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Neutron Activation Analysis Applied to the Determination of Heavy Metals and Other Trace Elements in Sediments from Sepetiba Bay (RJ), Brazil

Fábio **Pellegatti** (1), Ana M.G. **Figueiredo** (1)* and Julio C. **Wasserman** (2)

(1) IPEN-CNEN/SP, Caixa Postal 11049, CEP 05422-970, São Paulo, SP, Brasil
(2) Programa de Pós-Graduação em Ciência Ambiental/Departamento de Geoquímica -UFF Outeiro de São João Batista s/no., Niterói, Rio de Janeiro, 24020-150, Brasil
* Corresponding author. e-mail: grafigue@curiango.ipen.br

In this work, instrumental neutron activation analysis (INAA) was applied to the determination of the elements As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Nd, Rb, Sc, Sm, Ta, Tb, Th, U, Yb, Zn in twenty eight bottom sediment samples from Sepetiba Bay, Rio de Janeiro, Brazil. With the concentration data obtained, contour maps were prepared, by using Kriging method, to show the spatial distribution of the studied elements in the Bay. The elements Co, Cr, Cs, Fe, Sc, Ta and Zn showed similar behaviour in the sediments, with higher concentrations along the northern coast of the bay, where the fluvial water inputs are concentrated. The distribution of U, rare earth elements and Ba in the Bay indicates that these elements are not deposited as contaminants.

Keywords: neutron activation analysis, heavy metals, trace elements, marine sediments.

Dans ce travail, les éléments suivants, As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, La Lu, Nd, Rb, Sc, Sm, Ta, Tb, Th, U, Yb et Zn ont été analysés par activation neutronique instrumentale dans vingt huit sédiments de fond de la baie de Sepetiba, Rio de Janeiro, Brésil. Par krigeage et à partir des concentrations obtenues, nous avons établi des cartes de la répartition spatiale des éléments étudiés dans la baie. Co, Cr, Cs, Fe, Sc, Ta et Zn ont des comportements similaires dans les sédiments, avec des concentrations plus importantes le long de la côte nord de la baie, où les apports en eau fluviale sont concentrés. La distribution en U, Terres Rares et Ba indique que ces éléments ne sont pas déposés comme polluants dans la baie.

Mots-clés : analyse par activation neutronique, métaux lourds, éléments en traces, sédiments marins.

Nowadays, the pollution of aquatic systems by heavy metals and other toxic elements from industrial waste and other activities have caused a modification in the natural cycle of these elements, increasing their dispersion in the environment. The study of the distribution of metals in sediments is very important from the point of view of environmental pollution because sediment concentrates metals from aquatic systems, and represents an appropriate medium to monitor contamination (Moore and Ramamoorthy 1993, Foster and Charlesworth 1996). One of the objectives of the study of metal pollution in estuarine sediments is to elucidate the origin of the pollution.

The determination of heavy metals and other trace elements in sediments, usually at $\mu g\ g^{-1}$ or $ng\ g^{-1}$ levels, is a very difficult task that requires sensitive and accurate analytical methods. Neutron activation analysis (NAA) is well recognised as an accurate analytical technique, and has been used in the certification of different reference materials (Al-Jundi *et al.* 1993). Instrumental neutron activation analysis (INAA) has been widely applied to the analysis of sediments, allowing the determination of elements such as As, Ba, Co, Cr, Cs, Fe, Hf, Hg, Mn, Rb, Sb, Sc, Se, Ta, Th, U, Zn and rare earth elements (REE): La, Ce, Nd, Sm, Eu, Tb, Yb and Lu (Fong and Chatt 1987, Golchert *et al.* 1991).

Sepetiba Bay, located about 60 km south of the city of Rio de Janeiro, Brazil, is one of the most important fishery areas in the State of Rio de Janeiro. A large harbour has encouraged considerable industrial

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investment in this region which, since the 1970's, has undergone a rapid industrial expansion, leading to high levels of pollution by metals. For the last two decades, an industrial park composed of about 400 industrial plants, mainly involved in metallurgical activities, has been established in the Sepetiba Bay basin, releasing its industrial waste either directly into the Bay or indirectly through local rivers. Contamination in the Bay for some metals, such as zinc, has been already reported (Barcellos *et al.* 1998, Dornelles 1997). Some authors have studied the distribution and behaviour of other heavy metals, but only few elements have been targeted (Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn; Lacerda *et al.* 1987, Wasserman *et al.* 1991, Quevauviller *et al.* 1992). This is due mainly to the fact that the analytical technique most employed has been atomic absorption spectrometry, which does not have simultaneous multi-elemental capabilities.

In this work, instrumental neutron activation analysis (INAA) is applied to the determination of the elements As, Ba, Co, Cr, Cs, Fe, Hf, Rb, Sc, Th, U, Zn and REE in twenty eight sediment samples from Sepetiba Bay. The objective of this work is to test the potential of INAA to determine more than twenty elements (metals, semi-metals, non-metals, actinides and lanthanides) in bottom sediments of aquatic systems, and thus provide new information about the distribution and behaviour of these elements in Sepetiba Bay.

Sampling procedure

Samples were collected at twenty eight stations distributed throughout Sepetiba Bay (Figure 1). The stations had been chosen previously in order to obtain information about regions of interest within the Bay. The exact position of each station was determined by use of a geographical positioning system, with an accuracy of 50 m. The sediment samples were collected by using a stainless steel Van Veen-like bottom grab (Rubio and Ure 1993). After collection, the samples were immediately put into polyethylene trays, discarding parts that had been in contact with metal, to avoid contamination. Samples were transferred to polyethylene bags, stored at 4 °C, and transported to the laboratory and frozen at -20 °C.

Analytical procedure

Each sample was split in two parts. One part was used for granulometric analysis (fraction ‹ 63 μm). The other part was dried at 40 °C in a ventilated oven for three days, and the samples were carefully ground in agate mortars and stored in polyethylene bags until analysis. For granulometric analysis, the samples were wet sieved through a 63 μm nylon sieve, both the passed and retained fractions were dried, weighed and the fraction ‹ 63 μm was calculated.

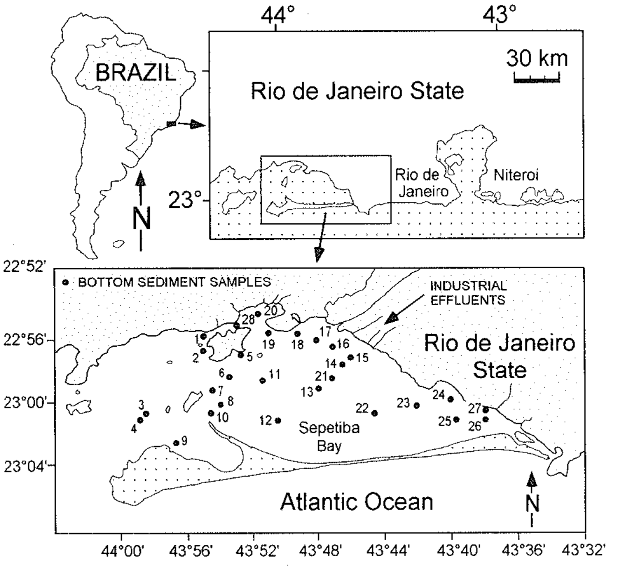

Figure 1. Study area and location of sampling points.

INAA

One hundred mg of the sample were accurately weighed in polyethylene bags. Elemental synthetic calibration samples of the analysed elements were prepared by pipetting convenient aliquots of standard solutions (SPEX) onto 1 cm^2 pieces of Whatman No. 40 filter paper. These calibration samples were then sealed in polyethylene bags. Unknown and calibration samples were irradiated for 8 hours at a thermal neutron flux of 10^{13} n cm^{-2} s^{-1} at the IEA-R1m nuclear reactor of IPEN. The measurements of the induced gamma-ray activity were carried out using a GMX20190 hyperpure Ge detector (Canberra). The multi-channel analyser was a 8192 channel Canberra S-100 plug-in-card in a personal computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma-ray of ^{60}Co. Two series of counts were performed: the first one five days after irradiation and the second one 15 days after irradiation. The counting times varied from 1 to 2.5 hours. The gamma-ray spectra were processed by using the SAMPO 90 gamma-ray software (Aarnio *et al.* 1992), which locates peak positions and calculates the energies and net areas. The radioisotopes used to determine the

Table 1.
Radioisotopes used, their main nuclear characteristics and time of decay before counting

Element	Radioisotope	Half-life	Energy (keV)	Decay after irradiation before counting (d)
As	^{76}As	26.3 hr	559.2	5
Ba	^{131}Ba	11.5 d	496.3	15-20
Ce	^{141}Ce	32.5 d	145.4	15-20
Co	^{60}Co	5.24 yr	1332.2	15-20
Cr	^{51}Cr	27.8 d	320.0	15-20
Cs	^{134}Cs	2.7 yr	795.8	15-20
Eu	^{152}Eu	12.2 yr	1407.5	15-20
Fe	^{59}Fe	45.1 d	1098.6	15-20
Hf	^{181}Hf	44.6 d	482.2	15-20
La	^{140}La	47.27 hr	328.6	5
			1595.4	
Lu	^{177}Lu	6.75 d	208.4	5
Nd	^{147}Nd	11.1 d	91.4	5
			531.0	15-20
Rb	^{86}Rb	18.66 d	1076.6	15-20
Sb	^{122}Sb	2.70 d	564.2	5
	^{124}Sb	60.2 d	1691.0	15-20
Sc	^{46}Sc	83.9 d	889.4	15-20
Sm	^{153}Sm	47.1 hr	103.2	5
Ta	^{182}Ta	115.1 d	1188.8	15-20
			1221.6	
Tb	^{160}Tb	73 d	879.4	15-20
Th	^{233}Pa	27 d	311.8	15-20
U	^{239}Np	2.35 d	277.5	5
Yb	^{175}Yb	101 hr	396.1	5
	^{169}Yb	30.6 d	197.8	15-20
Zn	^{65}Zn	245 d	1115.4	15-20

Table 2.
Results obtained for the certified reference materials Buffalo River Sediment (NIST 2704) and Estuarine Sediment (NIST 1646a) (μg g^{-1})

Element	Buffalo River Sediment SRM 2704	Certified values[a]	Estuarine Sediment SRM 1646a	Certified values[b]	Detection limit (Currie 1968) (μg g^{-1})
As	23.2 ± 0.8	23.4 ± 0.8	6.7 ± 0.1	6.23 ± 0.21	1.4
Ba	408 ± 14	414 ± 12	209 ± 6	(210)	23
Co	12.5 ± 0.1	14.0 ± 0.6	4.6 ± 0.1	(5)	0.02
Cr	135 ± 1	135 ± 5	40.8 ± 0.7	40.9 ± 1.9	1.9
Cs	5.8 ± 0.1	(6)	1.27 ± 0.03	-	0.2
Fe	37600 ± 700	41100 ± 1000	20500 ± 500	20080 ± 390	7
Hf	8.06 ± 0.08	(8)	11.86 ± 0.09	-	0.069
Rb	91 ± 4	(100)	34.3 ± 0.8	(38)	5.9
Sb	3.77 ± 0.06	3.79 ± 0.15	-	(0.3)	0.082
Sc	11.4 ± 0.2	(12)	4.8 ± 0.1	(5)	0.012
U	3.0 ± 0.2	3.13 ± 0.13	2.0 ± 0.1	(2)	0.15
Zn	476 ± 5	438 ± 12	50.1 ± 1.6	48.9 ± 1.6	0.3
La	30 ± 1	(29)	18.5 ±0.1	(17)	0.06
Ce	66 ± 1	(72)	38.6 ± 0.2	(34)	0.3
Nd	20.0 ± 0.9	-	18 ± 2	(15)	6
Sm	6.5 ± 0.1	(6.7)	3.30 ± 0.04	-	0.014
Eu	1.25 ± 0.01	(1.3)	0.63 ± 0.01	-	0.097
Tb	0.90 ± 0.02	-	0.44 ± 0.03	-	0.23
Yb	2.91 ± 0.03	(2.8)	1.4 ± 0.1	-	0.15
Lu	0.58 ± 0.01	(0.6)	0.26 ± 0.01	-	0.015

[a] National Institute of Standards and Technology (NIST), Certificate of Analysis Standard Reference Material – Buffalo River Sediment 2704, NIST, Gaithersburg, 1990. [b] National Institute of Standards and Technology (NIST), Certificate of Analysis Standard Reference Material – Estuarine Sediment 1646a, NIST, Gaithersburg, 1995. Figures in parentheses are information values. Reference materials uncertainties are 95% confidence limits and data uncertainties are one standard deviation of six replicate analyses.

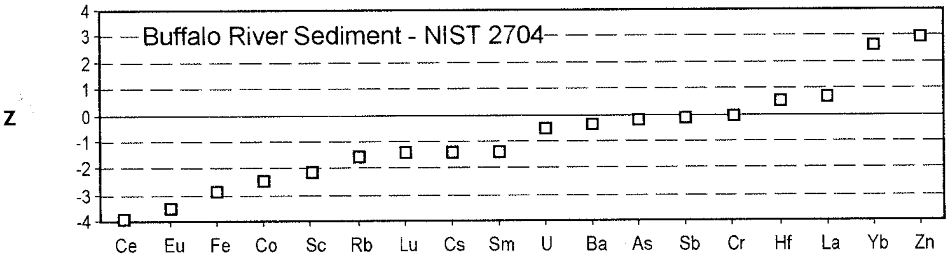

Figure 2. Control chart (z-values) for the analysed elements in the Buffalo River Sediment (NIST SRM 2704) reference material.

analysed elements and their main decay characteristics are presented in Table 1.

Precision and accuracy of the method

The precision and accuracy of the results were verified by the analysis of the certified reference materials Buffalo River Sediment (NIST SRM 2704) and Estuarine Sediment (NIST SRM 1646a). The results obtained (mean of six replicate analyses), as well as certified and proposed values and detection limits, calculated by using Currie's criterion (Currie 1968), are shown in Table 2. The errors associated with the data represent one standard deviation. It can be seen that the data obtained agreed with certified values. For the Buffalo River Sediment, the relative errors were less than 5% for most elements, excepting Ce, Co, Fe, Rb and Zn (relative errors from 8 to 10%). Figure 2 shows the standardized difference or z-value for the Buffalo River Sediment reference material, calculated as reported by Bode (1996). The z-value of a result is given by:

$$z_i = (C_i - C_{ref,i}) / (\sigma^2_i + (\sigma^2_{ref,i}))^{1/2} \qquad (1)$$

where:

C_i = analysed concentration of the element i in the reference material.

$C_{ref,i}$ = concentration of the certified or consensus value for the element i.

σ_i = uncertainty of the analysed concentration of element i in the reference material.

$\sigma_{ref,i}$ = uncertainty of the certified consensus value for the element i.

If $|z| < 3$, the analysed can be considered to agree with the certified/consensus value at the 99% confidence level. It can be observed that only the results obtained for Eu and Ce presented $|z| > 3$. It should be noticed that the reference material values for these elements are information values.

In the case of the Estuarine Sediment, relative errors were below 10% for all the analysed elements, excepting Ce and Nd, which presented relative errors of 13.5 and 20%, respectively. However, for this reference material, only information values are available for the REE: La, Ce and Nd, and there are no data for the concentration levels of the REE: Sm, Eu, Tb, Yb and Lu. Results presented in Table 2, therefore make a contribution to concentration values of REE in this reference material.

The reproducibility of the analysis was good, considering the concentration level of the majority of the analysed elements ($\mu g\ g^{-1}$), showing relative standard deviations ranging from 0.5 to 7%. The detection limits are adequate for the determination of trace elements in this kind of matrix.

Results

The results obtained are presented in Tables 3 to 5. The results correspond to one determination, and the uncertainties (1*s*) were calculated considering the statistical errors in counting spectra from unknown and calibration samples. In Table 6 a comparison is made between average (and standard deviation) values from this study and the mean shale of Wedepohl (1995). Among the elements presented, only U and, to a greater extent, Zn values exceed the mean shale (Wedepohl 1995) and only Zn can be considered enriched in the whole Sepetiba Bay. Francisco and Cunha (1977) observed the presence of U- and Th-bearing rocks that may also contain rare earth elements. Monazite sands have also been observed in a number of sites in Sepetiba Bay, containing concentrations of up to 6% m/m Th and 0.32% m/m U (Leonardos and Santos 1972). Although some determinations of the

Table 3.
Results (μg g^{-1}) obtained for bottom sediments from Sepetiba Bay (Stations 1-10)

Element	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
As	7.0 ± 0.3	9.3 ± 0.4	1.5 ± 0.1	0.8 ± 0.1	1.6 ± 0.1	4.1 ± 0.2	2.4 ± 0.1	5.2 ± 0.2	7.0 ± 0.4	5.0 ± 0.2
Ba	680 ± 11	378 ± 9	315 ± 6	300 ± 5	376 ± 7	182 ± 7	393 ± 15	337 ± 6	283 ± 9	357 ± 18
Ce	111.6 ± 0.7	7 ± 1	24.8 ± 0.1	7.52 ± 0.07	82.4 ± 0.3	56.1 ± 0.3	63.3 ± 0.5	28.0 ± 0.2	89.3 ± 0.6	63.8 ± 0.3
Co	11.7 ± 0.1	11.4 ± 0.1	1.57 ± 0.02	0.70 ± 0.01	2.27 ± 0.03	3.87 ± 0.04	3.8 ± 0.1	2.82 ± 0.03	10.9 ± 0.1	6.2 ± 0.1
Cr	57 ± 2	70 ± 1	17.6 ± 0.4	3.57 ± 0.07	14.7 ± 0.3	25.3 ± 0.5	22 ± 1	18.4 ± 0.6	72 ± 2	43 ± 2
Cs	5.04 ± 0.09	5.90 ± 0.09	0.81 ± 0.03	0.33 ± 0.02	0.64 ± 0.03	1.84 ± 0.05	1.42 ± 0.08	1.06 ± 0.04	5.6 ± 0.1	2.6 ± 0.1
Eu	1.93 ± 0.04	1.61 ± 0.03	0.39 ± 0.01	0.19 ± 0.01	0.67 ± 0.02	0.79 ± 0.02	0.65 ± 0.04	0.41 ± 0.01	1.36 ± 0.03	0.85 ± 0.04
Fe (% m/m)	4.11 ± 0.06	4.38 ± 0.08	0.62 ± 0.01	0.18 ± 0.01	0.87 ± 0.02	1.56 ± 0.03	1.35 ± 0.01	2.58 ± 0.04	3.92 ± 0.06	2.16 ± 0.01
Hf	11.8 ± 0.1	5.53 ± 0.05	6.77 ± 0.05	1.89 ± 0.02	8.9 ± 0.1	3.17 ± 0.03	6.52 ± 0.08	3.91 ± 0.03	4.11 ± 0.04	9.9 ± 0.1
La	64.1 ± 0.2	60.0 ± 0.2	11.9 ± 0.1	3.94 ± 0.05	46.2 ± 0.2	28.4 ± 0.2	77.5 ± 0.4	12.2 ± 0.1	46.2 ± 0.2	77.7 ± 0.5
Lu	0.42 ± 0.01	0.35 ± 0.01	0.18 ± 0.01	0.05 ± 0.01	0.14 ± 0.01	0.15 ± 0.01	0.14 ± 0.01	0.09 ± 0.01	0.30 ± 0.01	0.30 ± 0.01
Nd	52 ± 10	51 ± 9	13 ± 2	3.0 ± 0.6	32 ± 6	27 ± 5	35 ± 9	10 ± 2	38 ± 7	42 ± 9
Rb	112 ± 2	103 ± 1	32.5 ± 0.7	29.4 ± 0.6	35.9 ± 0.8	34 ± 1	49 ± 2	47 ± 1	83 ± 2	61 ± 2
Sc	14.10 ± 0.04	13.99 ± 0.09	1.86 ± 0.01	0.61 ± 0.01	2.63 ± 0.01	4.92 ± 0.05	3.94 ± 0.03	2.61 ± 0.01	13.05 ± 0.04	6.72 ± 0.04
Sm	8.6 ± 0.1	8.5 ± 0.1	2.50 ± 0.03	0.60 ± 0.01	4.96 ± 0.06	4.21 ± 0.01	10.2 ± 0.1	1.93 ± 0.03	6.3 ± 0.1	10.2 ± 0.1
Ta	1.51 ± 0.04	1.32 ± 0.04	0.39 ± 0.02	0.12 ± 0.00	0.30 ± 0.02	0.60 ± 0.03	0.58 ± 0.05	0.36 ± 0.02	1.14 ± 0.04	0.92 ± 0.06
Tb	0.89 ± 0.05	0.87 ± 0.05	0.24 ± 0.02	0.08 ± 0.01	0.37 ± 0.02	0.34 ± 0.03	0.41 ± 0.05	0.17 ± 0.02	0.64 ± 0.04	0.51 ± 0.06
Th	3.9 ± 0.1	3.9 ± 0.2	1.3 ± 0.1	*	2.1 ± 0.1	2.1 ± 0.1	3.2 ± 0.2	0.9 ± 0.1	2.8 ± 0.2	3.1 ± 0.2
U	15.5 ± 0.1	16.4 ± 0.1	3.28 ± 0.03	1.13 ± 0.01	16.5 ± 0.1	5.49 ± 0.03	9.7 ± 0.1	3.36 ± 0.02	12.85 ± 0.08	9.8 ± 0.1
Yb	2.32 ± 0.07	2.00 ± 0.05	0.94 ± 0.03	0.26 ± 0.01	0.74 ± 0.02	0.84 ± 0.03	0.93 ± 0.07	0.51 ± 0.02	1.72 ± 0.05	1.9 ± 0.1
Zn	637 ± 30	810 ± 18	78 ± 2	37.0 ± 0.8	58 ± 1	241 ± 5	174 ± 22	97 ± 3	986 ± 25	500 ± 64

Uncertainties are 1s and were calculated considering the errors in the counting rates of unknown and calibration samples. * not determined.

Table 4.
Results (μg g^{-1}) obtained for bottom sediments from Sepetiba Bay (Stations 11-20)

Element	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20
As	3.7 ± 0.1	6.3 ± 0.6	8.1 ± 0.5	11 ± 1	9.1 ± 0.9	7.9 ± 0.3	9.7 ± 0.6	6.8 ± 0.2	7.1 ± 0.4	10.6 ± 0.4
Ba	413 ± 14	314 ± 9	280 ± 10	249 ± 13	195 ± 11	270 ± 10	209 ± 10	285 ± 17	335 ± 17	396 ± 17
Ce	93.5 ± 0.5	89.8 ± 0.4	87.4 ± 0.4	116.5 ± 0.6	108.3 ± 0.5	124.9 ± 0.6	120.2 ± 0.8	111.9 ± 0.6	129.0 ± 0.6	135.5 ± 0.7
Co	2.9 ± 0.1	9.7 ± 0.1	7.8 ± 0.1	9.7 ± 0.1	10.8 ± 0.1	15.9 ± 0.1	12.5 ± 0.1	11.1 ± 0.1	11.7 ± 0.1	11.5 ± 0.1
Cr	18 ± 1	68.2 ± 0.5	58.2 ± 0.5	76.4 ± 0.8	87.7 ± 0.7	91.4 ± 0.6	141 ± 4	86 ± 2	79 ± 2	66 ± 2
Cs	1.2 ± 0.1	5.5 ± 0.1	4.5 ± 0.1	5.8 ± 0.1	6.5 ± 0.1	8.5 ± 0.1	7.1 ± 0.3	6.7 ± 0.2	7.0 ± 0.2	5.8 ± 0.2
Eu	0.74 ± 0.03	1.47 ± 0.03	1.26 ± 0.03	1.65 ± 0.04	1.68 ± 0.03	2.16 ± 0.04	1.80 ± 0.04	1.74 ± 0.05	2.05 ± 0.05	1.86 ± 0.05
Fe (% m/m)	1.54 ± 0.01	4.7 ± 1.3	4.5 ± 1.2	5.3 ± 1.5	5.7 ± 1.6	7 ± 2	5.16 ± 0.07	4.42 ± 0.05	4.41 ± 0.05	4.48 ± 0.05
Hf	11.2 ± 0.1	5.84 ± 0.05	6.37 ± 0.05	5.52 ± 0.05	2.50 ± 0.03	3.28 ± 0.03	2.25 ± 0.03	3.93 ± 0.06	4.62 ± 0.06	6.05 ± 0.07
La	115.3 ± 0.7	48.0 ± 0.2	43.6 ± 0.2	62.4 ± 0.3	60.1 ± 0.2	73.7 ± 0.3	73.9 ± 0.3	52.2 ± 0.1	68.1 ± 0.3	69.1 ± 0.1
Lu	0.15 ± 0.09	0.32 ± 0.01	0.26 ± 0.01	0.33 ± 0.01	0.31 ± 0.01	0.44 ± 0.01	0.37 ± 0.01	0.31 ± 0.01	0.33 ± 0.01	0.32 ± 0.01
Nd	49 ± 10	54 ± 14	62 ± 14	64 ± 16	59 ± 14	56 ± 13	51 ± 10	41 ± 7	55 ± 9	55 ± 9
Rb	51 ± 2	88 ± 1	75 ± 1	86 ± 2	96 ± 2	136 ± 2	102 ± 2	97 ± 3	107 ± 3	113 ± 3
Sc	3.16 ± 0.02	12.88 ± 0.04	10.48 ± 0.03	13.61 ± 0.04	14.86 ± 0.04	18.87 ± 0.04	16.18 ± 0.05	15.2 ± 0.1	16.9 ± 0.1	14.88 ± 0.05
Sm	12.3 ± 0.1	6.8 ± 0.1	6.4 ± 0.1	8.2 ± 0.2	7.7 ± 0.1	10.7 ± 0.2	8.2 ± 0.1	7.2 ± 0.1	9.4 ± 0.1	9.4 ± 0.1
Ta	0.66 ± 0.05	1.22 ± 0.03	1.03 ± 0.03	1.52 ± 0.05	1.68 ± 0.04	2.16 ± 0.04	1.78 ± 0.05	1.45 ± 0.06	1.61 ± 0.06	1.36 ± 0.06
Tb	0.54 ± 0.05	0.74 ± 0.04	0.65 ± 0.04	0.78 ± 0.04	0.84 ± 0.05	1.06 ± 0.05	0.80 ± 0.05	0.84 ± 0.09	1.01 ± 0.09	0.96 ± 0.09
Th	3.8 ± 0.3	2.9 ± 0.1	2.8 ± 0.1	3.7 ± 0.2	2.7 ± 0.1	4.1 ± 0.1	3.4 ± 0.1	3.7 ± 0.1	4.9 ± 0.2	3.5 ± 0.2
U	14.2 ± 0.1	13.4 ± 0.1	12.1 ± 0.1	19.6 ± 0.1	16.3 ± 0.1	17.5 ± 0.1	17.3 ± 0.2	18.2 ± 0.1	20.2 ± 0.1	20.6 ± 0.1
Yb	0.97 ± 0.07	1.6 ± 0.1	1.55 ± 0.04	1.87 ± 0.05	1.79 ± 0.05	2.57 ± 0.06	2.20 ± 0.07	1.86 ± 0.09	2.10 ± 0.09	1.99 ± 0.09
Zn	151 ± 20	881 ± 275	1272 ± 398	2400 ± 751	2644 ± 827	2070 ± 648	2894 ± 75	1677 ± 27	633 ± 10	1343 ± 22

Uncertainties are 1s and were calculated considering the errors in the counting rates of unknown and calibration samples.

Table 5.
Results (μg g⁻¹) obtained for bottom sediments from Sepetiba Bay (Stations 21-28)

Element	S21	S22	S23	S24	S25	S26	S27	S28
As	12.1 ± 0.4	7.8 ± 0.4	6.6 ± 0.6	8.0 ± 0.5	6.5 ± 0.5	6.3 ± 0.4	8.0 ± 0.3	8.1 ± 0.5
Ba	246 ± 15	273 ± 13	223 ± 8	265 ± 8	230 ± 9	320 ± 8	328 ± 9	649 ± 11
Ce	110.2 ± 0.6	88.9 ± 0.4	84.3 ± 0.5	104.0 ± 0.7	91.1 ± 0.6	100.7 ± 0.6	127.2 ± 0.7	128.3 ± 0.8
Co	9.7 ± 0.1	8.4 ± 0.1	9.5 ± 0.1	10.3 ± 0.1	10.2 ± 0.1	10.4 ± 0.1	11.3 ± 0.1	11.1 ± 0.1
Cr	76 ± 2	63 ± 2	67 ± 3	70 ± 3	71 ± 3	65 ± 3	73 ± 3	54 ± 2
Cs	5.9 ± 0.1	4.9 ± 0.1	5.5 ± 0.1	5.7 ± 0.1	5.6 ± 0.1	5.1 ± 0.2	7.4 ± 0.1	2.1 ± 0.1
Eu	1.51 ± 0.04	1.29 ± 0.04	1.45 ± 0.04	1.57 ± 0.04	1.45 ± 0.04	1.57 ± 0.04	1.77 ± 0.04	2.13 ± 0.04
Fe (% m/m)	4.34 ± 0.05	3.51 ± 0.04	3.97 ± 0.04	4.37 ± 0.04	4.02 ± 0.04	4.06 ± 0.04	4.58 ± 0.04	4.10 ± 0.06
Hf	4.95 ± 0.05	5.08 ± 0.06	3.63 ± 0.04	8.22 ± 0.07	3.42 ± 0.04	6.94 ± 0.06	7.45 ± 0.06	17.5 ± 0.1
La	58.3 ± 0.3	45.7 ± 0.2	43.1 ± 0.2	53.6 ± 0.2	47.7 ± 0.2	53.4 ± 0.2	68.3 ± 0.2	65.9 ± 0.2
Lu	0.39 ± 0.01	0.24 ± 0.01	0.28 ± 0.01	0.35 ± 0.01	0.28 ± 0.01	0.34 ± 0.01	0.37 ± 0.01	0.40 ± 0.01
Nd	45 ± 7	37 ± 6	41 ± 9	42 ± 10	38 ± 9	41 ± 9	52 ± 11	54 ± 10
Rb	89 ± 2	77 ± 2	82 ± 2	93 ± 2	89 ± 2	99 ± 2	105 ± 2	111 ± 2
Sc	13.35 ± 0.05	10.81 ± 0.04	12.58 ± 0.04	13.00 ± 0.04	12.76 ± 0.04	12.28 ± 0.03	13.56 ± 0.04	14.38 ± 0.04
Sm	8.1 ± 0.1	6.5 ± 0.1	5.9 ± 0.1	7.4 ± 0.1	6.3 ± 0.1	7.0 ± 0.1	8.8 ± 0.1	8.7 ± 0.1
Ta	1.35 ± 0.05	1.03 ± 0.05	1.20 ± 0.04	1.41 ± 0.04	1.26 ± 0.04	1.42 ± 0.04	1.57 ± 0.05	1.49 ± 0.04
Tb	0.89 ± 0.08	0.66 ± 0.07	0.68 ± 0.04	0.75 ± 0.05	0.67 ± 0.04	0.79 ± 0.05	0.90 ± 0.05	0.86 ± 0.05
Th	4.3 ± 0.2	3.2 ± 0.2	2.9 ± 0.1	3.3 ± 0.1	3.0 ± 0.1	3.0 ± 0.1	3.0 ± 0.1	5.3 ± 0.5
U	17.1 ± 0.1	12.9 ± 0.1	12.7 ± 0.1	16.7 ± 0.1	13.6 ± 0.1	15.3 ± 0.1	20.5 ± 0.1	18.9 ± 0.1
Yb	2.29 ± 0.09	1.53 ± 0.07	1.61 ± 0.06	2.01 ± 0.01	1.72 ± 0.06	1.89 ± 0.06	2.13 ± 0.07	2.17 ± 0.06
Zn	1404 ± 23	1001 ± 16	1164 ± 66	873 ± 49	687 ± 39	542 ± 31	743 ± 42	1011 ± 26

Uncertainties are 1s and were calculated considering the errors in the counting rates of unknown and calibration samples.

Table 6.
Comparison between average values and reference values from the literature

Element	Average values ± 1 SD (n=28) (μg g⁻¹)	Shale (a) (μg g⁻¹)
As	6.7 ± 2.9	13
Ba	324 ± 114	550
Ce	89 ± 36	80
Co	8.6 ± 3.9	19
Cr	59 ± 30	90
Cs	4.5 ± 2.4	5
Eu	1.36 ± 0.56	0.95*
Fe (% m/m)	3.64 ± 1.65	5.5
Hf	6.1 ± 3.4	4
La	55 ± 23	40
Lu	0.28 ± 0.10	0.6
Nd	43 ± 15	26*
Rb	82 ± 29	140
Sc	11 ± 5	15
Sm	7.3 ± 2.7	7.2
Ta	1.16 ± 0.50	1.7
Tb	0.68 ± 0.26	0.64*
Th	3.2 ± 0.9	12
U	14 ± 5	3.2
Yb	1.64 ± 0.59	3.2
Zn	965 ± 785	100

* Upper continental crust.

(a) Reimann and de Caritat (1998); Wedepohl (1995).

elements Eu, Nd and Tb are higher than the reference values, it must be emphasised that because mean shale values for these elements are not available, mean upper continental crust values were used instead. These reference values are usually lower than the values found in the sediments.

Comparison with mean shale values in Table 6 permits a rough evaluation of the state of contamination to be made. Unfortunately, no detailed description of the geology of the region has yet been made that would permit establishing good background levels. It can be seen in Tables 3-5 that the majority of the elements presented higher concentrations at the northern coast of the bay (Stations 14, 15, 16 and 17). This behaviour was expected since, according to Lacerda *et al.* (1987), the clockwise circulation pattern of the water within the bay (Signorini 1980) produces a preferential depositional area along the northern coast. The input of the riverine water into the bay is concentrated along the northern coast, where five rivers are responsible for 95% of the input of fluvial water in the bay. These rivers receive industrial wastes from the industrial park, some 3 km from the coast (Lacerda *et al.* 1987).

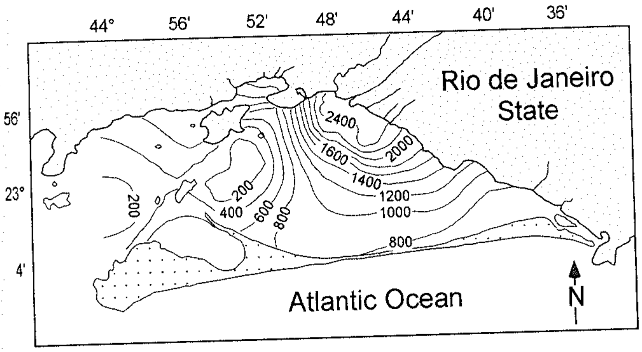

Figure 3. Contour map for Zn (contours in µg g^{-1}).

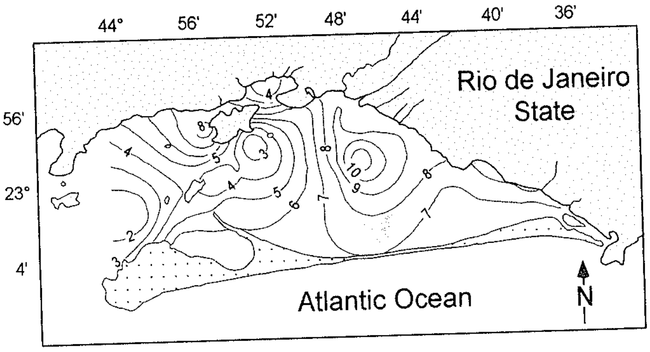

Figure 4. Contour map for As (contours in µg g^{-1}).

Particle size distribution has been shown to be a major factor controlling metal concentrations (Forstner 1989), the accumulation of metals occurring mainly in the fine grained portion of the sediments (the fraction smaller than 63 µm). The percentage of fine grained sediments in the samples analysed did not show a significant variation, ranging from 60 to 70%, hence, variations in concentration in the samples studied here are due to other parameters.

With the data shown in Tables 3-5, contour maps were prepared, by using the Kriging method, with a linear variogram, to show the spatial distribution of the studied elements in the bay. The software "SURFER" was used in this study.

The heavy metals Zn, Co, Cr and Fe showed a similar behaviour, with higher concentrations along the northern coast, mainly near the input of the fluvial water. To illustrate this group, the contour map for Zn is shown in Figure 3. The distribution of these metals followed the distribution pattern of the sediment deposition from the rivers and of the water surface currents in the Bay (Lacerda *et al.* 1987), indicating that their main source was the industrial park. The industrial activities include zinc smelters, coal combustion plants, steel works, iron ore treatment plants and other small scale sources. In the particular case of Zn, the gradient of concentration is very high, ranging from 2400 µg g^{-1} (near the mouth of the rivers) to 200 µg g^{-1} along the southern coast of the bay. Zinc is a well known contaminant in Sepetiba Bay, but concentration levels have been previously reported to reach not more than 1000 µg g^{-1} (Lacerda *et al.* 1987, Dornelles 1997, Wasserman *et al.* 1991, Barcellos *et al.* 1991, Barcellos 1995, Barcellos *et al.* 1998). In recent research in the same area, Wasserman *et al.* (2001) observed that sediment profiles in the northern coast mangrove stands present decreasing concentrations of Zn from top to bottom, confirming the anthropogenic origin of this element. Concentrations in the bottom layers of the cores reach values as low as 22 µg g^{-1}, that was considered as the background level for the region.

Wasserman *et al.* (2001) observed that, although As constitutes a common pollutant in regions of considerable industrial activity, arsenic profiles in sediment did not follow the shape expected of a contaminant element (high concentrations in the top and low concentrations in bottom layers). In this work, although As showed higher levels along the northern coast and increasing concentration towards the centre of the bay, suggesting that its origin should be the industrial park (Figure 4), the concentrations were low when compared to the mean shale (Table 6). This observation may indicate that anthropogenic inputs are not significant.

The elements Cs, Rb, Sc and Ta are also present at higher levels along the northern coast in relation to the southern coast. On the other hand, these elements exhibited average concentration values lower than mean shale (Table 6). One possible explanation for such behaviour may be the variations in detrital deposition in relation to the hydrodynamics of the Bay, producing a preferential depositional area along the northern coast. To illustrate this group, Figure 5 presents the contour map for Sc.

The REEs La, Sm and Nd showed two points of higher concentrations, in the northern coast and in the centre of the Bay, and Yb showed a region of higher levels in the mouths of the rivers. Figure 6 shows the contour map for La. The REEs Ce, Eu, Tb and Lu, and the element Hf were uniformly distributed along the bay. As stated by Francisco and Cunha (1977) and Leonardos and Santos (1972), the REE should be

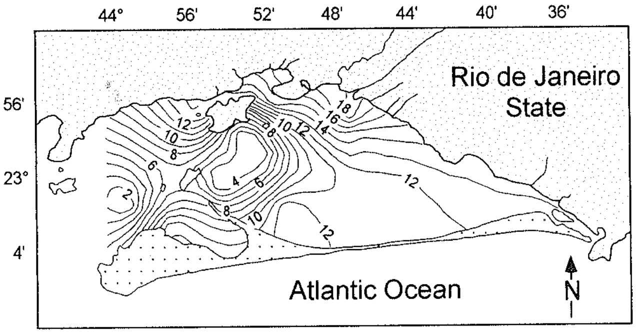

Figure 5. Contour map for Sc (contours in µg g^{-1}).

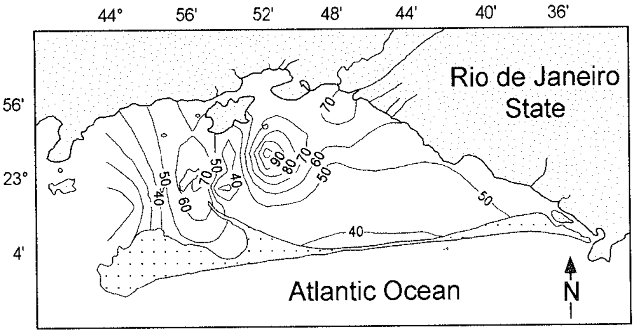

Figure 6. Contour map for La (contours in µg g^{-1}).

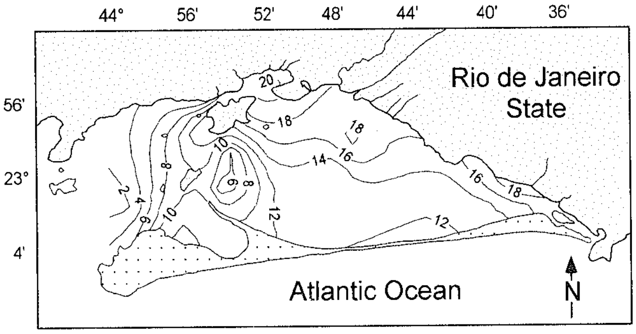

Figure 7. Contour map for U (contours in µg g^{-1}).

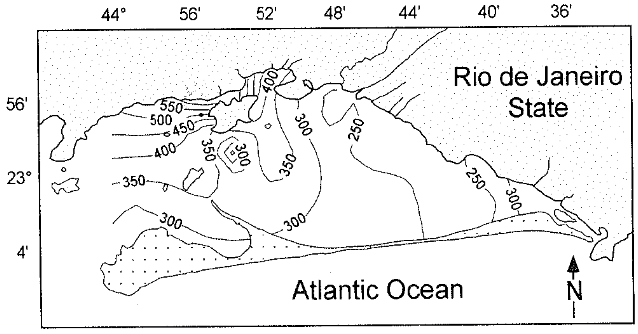

Figure 8. Contour map for Ba (contours in µg g^{-1}).

associated with the U- (Figure 7) and Th-bearing rocks or monazite sands. Uranium and Th exhibited higher concentrations along the whole northern coast, and did not show any special area of accumulation. These results suggest that REE, U, Th and Hf derive from the continental lithologies and have a natural dispersion in the Bay, showing a geochemical behaviour compatible with the associated environment.

The element Ba showed a higher level of concentration at the northwest coast of the Bay (Figure 8). This region is a marine sediment depositional area (Lacerda *et al.* 1987), which indicates that sea water is the main source of this element.

Conclusions

Instrumental neutron activation analysis has been shown to be a very appropriate analytical method to determine trace elements in marine sediments, providing information about concentration levels of elements such as heavy metals, semimetals, non-metals, rare earths and actinides. The great advantage of this method is its multi-elemental and non-destructive capabilities, allowing the determination of up to twenty four elements without requiring the chemical dissolution of the sample. On the other hand, lead, a very important element from the point of view of environmental contamination, cannot be detected by INAA, due to its unfavourable nuclear characteristics in relation to neutron activation. Elements such as Cd, Hg, Sb and Se are difficult to detect accurately by INAA at the ng g^{-1} level. In these cases, radiochemical neutron activation analysis (RNAA) should improve the detection limits.

The results obtained for the reference materials Buffalo River Sediment and Estuarine Sediment demonstrate the accuracy of the method. The concentration data for the Estuarine Sediment CRM are a contribution to concentration levels in this reference material. The contour maps obtained from the INAA data may be used to identify possible sources of contamination. This can be seen particularly in the case of the contour map for Zn (Figure 3), where an industrial park is clearly the source of this element in the Bay. In a similar way, it was possible to conclude from the contour maps of U (Figure 7), REE (Figure 6) and Ba (Figure 8) that these elements are not contaminants in the Bay.

The data presented herein also confirmed results obtained in previous studies in the Bay, and especially confirm the increasing contamination by Zn. For other elements, this work contributes to the knowledge of their concentration and distribution in Sepetiba Bay.

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