Anthropic sources (of metals and metalloids) include industrial and domestic wastes and sewage effluents which are originated from nearby urban centers, and draining into rivers, bays, estuaries, lakes[1].

In studies about contamination of aquatic systems, sediments have been widely used, because they act as a reservoir to a lot of chemical substances. Most of the contaminants leave their fingerprint in sediments samples. Therefore, this geological matrix can provide information about the history of the environment studied[2]. For instance, in estuaries where sediments from different sources are mixed, knowing the origin of sediments is especially helpful in identifying the fate of pollutants and nutrients and tracing the possible cycles of particulate matter in the estuarine system[3].

The aims of present work were to determine As, Cd, Cu, Ni, Pb and Zn contents in sediments collected from Sepetiba bay, Rio de Janeiro. These elements are considered very important in environmental studies, because they are commonly used in industrial activities. The analytical techniques used were Neutron Activation Analysis (NAA), Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and Inductively Coupled Plasma – Optical Emission Spectrometry (ICP OES). A multivariate statistical approach (Principal Component Analysis, PCA) was adopted to identify pollution sources and to separate natural from anthropic contributions. Besides, a geostatistic approach was used to check the spatial distribution of the elements studied. The factor scores obtained were interpolated by ordinary kriging using SURFER® 6.01 for Windows.

2. EXPERIMENTAL

2.1. Study Area

Located at the latitude of 22º54' and 23º04'S longitude of 43º34' and 44º10'W at Rio de Janeiro State, Brazil. Sepetiba Bay has important touristic and industrial activities that have led to a set of impacts on the environment. The surroundings of the bay show the fastest growing rates of industrialisation and urbanisation of the region provided by transportation facilities (roads and railways), cheap and available land and good freshwater supply. Large population inflows and the construction of a large harbour in the early 70s made the area further attractive for industrial development. Nowadays, there are about 400 industries that can be grouped into: pyrometallurgic, aluminium plants and electricity power plants. This industrial park is responsible for the inputs of large amounts of toxic elements in the surrounding environments, attaining the coastal area through the rivers or atmospheric deposition[3]. The most important environmental accident in Sepetiba bay happened in 1995. A metallurgical plant, which produced zinc from calamine ore, discharged a lot of wastes into the bay. Among these wastes, which constitute serious contaminants in the bay, there were As, Zn and Cd[4,5].

2.2 Sampling Sites

The sediment sampling was in August/2003. The samples were collected from 65 previously chosen sites (Fig 1). A Van Veen sampler[6] was used to collect the samples. A fraction of sediment that was not in contact with the surface of the grab was separated and placed in plastic ziplock bags and immediately cooled to 4 °C for transportation. In order to have representative results, the samples were collected from a very dense network of stations. This was necessary because it was aimed to analyse the spatial distribution of the metals.

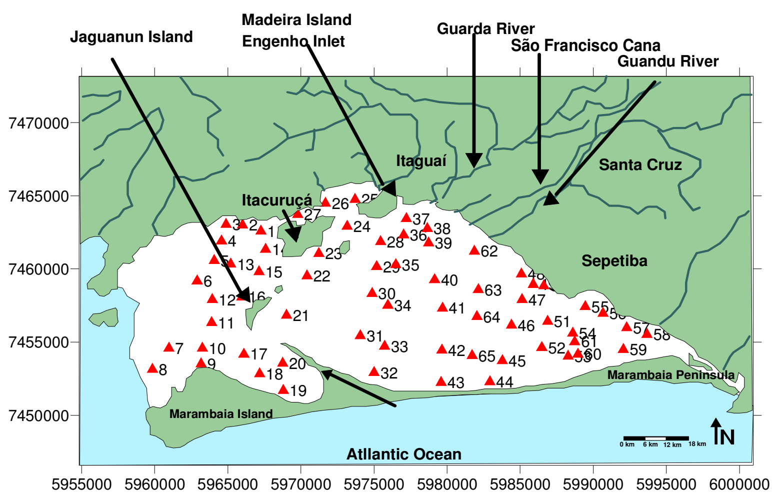

Figure 1. Location of the study area and positioning of the sampling stations.

2.3 Analytical Procedures

In the laboratory, the samples were frozen and stored at -20 °C. Within a few weeks, the samples were dried at less than 40 °C for three days, grounded with an agate mortar and stored in sealed plastic bags until analysis.

2.3.1 Granulometric analysis

Granulometric analysis was done by wet sieving samples through a 63 µm nylon, followed by the drying of both passed and retained fractions, that were weighted and the fraction smaller than 63 µm was calculated.

2.3.2 Organic carbon

The samples were pre-weighted in special silicate crucibles and treated with HCl 1 mol L^{-1} in order to completely eliminate carbonates. Organic carbon was measured in CHN equipment (Perkin Elmer, 2400 CHN).

2.3.3 NAA

About 100 mg of the sample were accurately weighed, in polyethylene bags, to determine As and Zn contents. Elemental synthetic standards of these elements were prepared by pipetting convenient aliquots of standard solutions (SPEX) onto 1 cm^2 pieces of Whatman nº 40 filter paper. The standards were then sealed in polyethylene bags. Samples and standards were irradiated for 16 hours at a thermal neutron flux of 10^{13} n cm^{-2} s^{-1} at the IEA-R1 nuclear reactor of IPEN. The measurements of the induced gamma-ray activities were performed in two series of countings: the first one five days after irradiation, to determine As contents and the second one 15 days after irradiation, to determine Zn contents.

2.3.4 GFAAS and ICP OES

About 250 mg of sediment were weighted, and the EPA 3052 method[7] was used for the total digestion of samples. Cd and Pb contents was determined by using GFAAS and Cu and Ni contents were determined by using ICP OES[8].

2.3.5 Statistical Analysis

Factorial analysis with Extraction Principal Components (PCA) is a multivariate method which facilitates the reduction, transformation and organization of original data by the use of intricate mathematical techniques, which eventually results in sample form of factor model. This statistical tool creates a new set of uncorrelated variables, which are the linear combination of the original ones with the same amount of information.[9]. The interpretation of dominant factors was made by taking into account the highest factor loadings on chemical elements. The statistical analysis was done by using rhe STATISTIC® 6.0 program for Windows. Spatial visualisation of the results of the factor analysis were mapped by kriging ordinary interpolation , using the Golden Software Surfer® 7.0 for Windows. The theoretical details of the PCA and the principle of the ordinary kriging model are known in statistical works[9,10].

3. RESULTS AND DISCUSSION

3.1 Granulometric Analysis

Granulometry may constitute a good control of the element contents[11]. This procedure assumes that elements are exclusively associated with the fine grained portion of the sediments (< 63 µm). This is consistent with the fact that the specific surface in fine grained sediments is larger than in coarse sediments, and therefore, fine grained sediments are more reactive than coarse sediments. Nonetheless, the granulometric correction should be carefully considered since the assumption that metals are strictly associated with fine grained sediments is not always correct, mainly when grained fraction is very small[12]. Granulometric analysis showed fine grained sediments are predominant in Sepetiba bay. The granulometric correction provided very high contents to the metals and did not reflect the true contamination in the environment studied. Figure 2 shows the granulometric distribution of fine grained sediment in Sepetiba bay.

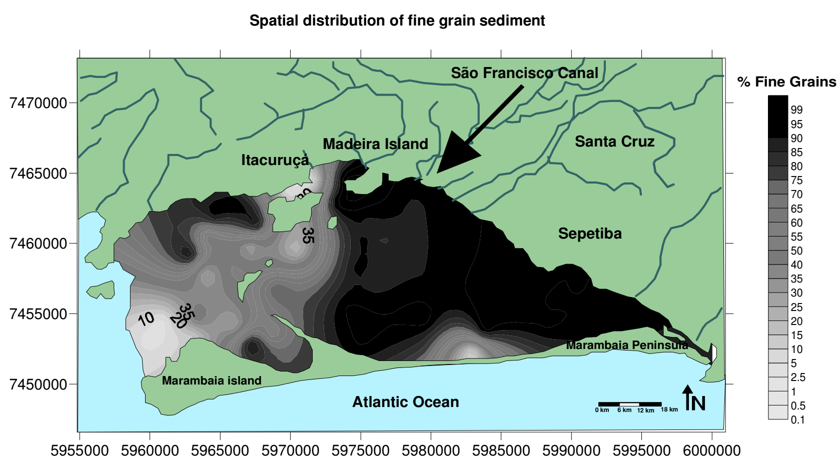

Figure 2: Spatial distribution of fine grain sediment in Sepetiba bay.

3.2 Organic Carbon

The results obtained to the organic matter showed contents between 2% and 3% for most of the analyzed samples. The highest values were observed in the East portion of the bay, because there are a lot of mangroves in this region. The fate of metal ion in the environment is related to its ability to combine with other entities, such as organic matter, surface of microorganisms and ions. As organic matter, microorganism may affect the chemical speciation of metal ions and control metal bioavailability and/or toxicity in aquatic systems[13]. Figure 3 presents the spacial distribution of organic carbon in Sepetiba bay.

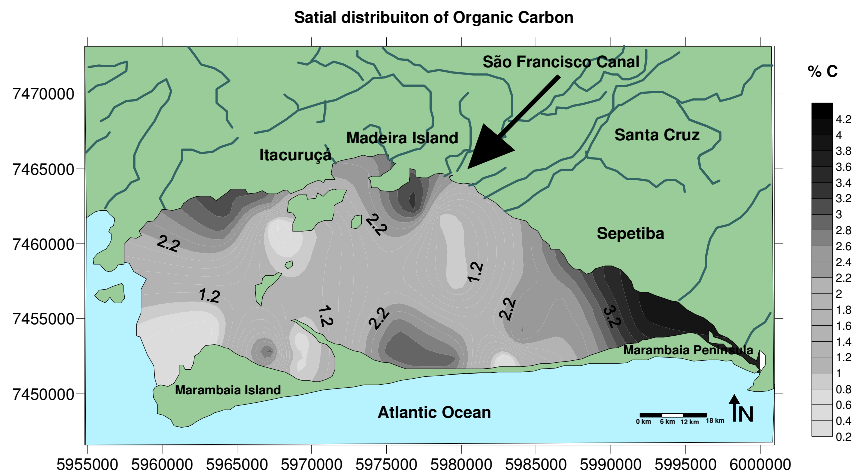

Figure 3: Spatial distribution of organic carbon in Sepetiba bay.

3.3 Metals and As Contents

The metals and As mean contents obtained for the samples analyzed are presented in Table 1. Generally, the highest values of the elements were observed in the Northeast and Southeast portions of Sepetiba bay, except to Ni, which presented the highest contents in the Northweast. This fact may indicate that Ni presents a different source or different behaviour related to other elements studied.

Table 1: Mean contents, standard deviation (SD) and range contents obtained to sediments samples from Sepetiba bay, in mg kg^{-1}.

Element	Mean and SD (mg kg^{-1})	Range (mg kg^{-1})
As	8 ± 4	1 – 14
Cd	2 ± 1	0.02 – 7.4
Cu	14 ± 8	1.6 – 33.0
Ni	16 ± 8	1.8 – 26.9
Pb	30 ± 14	2.9 – 69.5
Zn	600 ± 491	23.7 - 1941

3.4 PCA

The results of PCA for data sets are reported in Table 2. According to the results of initial eigenvalues, two principal components were considered, which accounted 71% of the total variance. The factor loadings indicated that Cu, Pb and Ni presented good correlation to sediment grain sizes and organic carbon and were associated to the first component (F1), while As, Cd and Zn were associated to second factor (F2).

F1: according to previous works[3,14,15], there is not a strong contamination in Sepetiba bay due to the presence of Cu, Ni and Pb. Nonetheless, in the region there are several plants which release their wastes into the rivers which flow into the bay, increasing the contents of metals, including Cu, Ni, and Pb. Therefore, the results of PCA method suggest these elements have a different source when compared to As, Cd and Zn, however one cannot conclude whether the origin of Cu, Ni and Pb come from, mostly, natural or anthropic sources.

F2: the second factor included As, Cd and Zn. This result suggested these elements have their origin associated to a metallurgical plant which caused an important environmental accident in Sepetiba bay, in nineties[16]. The wastes from the metallurgical plants presented high contents of As, Cd and Zn. These wastes have been damaging Sepetiba bay since the metallurgical plant started working, until the last year, when the federal authorities required Rio de Janeiro State started a work to recover Sepetiba bay[16,17].

Table 2: Factor loadings, eigenvalues and total variance (%).

Variables	F1	F2
Zn		0.876146
Cd		0.616871
Pb	0.598235	
Cu	0.640587	
Grain size	0.853517	
Organic carbon	0.778422	
As		0.844442
Ni	0.904853	
Eigenvalues **Total variance (%)**	4.441257 55.51572	1.154147 14.42684

3.5 Geostatistic

A geostatistic approach[9] was adopted to check the interpretation of PCA results as well as the spatial distribution factor scores in Sepetiba bay. Both raw data and factor scores were interpolated by ordinary kringing using SURFER® 6.01 for Windows. The obtained isoline maps were projected on a regional map.

F1 scores of data set are presented in Figure 4 and are associated to Cu, Ni and Pb. Figure 4 allows observing that the spatial distribution of F1 scores had the same way along Sepetiba bay. Therefore, geostatistic approach did not allow the identification of the most important source for Cu, Ni and Pb in Sepetiba region either.

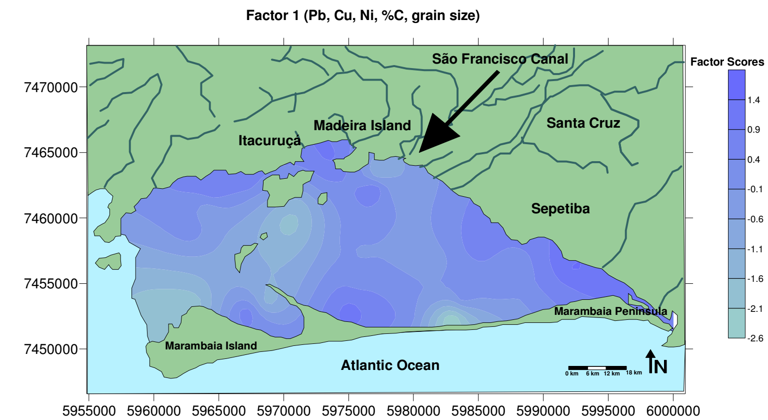

Figure 4: Spatial distribution of F1 scores in Sepetiba bay.

F2 scores of data set are presented in Figure 5 and are associated to As, Cd and Zn. Figure 5 allows observing the highest values of F2 scores were found in the Northeast region of Sepetiba bay, close to the mouths of the main rivers of Sepetiba, which provide a lot of wastes to the bay. Therefore, geostatistic approach allowed concluding that the most important source to As, Cd and Zn is an anthropic one.

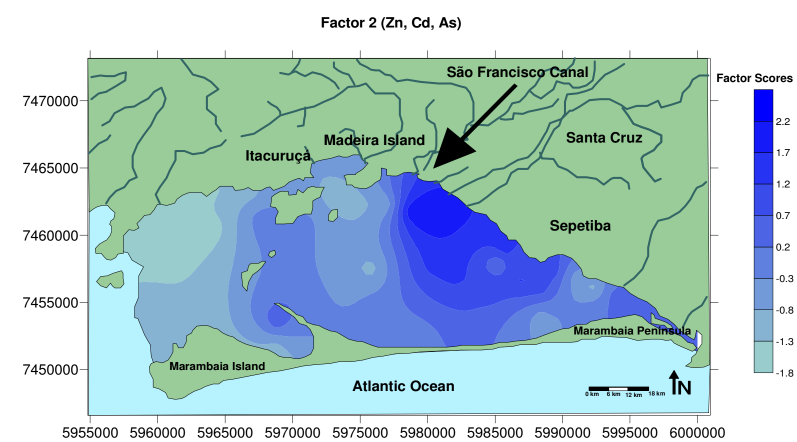

Figure 5: Spatial distribution of F2 scores in Sepetiba bay.

4. CONCLUSIONS

The results of PCA performed on six elements (As, Cd, Cu, Ni, Pb and Zn) identified two main factors controlling their variability in sediments from Sepetiba bay. Geostatistic approach provided useful information and supported the information obtained in PCA approach. According to the study, the variability of Cu, Ni and Pb, associated in the same factor, could not be identified as natural or anthropic source, mostly. As, Cd and Zn contents are controlled by a long-term anthropic activity connected with a metallurgical plant located in Sepetiba bay.

From a methodological point of view, multivariate statistics were found to be a powerful tool for the identification of factors controlling the variability of geochemical data for the interpretation of results, while geostatistic approach allows evidencing spatial relationships between the cases studied.

ACKNOWLEDGMENTS

The authors acknowledge to CNPq that financed this work, IPEN and UFF.

REFERENCES

1. M. Singh, G. Müller and B. Singh, "Heavy metals in freshly deposited stream sediments of rivers associated with urbanization of the Ganga Plain, India", *Water, Air and Soil Pollution*, **141**, pp. 35-54 (2002).
2. B. H. Shomar, G. Müller and A. Yahya, " Seasonal variations of chemical composition of water and bottom sediments in the wetland of Wadi Gaza, Gaza Strip", *Wetlands Ecology and Management*, **13**, pp. 419-431 (2005)
3. C. Barcellos and L. D. Lacerda, "Cadmium and zinc source and assessment in Sepetiba bay and basin region", *Environm. Acad. Pub.*, **29**, pp. 183-199 (1994).
4. F. Pellegatti, A. M. G. Figueiredo and J. C. Wasserman, "Neutron activation analysis applied to determination of heavy metals and other trace elements in sediments fro Sepetiba bay (RJ), Brazil", *Geostandards Newsletter – The Journal of Geostandards and Geoanalysis*, **25**(2), (2001).
5. L. D. Lacerda and M. L. Fiszman, "Metais pesados no pescado da baía de Sepetiba", *Ciênc. Cult.*, **37**, pp. 297-302 (1985).
6. R. Rubio and A. M. Ure, "Approaches to Sampling and Sample Pretreatments for Metal Speciation in Soils and Sediments. International", *J. Environ. Anal. Chem.*, **51**, pp. 205-217 (1993).
7. US-EPA United States Environmental Protection Agency "*Method 3052: microwave assisted digestion of sediments, sludges, soils and oils***.** 2003. Disponível em: <http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3051.pdf> - Acesso em 07/05/2004.
8. M.E. B. Cotrim, "*Avaliação da Qualidade da água na bacia hidrográfica do Ribeira de Iguape com vistas ao abastecimento público"***.** Tese (Doutorado) – Instituto de Pesquisas Energéticas e Nucleares – Universidade de São Paulo, São Paulo, 2006.

9. A. Facchinelli, E. Sacchi, L. Mallen "Multivariate statistical and GIS-based approach to identify heavy metal sources in soils", *Environmental Pollution*, **114**, pp. 313-324 (2000).
10. P.M.B. Landim, *"Análise estatística de dados geológicos multivariados"*. Texto Didático - DGA, IGCE, UNESP/Rio Claro, Lab. Geomatemática, 2000.
11. U. Förstner and W. Salomons, "Trace metals analysis on polluted sediments. Part I: Assessments of sources and intensities", *Environ. Technol. Lett.*, **1**, pp. 495-505 (1980).
12. J.C. Wasserman, A. M. G. Figueiredo, F. Pellegatti and E. V Silva-Filho, "Elemental composition of sediment cores from a mangrove environment using neutron activation analysis", *J. Geochem. Explor.*, **72**, pp. 129-146 (2001).
13. A. T. Lombardi, T. M. R. Hidalgo, A. A. H Vieira, "Copper complexing properties of dissolved organic materials exuded by freshwater microalgae Scenedesmus acuminatus (Chlorophyceae)", Chemosphere, 60(4), pp. 453-459 (2005).
14. FEEMA - Fundação Estadual de Engenharia do Meio Ambiente *"Levantamento de metais pesados no Estado do Rio de Janeiro",* Rio de Janeiro, 1986.
15. C. S. Karez, V. F. Magalhães and W. C. Pfeiffer, "Trace metal accumulation by algae in Sepetiba bay, Brazil", *Environ. Pollut.*, **83(9)**, pp. 351-356 (1994).
16. L. M. O. Pinto, *"Implicações da contaminação por metais pesados no meio ambiente da baía de Sepetiba e entorno: o caso da Cia Mercantil Ingá"*, Dissertação (Mestrado) – Universidade Federal Fluminense, Niterói – RJ, 2005.
17. J. A. Medeiros and M. L. C.Pinto, "Projeto Ingá rejeito zero, reciclagem de efluentes e rejeitos industriais com zinco, cádmio, chumbo e arsênio: uma solução de tecnologia química para o problema ambiental na baía de Sepetiba", *In: Encontro Nacional Sobre Contaminantes Inorgânicos,* Belo Horizonte, 25-27 de outubro, 10,pp. 25-26 (2006).