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Determination of heavy metals and other elements in bottom sediments from Sepetiba bay, Rio de Janeiro, by Instrumental Neutron Activation Analysis

Fábio Pellegatti¹, Ana M. G. Figueiredo¹ and Julio C. Wasserman²

 ¹Instituto de Pesquisas Energéticas e Nucleares - IPEN-CNEN/SP Caixa Postal 11049, CEP 05422-970, São Paulo, Brasil
² Depto. de Geoquímica – UFF, Outeiro de São João Batista s/ nº CEP 24020-150, Niterói, Rio de Janeiro, Brasil

INTRODUCTION

The Sepetiba bay, located about 60 km from the city of Rio de Janeiro, is a semienclosed salt-water body with 519 km² in area. In Sepetiba bay, industry, tourism and urban expansion have been considerable for the last three decades, leading to a series of impacts on the environment. The construction of a large port in the early 70's made the area particularly attractive for industrial development. \tilde{A} industrial park composed by about 400 plants, basically metallurgical, is responsible for the input of large amounts of metals in the environment, releasing their effluents either directly into the bay or through the local rivers. Many authors have studied the distribution and behavior of heavy metals in the bay (Lacerda *et al.*, 1987; Barcellos *et al.*, 1998), but only a few elements have been focused (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn). This is probably due to the fact that the analytical technique usually employed is Atomic Absorption Spectrometry, which is not a multielemental technique.

In the present work, Instrumental Neutron Activation Analysis (INAA) was applied to the determination of the elements As, Ba, Co, Cr, Cs, Fe, Hf, Rb, Sc, Ta, Zn, rare earth elements (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu), U and Th in bottom sediment samples from Sepetiba bay.

MATERIAL AND METHODS

Sampling and Sample Preparation: Samples were collected in 28 stations distributed throughout Sepetiba bay (Fig. 1). The sediment samples were collected by using a Van Veen like bottom sampler. After the collection, the sample was

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immediately transferred to a polyethylene recipient (parts in contact with metal were discarded) and separated in two parts, one for INAA and the other for granulometric analysis (fraction < 63 μ m). The samples were frozen and stored at – 20°C. They were then dried in a oven at 40°C for three days, grind in agata mortars and stored in polyethylene bags for INAA.

INAA: The sediment samples were irradiated at the IEA-R1m nuclear reactor at the Instituto de Pesquisas Energéticas e Nucleares (IPEN) for 8 hours at a neutron flux of 10¹³ n cm⁻² s⁻¹. The measurements of the induced gamma-ray activity were carried out in a GMX20190 hyperpure Ge detector (CANBERRA). The multichannel analyser was a 8192 channel CANBERRA S-100 plug-in-card in a PC computer. The gamma-ray spectra were processed by using the program SAMPO90. The accuracy and precision of the method were verified by the analysis of the reference materials Buffalo River Sediment (NIST 2704) and Estuarine Sediment (NIST 1646a), showing analytical precision and relative errors better than 10%

RESULTS

Mean values and ranges of metal concentrations are presented in Table 1.

The elements Zn, Cr, Co, Fe, Ta, Sc, and Cs presented similar behavior, showing higher concentration along the northern coast of the bay, where the fluvial water inputs to the bay are concentrated. The distribution of these metals follows the pattern of sediment deposition from rivers and surface currents (Lacerda, 1987), indicating that their main source is the industrial park. For Zn, the concentration is considerably higher near the entrance of the rivers into the bay (2900 μ g g⁻¹), decreasing to about 200 ppm along the south coast of the bay. Zn is a well known contaminant of the bay, but concentration levels have been reported to reach not more than 1000 μ g g⁻¹ (Dornelles, 1997, Barcellos et al., 1998). Nonetheless, the values reported in this work can be attributed to an accidental release of Zn by a melting industry adjacent to the bay, in February 1996 (ALERJ, 1996).

Arsenic presented higher concentrations along the northeast coast with a tendency of increasing the concentration levels to the center of the bay. This behavior may

indicate that its origin is the industrial park, but transport of this element to the center of the bay may have occurred.

Rare earth elements did not show any general behavior and the distribution throughout the bay varied from element to element. U and Th exhibited higher levels along all the north coast, and did not present any special area of concentration. These results suggest that rare earth elements, U and Th, derive from the neighboring lithology and have a natural dispersion in the bay, presenting a geochemical behavior related to the associated environment.

Ba and Hf reached their highest concentrations along the northwest coast of the bay, a marine sediment depositional area, indicating that it is originated from natural sources.

The results presented in this work confirmed previous studies about the anthropogenic origin of elements such as Zn and Cr in the bay. For the other analysed elements, this work is a contribution to the knowledge of their concentration and distribution in Sepetiba bay.

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FIGURE 1 – Study area and location of sampling points

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TABLE 1 – Mean values and ranges of heavy metal and other element concentrations in Sepetiba bay bottom sediments (n=28) in $\mu g g^{-1}$

Element	Mean	Range	Element	Mean	Range
As	6,7	0,8 - 320	Nd	42,8	3 - 99
Ва	324,3	182 - 680	Rb	81,5	12,28 - 136
Се	88,8	7 - 135,5	Sc	10,9	0,61 - 8,87
Со	8,6	0,7 - 65	Sm	7,3	0,6 - 12,3
Cr	59,1	3,57 - 141	Та	1,2	0,12 - 2,16
Cs	4,5	0,33 - 8,5	ТЬ	0,7	0,08 - 3
Eu	1,4	0,19 - 4,06	Th	3,2	0,9 - 15,3
Fe(%)	3,6	0,18 - 7	U	14,0	1,13 - 20,6
Hf	6,1	1,89 - 53,4	Yb	1,6	0,26 - 542
La	54,7	0,34 - 115,3	Zn	964,6	37 - 2894
Lu	0,3	0,05 - 41	· · · · · · · · · · · · · · · · · · ·		



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