

## Elemental composition of sediment cores from a mangrove environment using neutron activation analysis

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### Abstract

The geochemistry of Sepetiba Bay was studied in four sediment cores using a multi-element approach. Two cores were sampled in the more contaminated eastern part of the bay and two cores were sampled in the western region. The aim was to determine whether less common elements like the rare earths or the actinides are associated with contaminant metals like zinc in the Bay. Samples were analysed by instrumental neutron activation analysis that permits the quantification of total concentrations of metals (Ba, Co, Cr, Cs, Fe, Hf, Rb, Sc, Zn), rare earth elements (Ce, Eu, La, Lu, Sm and Yb), actinides (Th, U), non-metals and semi-metals (As, Br). Organic carbon and total sulphur were also analysed. The results show very strong zinc contamination in the top layers (more than 1000  $\mu\text{g g}^{-1}$ ) and background concentrations in the bottom (15  $\mu\text{g g}^{-1}$ ). Elements like chromium which would be expected to be released by the heavy industries of Sepetiba Bay, did not show a contamination profile, and concentrations remained close to those of natural environments. No evidence of any association between the zinc and other potential contaminant elements could be identified in this work. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Sediment profiles; Multi-element approach; Geochemistry; Instrumental neutron activation analyses; Tropics; Sepetiba Bay

### 1. Introduction

Over the last few decades, the study of sediment cores has shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments. During the early sixties, sediment profiles from depositional areas were used to trace human activity, witnessed by anthropogenic contaminants like phosphorus (Livingstone and Boykin, 1962) and, later in the seventies, it was possible to distinguish radioactive isotope inputs due to nuclear tests (Robbins and Edgington, 1975). In

addition, the dating of sediment cores using radioactive tracers like  $^{210}\text{Pb}$  (Robbins and Edgington, 1975) permitted the precise quantification of the history of the inputs in a system (Abrão et al., 1996).

Even in the absence of reliable dating, sometimes it is possible to estimate sedimentation rates by carefully studying the concentration profile of a pollutant. A lot of work has shown that an increase in the concentrations in the surface layers should be attributed to the installation of a known polluting source, therefore, the enriched layers should correspond to the number of years after the installation of that source. Below these enriched layers, background concentrations should be measured (e.g. Quevauviller et al., 1992; Barrocas et al., 1993; Wasserman et al., 2001).

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A number of recent pieces of work have used sediment profiles to describe the contamination history of different environments. For instance, Pereira et al. (1998) studied mercury contaminated sediments in the lagoon of Aveiro (Portugal) where, from a set of four cores they could observe at least one that clearly presented enriched layers in the surface and background concentrations in the bottom, permitting the calculation of sedimentation rates. Even in remote areas, atmospheric contributions can be traced based on metal concentrations of undisturbed cores as done by Silva-Filho et al. (1998). Further, in a study of sediment cores from arctic and sub-arctic lakes, Landers et al. (1998) were able to estimate global fluxes of mercury, which yielded a model of the fallout distribution of this metal in the northern hemisphere.

Most of the contaminants can leave their fingerprint in sediments, the only condition is stability within the sedimentary column, i.e. no or insignificant post-depositional mobility is allowed. Although most of the elements can be studied that way, metals that are more widely applied in the industry like cadmium, chromium, copper, iron, mercury, nickel, lead and zinc constitute the bulk of the work presented in the literature (Förstner and Wittmann, 1983). This is due, on the one hand, to the obvious interest of researching metals that represent a potential danger for the degradation of the environment, and on the other hand, to the uneasiness of obtaining and interpreting data from multi-element analyses. Nonetheless, elements released by industrial or mining activities are seldom pure wastes. For instance, in a mining area of South Africa where pyrite (FeS) is a predominant mineral, acid leaching yields high concentrations of at least 24 elements (Liebenberg, 1972). In this case, treatment or transport of this iron ore may contaminate the environment. In Sepetiba Bay (Brazil), important amounts of iron are charged in ships with open air rolling carpets, spilling a red powder of the ore throughout the region that heavily contaminates the site with iron and possibly other metals (Lacerda et al., 1987; Wasserman et al., 1991).

In Sepetiba Bay, industry, tourism and urban expansion have significantly increased in the last three decades, leading to a series of impacts on the

environment. The surroundings and the catchment 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. Till date, there are some 400 industries that can be grouped into: pyrometallurgic (including two large steel plants), aluminium plants and electricity power plants. This industrial park is responsible for the inputs of large amounts of heavy metals in the surrounding environments, attaining the coastal area through the rivers, or through atmospheric deposition (Lacerda, 1983; Lacerda et al., 1987; Rodrigues, 1990; Pedlowisk et al., 1991; Wasserman et al., 1991; Barcellos, 1995; Marins et al., 1996; Barcellos et al., 1998). Among the metals that constitute serious contaminants in the bay, Zn and Cd were studied by various authors and specially by Barcellos et al., 1998 who observed mean concentrations in the sediments of 824 and 4.24  $\mu\text{g g}^{-1}$  respectively. In this same study, the authors measured the concentrations of these two metals in suspended matter with sediment traps, observing concentrations of 1087 and 4.10  $\mu\text{g g}^{-1}$  respectively. The comparison of the deposition rates observed in the studies of sediment cores (Japenga et al., 1988; Barcellos et al., 1991; Quevauviller et al., 1992) shows marked differences that are attributed to re-suspension, apparently an important process in this environment.

Although a great amount of research concerning heavy metal distribution and behaviour in Sepetiba Bay has been done in recent years only a few metals had the attention of the researchers. This is probably due to the fact that the technique utilised is frequently atomic absorption spectrometry that renders multi-element analysis more difficult.

In this work, a wide range of elements like metals (Ba, Co, Cr, Cs, Fe, Hf, Rb, Sc, Zn), rare earths (Ce, Eu, La, Lu, Sm and Yb), actinides (Th, U), non-metals and semi-metals (As, Br) was measured using instrumental neutron activation analysis (INAA), a technique that does not require previous extractions and yields reliable results. The geochemistry of the above-mentioned elements was studied in sediment cores from Sepetiba Bay in order to determine their

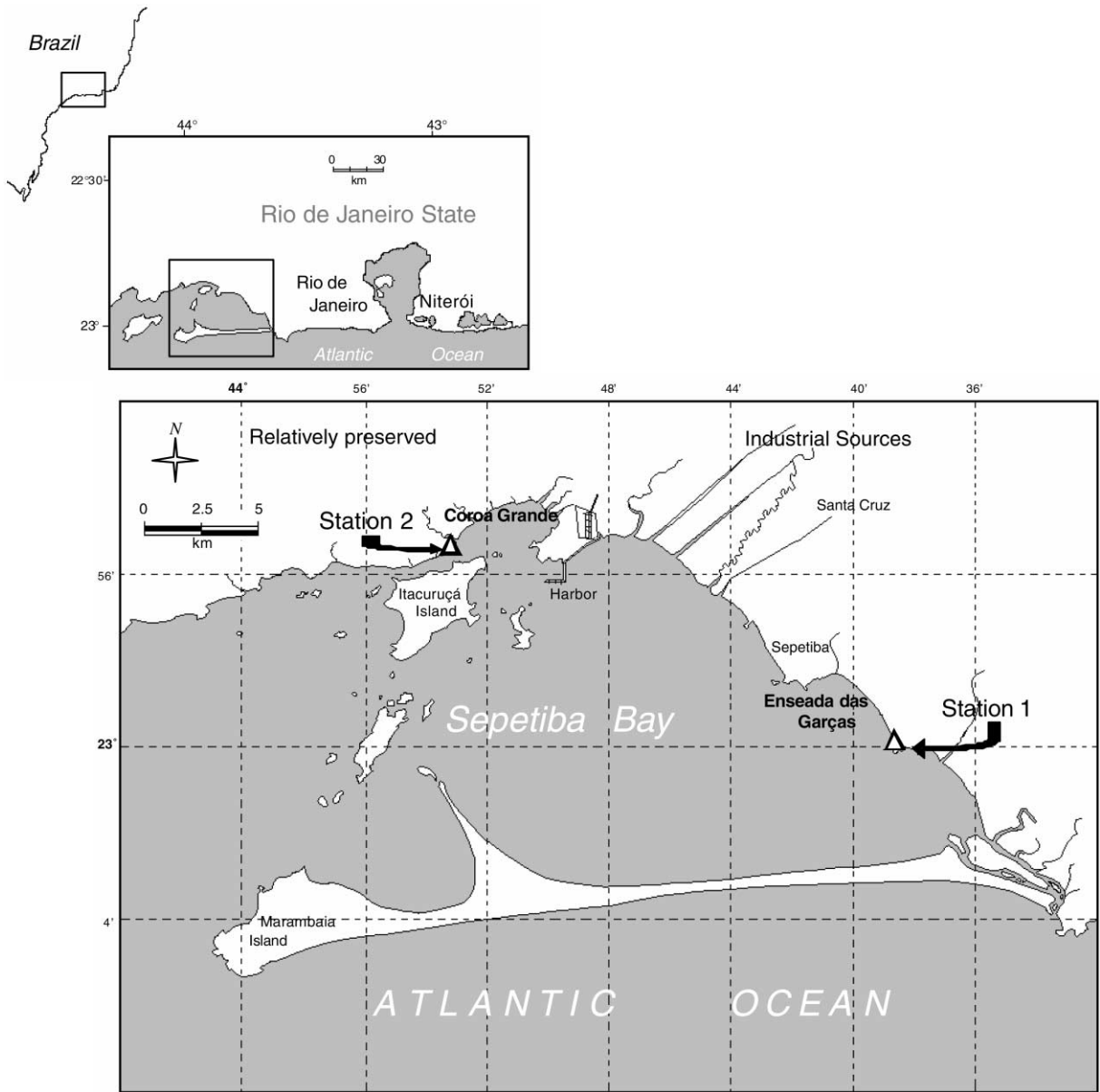


Fig. 1. Sampling location.

behaviour and associations with recognised pollutants (for example, zinc in Sepetiba Bay) used in the industries of the region. Two cores (cores 1 and 2) were sampled in the more polluted eastern part of the bay (station 1) and the remaining two cores (cores 3 and 4) were sampled in a less impacted portion of the bay (station 2).

## 2. Material and methods

### 2.1. Sampling procedures

Four sediment cores were hand sampled, two from each of the sampling sites in the Sepetiba Bay (Fig. 1). Station 1 is a large forest mangrove that is common in

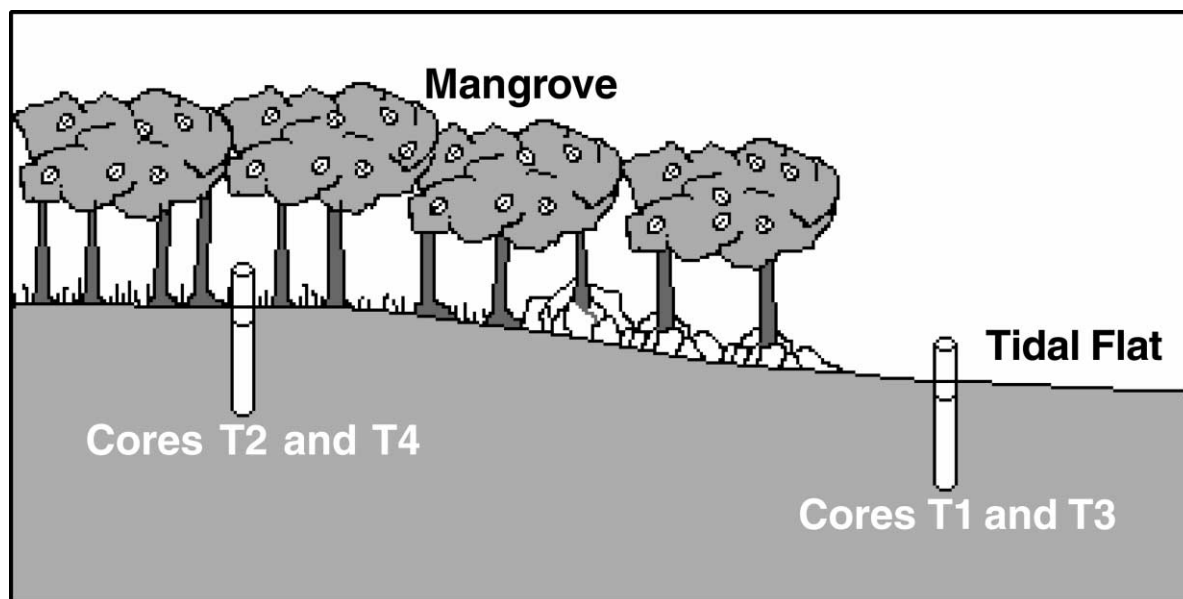


Fig. 2. Diagrammatic positioning of the sampled cores in the mangrove environment.

the eastern part of the bay. In this region, the flat relief, and the important fresh water supplies permitted the development of the majority of the industrial activity of the region. The eastern part of the bay is reported to be the most affected by metallic contamination, what is primarily explained by the hydrodynamic features of the bay. These hydrodynamic features engender extremely depositional conditions that characterise this area as a strong geochemical barrier for continental contaminants that, otherwise would easily reach the continental platform (Wasserman et al., 1991; Dornelles, 1993). In this Station, two cores were sampled, one from the tidal flat just in the edge of the mangrove (muddy flat). The second core was collected also in the tidal region, but within the mangrove trees (Fig. 2).

Station 2 is situated in the more preserved western part of the bay. The relief is considerably more abrupt with forested mountains diving directly into the sea. Fringe mangrove forests develop in the intertidal zone. The station is situated in the mouth of a small creek that is sourced in the neighbouring mountains. Two cores were also collected in this area, within the mangrove trees and in the edge of the tidal flat (Fig. 2).

Sampling was carried out with 1 m long PVC tubes

that were immediately sliced into 3 cm layers. The samples were stored in polyethylene bags at fridge temperature (4°C) and transported to the laboratory, where they were frozen to  $-20^{\circ}\text{C}$  until analyses.

## 2.2. Analytical procedures

*Sample treatment.* The frozen samples were divided into two aliquots, one for granulometric analysis (fraction  $<63\ \mu\text{m}$ ) and the second for the other analyses. Granulometric analysis was done by wet sieving samples through a nylon  $63\ \mu\text{m}$  sieve, followed by the drying of both passed fraction and retained fraction, that were weighted and the fraction  $<63\ \mu\text{m}$  was calculated. No drying of the sample is done prior to sieving. The second aliquot was dried in a ventilated oven at  $40^{\circ}\text{C}$  for three days, and the samples were carefully ground and stored in sealed polyethylene bags until analysis.

*Organic carbon and total sulphur.* The samples were pre-weighted in special silicate crucibles and treated with HCl 2N in order to completely eliminate carbonates. Droplets of HCl 2N were added until no bubbling was observed. Samples were then left to dry on a hot plate ( $60^{\circ}\text{C}$ ) for 16 h. Organic carbon was measured in a LECO induction furnace with infrared

Table 1

Results obtained for the reference materials Buffalo River Sediment (NIST 2704) and Estuarine Sediment (NIST 1646a). Standard deviations are based on six replicate analyses of reference materials. Values in brackets are information values

Element	Buffalo River Sediment ( $\mu\text{g g}^{-1}$ ) ( $n = 6$ )	Certified values ( $\mu\text{g g}^{-1}$ )	Estuarine Sediment ( $\mu\text{g g}^{-1}$ ) ( $n = 6$ )	Certified values ( $\mu\text{g g}^{-1}$ )	DL <sup>a</sup> ( $\mu\text{g g}^{-1}$ )
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
Br	5.3 ± 0.3	–	46 ± 2	–	0.3
Co	14.0 ± 0.7	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 (%)	4.21 ± 0.06	4.11 ± 0.10	2.05 ± 0.05	2.008 ± 0.039	7
Hf	8.06 ± 0.08	(8)	11.86 ± 0.09	–	0.069
Rb	102 ± 2	(100)	34.3 ± 0.8	(38)	5.9
Sb	3.77 ± 0.06	3.79 ± 0.15	–	(0.3)	0.082
Sc	12.3 ± 0.3	(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	30.0 ± 0.2	(29)	18.5 ± 0.1	(17)	0.06
Ce	66 ± 1	(72)	38.6 ± 0.2	(34)	0.3
Nd	28 ± 2	–	18 ± 2	(15)	6
Sm	6.9 ± 0.3	(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

<sup>a</sup> DL = Detection Limits, determined as 3 times the standard deviation of blanks.

detection. The measurement of total sulphur is made the same way but without acid leaching.

**Neutron activation analysis.** About 100 mg of the sample were accurately weighed in polyethylene vials. Elemental synthetic standards of the analysed elements were prepared by dissolving their respective oxides or salts (analytical grade) with adequate inorganic acids and diluting with distilled water. Aliquots of these solutions were pipetted onto 1 cm<sup>2</sup> pieces of Whatman no. 40 filter paper, evaporated to dryness under an infrared lamp, and sealed in polyethylene envelopes. Samples and standards were irradiated for 8 h at a thermal neutron flux of 10<sup>13</sup> n cm<sup>-2</sup> s<sup>-1</sup>, at the IEA-R1 nuclear reactor of the Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP). The measurements of the induced gamma-ray activity were carried out in a GMX20190 hyperpure Ge detector (CANBERRA). The multi-channel analyser was an 8192 channel CANBERRA S-100 plug-in-card in a PC computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma-ray of <sup>60</sup>Co. Two series of countings 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 h. The gamma-ray spectra were processed by using the SAMPO90 gamma-ray software which locates peak positions and calculates the energies and net areas. The accuracy and precision of the results were verified by the analysis of the reference materials *Buffalo River Sediment* (NIST SRM 2704) and *Estuarine Sediment* (NIST SRM 1646a). The results obtained for these standard reference materials, as well as certified and proposed values and detection limits ( $3\sigma$ ), are presented in Table 1. The reproducibility of the method was tested by six replicate analyses of the sample, and the errors associated with the data represent one standard deviation. Results agreed with the certified or information values, showing relative errors between 0 and 10% and good precision (relative standard deviations less than 15%). Although cadmium constitutes an important pollutant in Sepetiba Bay, it could not be measured because unreliable results were obtained for the low concentrations observed in Sepetiba Bay.

An extra experiment was performed to identify the amount of water insoluble bromine in some sediment samples (core 1, layers 0–3, 3–6 and 6–9 cm). The dried samples were leached in bi-distilled water and centrifuged. The overlying water was discarded and the procedure was repeated three times. The wet samples were dried, ground, homogenised and bromine concentrations were measured by neutron activation analysis as described above.

*Sediment enrichment factor for element concentrations.* To distinguish between natural enrichment and anthropogenic enrichment of elements, sediment enrichment factors were tested. A number of procedures have been established in the literature mainly based on comparisons with *conservative* elements or *background* values (Kemp, 1976; Martin and Meybeck, 1979; Förstner and Wittmann, 1983). The first problem is to select a *conservative* element, since elements that are conservative in a temperate environment may not be in a tropical one. The most used conservative element is aluminium (Kemp, 1976), due on the one hand, to its very high concentrations in clay minerals, and also due to the absence of significant anthropogenic sources. Unfortunately, aluminium analysis by INAA suffers from severe interferences in the presence of Si and P. These elements, by neutron activation, originate the radioisotope  $^{28}\text{Al}$ , (nuclear reactions:  $^{28}\text{Si}(n,p)^{28}\text{Al}$ ;  $^{31}\text{P}(n,\alpha)^{28}\text{Al}$ ), which is the same radionuclide obtained by neutron activation of aluminium (nuclear reaction:  $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$ ) (Erdtmann and Petri, 1986). Therefore, aluminium could not be conveniently quantified. Other conservative elements were considered such as Fe (Trefry and Presley, 1976) that although abundant in the sediments of the studied environment, is significantly affected by redox potentials that significantly varies within the core. More or less conservative elements like U and Th were also tested, but none of the studied profiles confirm that these elements have a conservative behaviour.

Granulometry may constitute a good control of the element concentrations (Förstner and Wittmann, 1983; Förstner, 1989). This procedure assumes that elements are exclusively associated with the fine grained portion of the sediments (fraction smaller than  $63\ \mu\text{m}$ ). 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 all metals are strictly associated with fine grained sediments is not always correct, mainly when fine grained fraction is very small. The layer 18–21 cm in core 3 is an example: considering the contents of fine grained fraction (0.40%), the granulometric correction would yield very high (and unreliable) concentrations of some elements, like iron (263.6%) or zinc (1.23%). These aberrations are attributed to the fact that iron and manganese oxide coatings present in the coarse sediments significantly contribute to the final concentrations. For these reasons, both granulometry corrected and total concentrations are presented in this work.

### 3. Results and discussion

#### 3.1. Core description (granulometry, organic carbon, and total sulphur)

As stated before, an important feature of the cores 1 and 3 is that both were sampled in the tidal flat just in front of the mangrove, while cores 2 and 4 were sampled within the trees (Fig. 2). Under the sedimentological view point Station 1 is a mangrove that was established on a sand bar, and the tidal flat just in front (core 1, Fig. 3) is muddy, explaining why core 2 could not be sampled deeper than 30 cm (Fig. 4, below this depth, sediment was sandy and too hard to be hand sampled). This sand bar was described as a feature associated with a higher sea level (Tinoco et al., 1993). Station 2 is fairly different from Station 1 since it is located in the mouth of a creek (Itingussú Creek). Although, core 3 is located in the tidal flat of Station 2, it presents a coarser granulometry (between 20 and 40% silt-clay, Fig. 5) probably due to the creek's current. Similar to core 1, core 4 presents fine grained sediments in the surface layers, and gets coarser in deeper layers (up to 60 cm, Fig. 6). This behaviour suggests that these two deeper sediment cores are reaching sand bars that are associated to lower sea level periods (Tinoco et al., 1993).

Cores 1, 3, and 4 present good correlation factors between organic carbon and total sulphur ( $r = 0.91$ ,  $p < 0.01$ ,  $n = 29$  for core 1;  $r = 0.69$ ,  $p < 0.01$ ,  $n = 16$  for core 3;  $r = 0.83$ ,  $p < 0.01$ ,  $n = 21$ ), suggesting

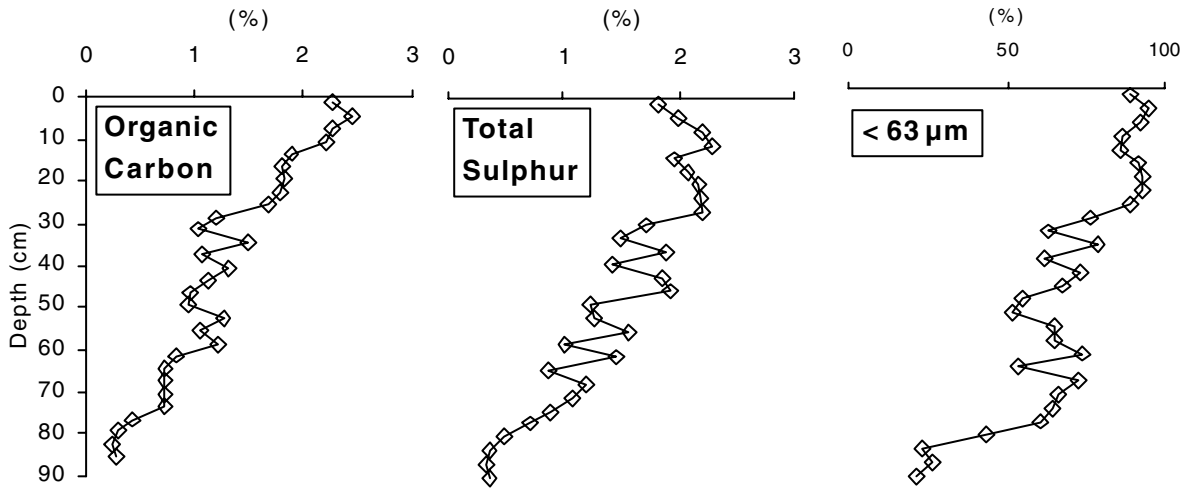


Fig. 3. Organic carbon, total sulphur and granulometry profiles in core 1.

that sulphur, that is largely provided by seawater sulphates, is reduced by sulphate reducing bacteria, that also require organic carbon (e.g. Lovley et al., 1996). For these three cores, there is a tendency for carbon contents to decrease with depth. This behaviour has been described elsewhere to be due to organic matter decomposition with burial time (Boudou, 1981; Wasserman et al., 1998). Core 2 is a particular case that can be explained by the presence of a considerable amount of roots, belonging to *Avicennia schauereiana*, trees. Clark et al. (1998) were able to develop a model that describes the

chemical changes promoted by the presence of *Avicennia* roots in sediment profiles. These authors established four main layers following redox patterns. The *upper oxidation zone* (UOZ) is the result of oxygen diffusion from the surface. About 5 cm deeper an *upper reduction zone* (URZ) appears due to the absence of oxygen supply. In tidal flats where mangrove trees do not grow, beneath this layer, sediments tend to be more and more reducing as it is deeper, but in areas where *Avicennia* stands are present, a *lower oxidation zone* (LOZ) appears at between 20 and 30 cm. This layer is coincident with

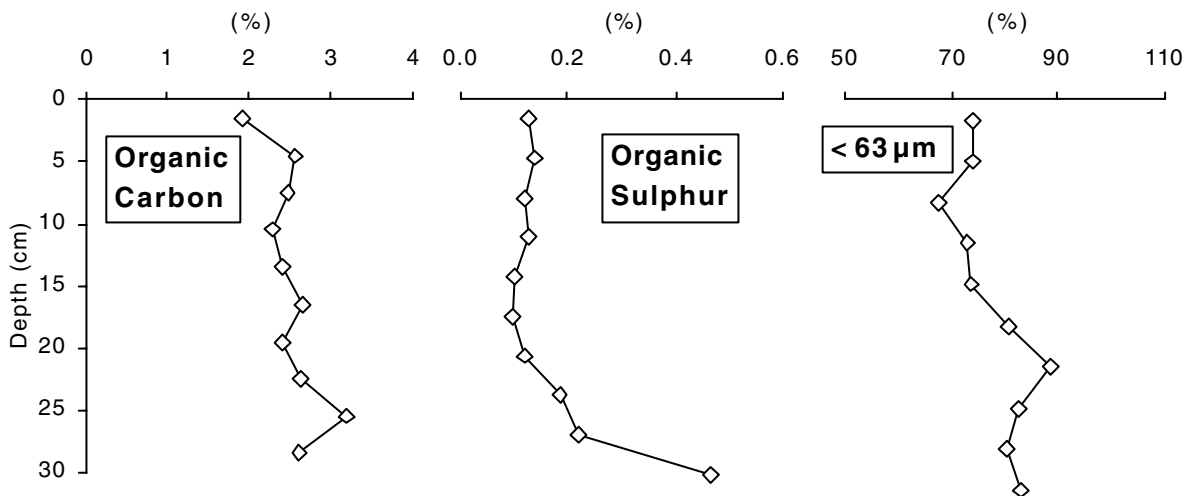


Fig. 4. Organic carbon, total sulphur and granulometry profiles in core 2.

Table 2

Average values in stations 1 (cores 1 and 2) and 2 (cores 3 and 4), compared to mean shale (used for calculations of Fe correction) and other sediments

Element	Station 1 <sup>a</sup> ( $\mu\text{g g}^{-1}$ ) ( $n = 39$ )	Station 2 <sup>a</sup> ( $\mu\text{g g}^{-1}$ ) ( $n = 40$ )	Student's Test <sup>b</sup>	Shale <sup>d</sup> ( $\mu\text{g g}^{-1}$ )	Other sediments ( $\mu\text{g g}^{-1}$ )
As	11.3 $\pm$ 2.4	4.5 $\pm$ 2.0	0.0000	13	2.9 <sup>c</sup>
Ba	363.5 $\pm$ 66.7	571.4 $\pm$ 99.5	0.0000	550	90 <sup>e</sup>
Br	120.3 $\pm$ 69.8	71.3 $\pm$ 39.6	0.0003	6	
Ce	285.3 $\pm$ 126.5	80.5 $\pm$ 27.9	0.0000	80	96 <sup>f</sup>
Co	9.3 $\pm$ 2.2	7.3 $\pm$ 5.6	0.0000	19	11 <sup>e</sup>
Cr	61.2 $\pm$ 14.0	32.8 $\pm$ 13.3	0.0000	90	31 <sup>e</sup>
Cs	4.8 $\pm$ 1.4	3.4 $\pm$ 1.3	0.0000	5	1 <sup>e</sup>
Eu	1.7 $\pm$ 0.2	1.3 $\pm$ 0.3	0.0000	0.95 <sup>e</sup>	
Fe (%)	4.0 $\pm$ 1.0	2.4 $\pm$ 1.0	0.0000	5.5	2.6 <sup>c</sup>
Hf	27.5 $\pm$ 12.1	10.5 $\pm$ 4.0	0.0000	4	16 <sup>g</sup>
La	133.1 $\pm$ 63.0	40.9 $\pm$ 14.2	0.0000	40	21 <sup>e</sup>
Lu	0.6 $\pm$ 0.2	0.2 $\pm$ 0.1	0.0000	0.6	
Rb	91.1 $\pm$ 20.2	106.3 $\pm$ 15.5	0.0003	140	91 <sup>f</sup>
Sc	11.5 $\pm$ 2.7	8.2 $\pm$ 3.0	0.0000	15	5 <sup>e</sup>
Sm	16.6 $\pm$ 7.1	6.3 $\pm$ 2.1	0.0000	7.2	
Th	61.4 $\pm$ 35.5	14.6 $\pm$ 4.5	0.0000	12	5 <sup>e</sup>
U	7.0 $\pm$ 2.6	5.2 $\pm$ 1.5	0.0004	3.2	2 <sup>e</sup>
Yb	3.3 $\pm$ 1.0	1.4 $\pm$ 0.3	0.0000	3.2	
Zn	309.1 $\pm$ 282.6	248.6 $\pm$ 236.9	0.3040	100	46 <sup>e</sup>

<sup>a</sup> Average of the concentrations of all layers of two cores sampled in each station.

<sup>b</sup> Between stations 1 and 2.

<sup>d</sup> Wedepohl, 1995; Reimann and de Caritat, 1998.

<sup>e</sup> Organic stream sediment, Finland (Lahermo et al., 1996).

<sup>f</sup> Stream sediment, Austria (Thalmann et al., 1988).

<sup>c</sup> Upper continental crust.

<sup>g</sup> Stream sediment, Germany (Roostai, 1997).

a considerable increase in the root biomass that flushes sediments with oxygen. Beneath this zone a *lower reduction zone* (LRZ) completely depleted in oxygen appears. In Sepetiba Bay the chemistry of the LOZ was already studied by Tanizaky (1994) and Marins et al. (1997). Nonetheless, it is difficult to explain why core 4, that was sampled among *Avicennia schauereiana* and *Laguncularia racemosa* trees, did not present elemental profiles that imply the presence of LOZ and LRZ as observed in the core 2.

The prevailing chemical conditions of the sediments will control the distribution of metals in the sedimentary column and the above mentioned work of Marins et al. (1997) is an example for mercury where oxidation will improve the mobilisation of this element. However, the chemical conditions established in the different layers remain constant for a very long period. Therefore an element that is mobile in a specific layer, will migrate to the adjacent layers until

it finds suitable conditions for trapping. When trapped, very seldom the element will become mobile again and that is why mangrove environments are called geochemical barriers (Wasserman et al., 1991) or contamination buffers (Clark et al., 1997). However, in extreme conditions (like very dry periods) it is possible that these chemical conditions change, releasing the elements to the environment. Then, the mangrove that is considered a trap for the elements will become a source (Clark et al., 1997).

### 3.2. Average concentrations and literature comparisons

Average concentrations of the measured elements in Sepetiba Bay, shale values, and sediment concentrations from the literature are presented in Table 2. This comparison indicates that although some of the elements present concentrations higher than other



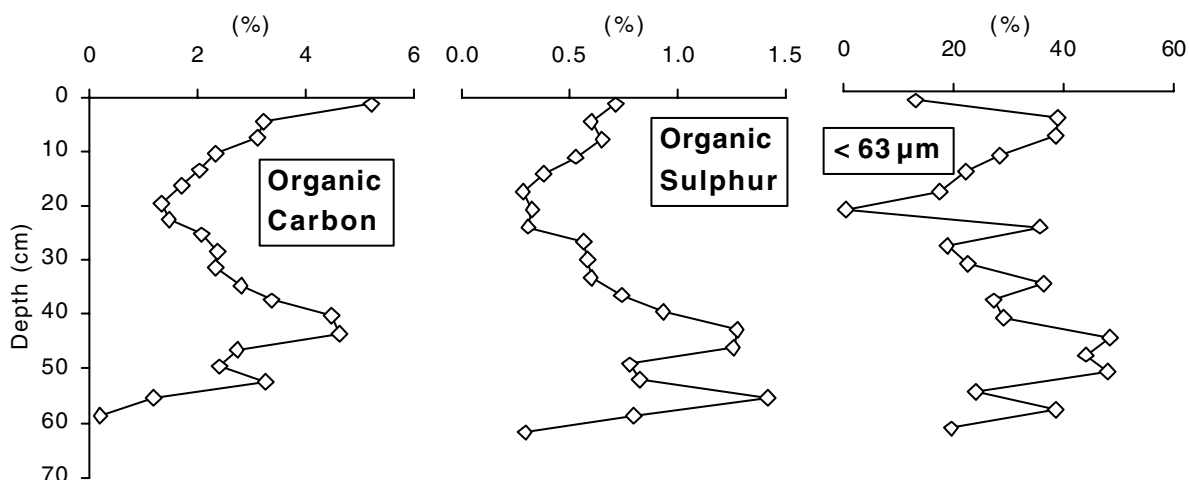


Fig. 5. Organic carbon, total sulphur and granulometry profiles in core 3.

sediments and mean shale, only bromine and zinc present significantly higher concentrations. High bromine concentrations are explained by its association with marine salts, and high mobility in the sediment (Reimann and de Caritat, 1998), while zinc is largely reported to be of anthropogenic origin in this region (Lacerda, 1983; Lacerda et al., 1987; Rodrigues, 1990; Barcellos et al., 1991; Wasserman et al., 1991; Barcellos, 1995).

Another important feature that can be observed in Table 2 is the higher concentrations for most elements in Station 1 (cores 1 and 2) compared to

Station 2 (cores 3 and 4; see Student's Test values, confirming differences between means for  $p < 0.01$ ). Only Ba presented significantly higher concentrations in Station 2 than in Station 1. This behaviour was largely expected since, as stated in Wasserman et al. (1991), the clockwise circulation pattern of the system engenders contaminants from the industrial sources (Fig. 1) to drift westward and settle in the north-western part of the bay (Station 1).

In the following sections element profiles are discussed. In order to optimise the presentation,

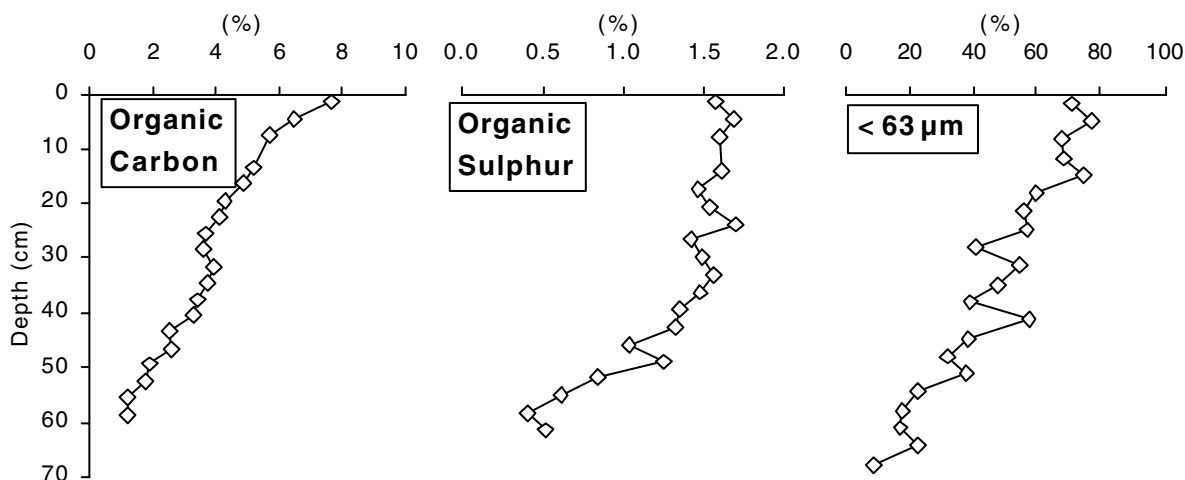


Fig. 6. Organic carbon, total sulphur and granulometry profiles in core 4.

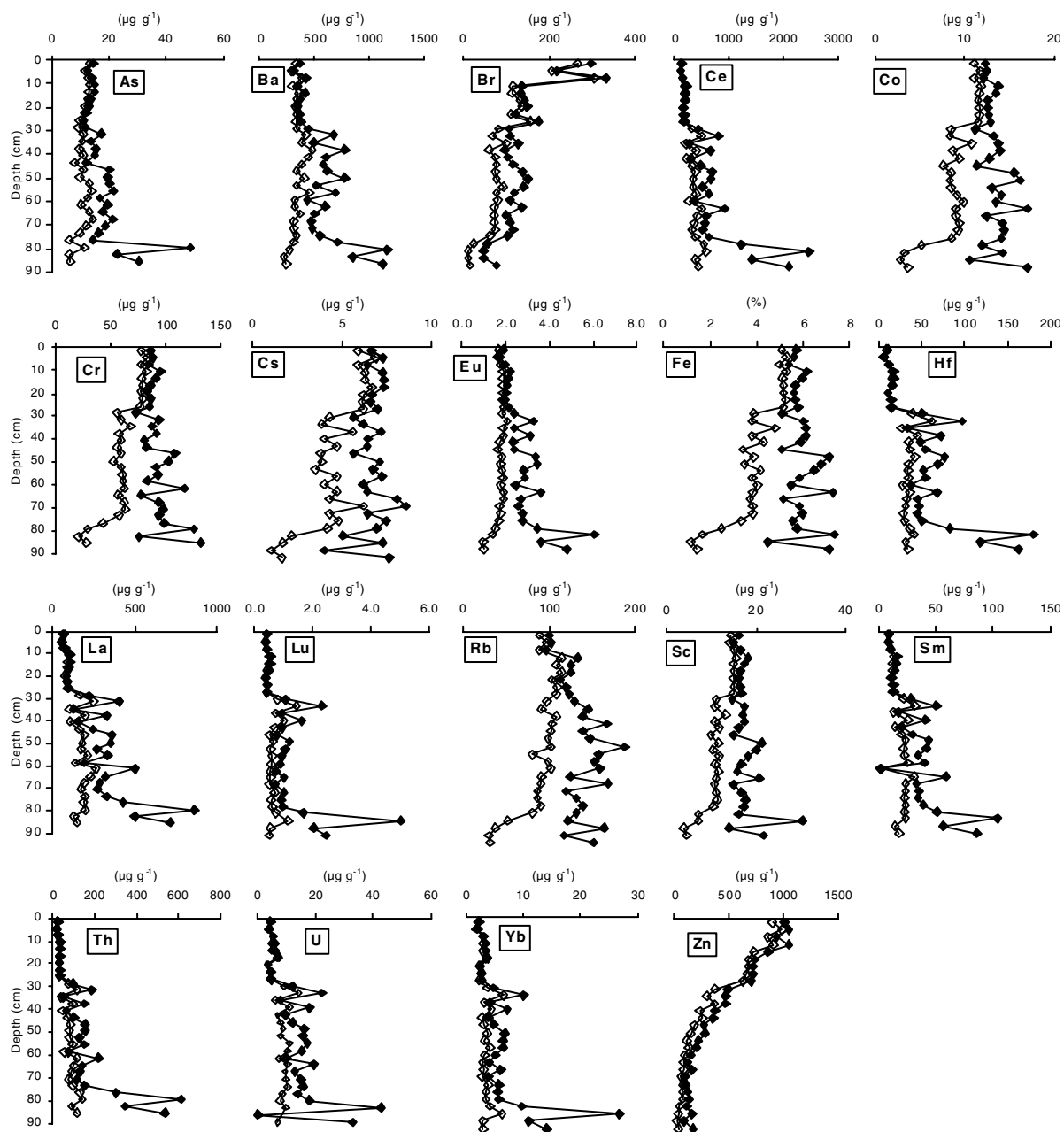


Fig. 7. Element concentration profiles in core 1. ( $\diamond$ ) Open diamonds correspond to total concentrations; ( $\blacklozenge$ ) closed diamonds correspond to granulometry corrected concentrations.

metals were separated into polluting elements (Zn, Cr, As, U and Fe), rare earth elements (Ce, Eu, La, Lu, Sc and Yb) and other elements (Co, Cs, Br, Sc, Th, Hf, Ba, Ru).

### 3.3. Profiles of the polluting elements

Except for core 2 that is considered as a root disturbed core, the other three present a clear zinc

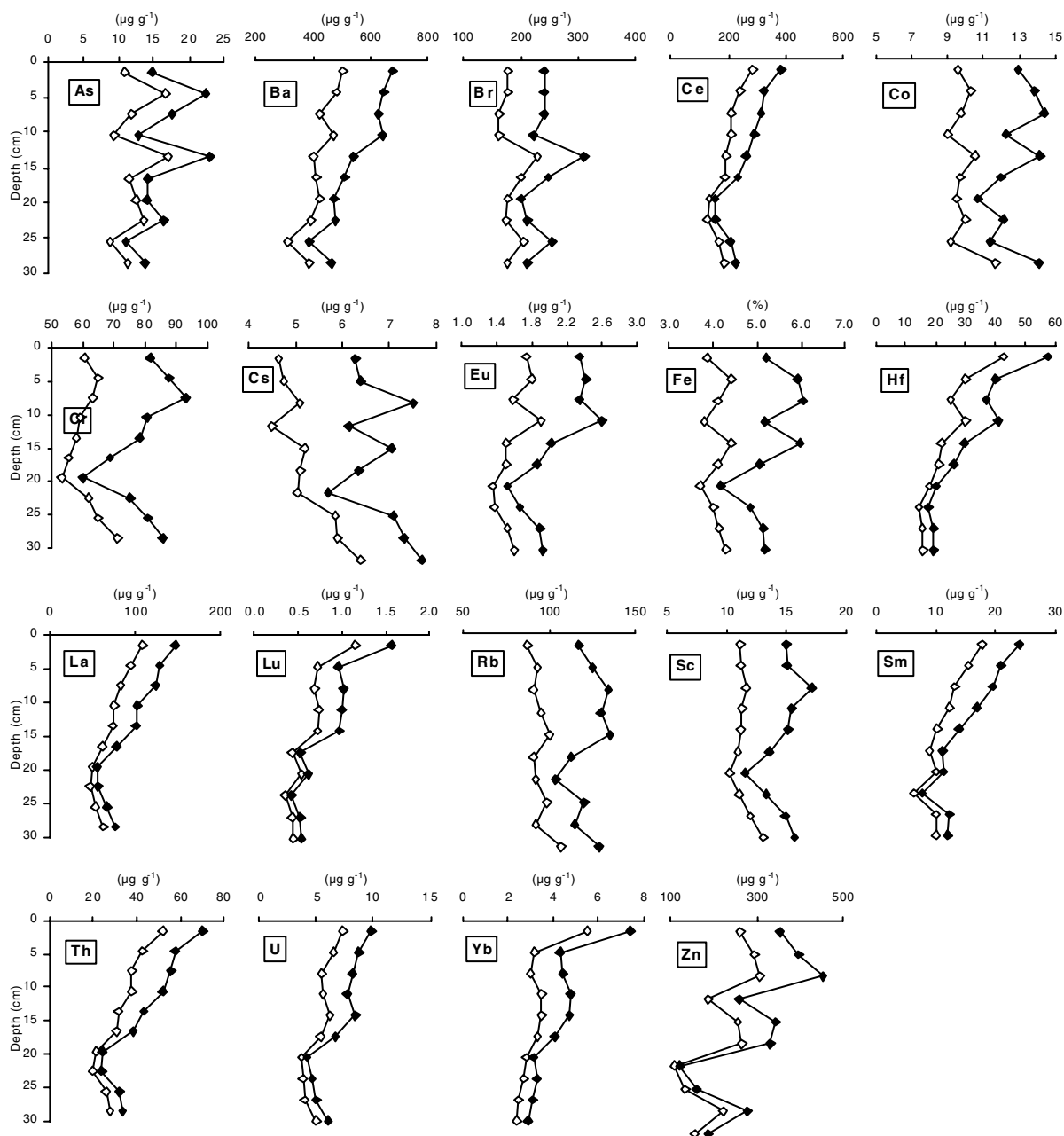


Fig. 8. Element concentration profiles in core 2. (◇) Open diamonds correspond to total concentrations; (◆) closed diamonds correspond to granulometry corrected concentrations.

contamination profile (Figs. 7–10). This was expected because other studies in the area have shown that industrial sources are responsible for the contamination of sediments with Zn, Cd, Pb and Cr (Lacerda,

1983). Concentrations of zinc tend to be higher in the top 30 cm, reaching more than  $1,000 \mu\text{g g}^{-1}$  (core 1, 3–6 cm) and show background levels at depths beneath 60 cm ( $15 \mu\text{g g}^{-1}$  at the level 57–60 cm of

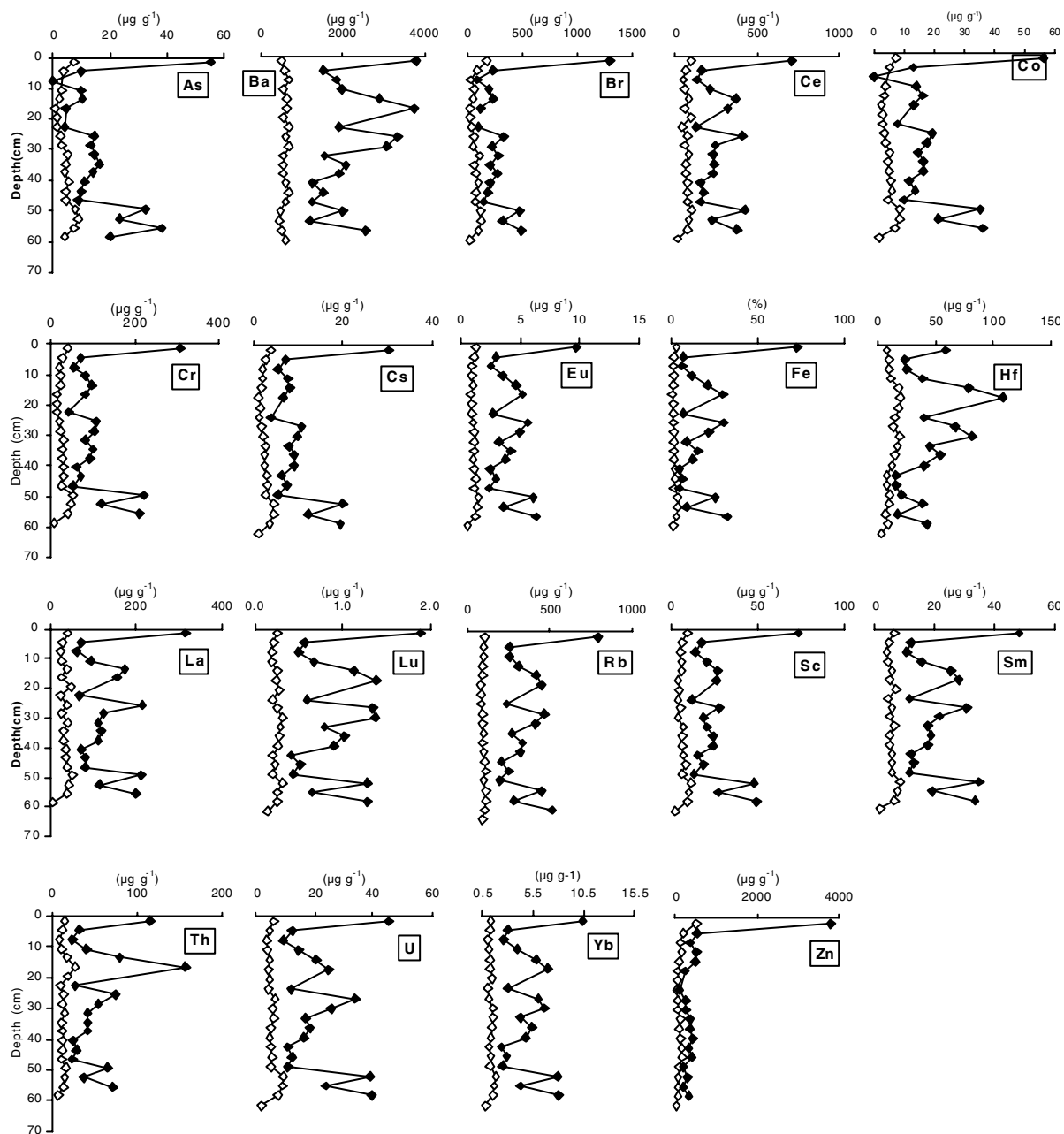


Fig. 9. Element concentration profiles in core 3. ( $\diamond$ ) Open diamonds correspond to total concentrations; ( $\blacklozenge$ ) closed diamonds correspond to granulometry corrected concentrations.

core 3). These results indicate an enrichment of almost 70 times for core 1 (as calculated by dividing of top concentrations by bottom concentrations), while Barcellos et al. (1998) calculated an enrichment

of not more than 15 times. Although their surface sediment concentrations are close to the values we have obtained in the present work, the differences in enrichment should be explained by the fact that these

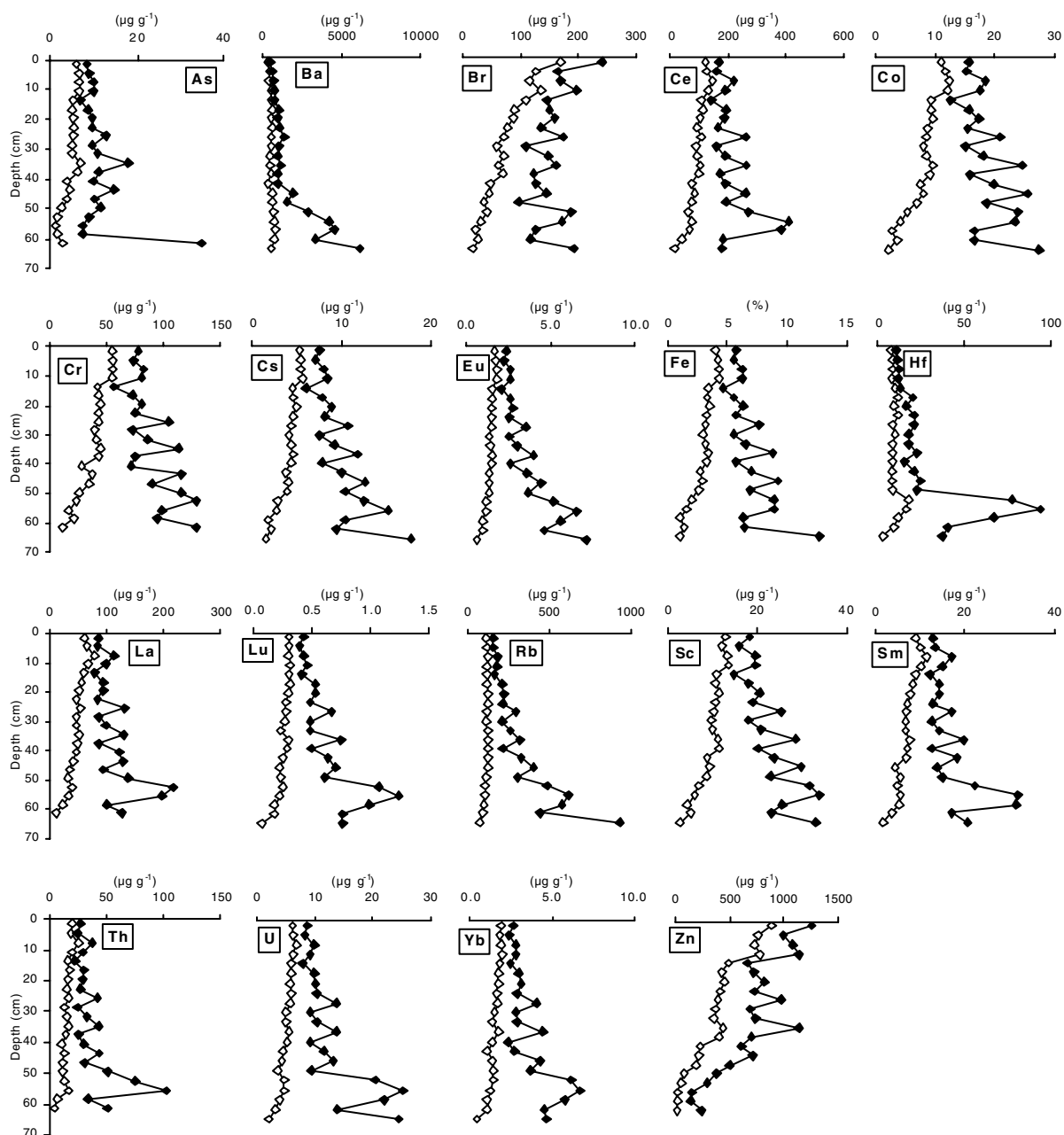


Fig. 10. Element concentration profiles in core 4. ( $\diamond$ ) Open diamonds correspond to total concentrations; ( $\blacklozenge$ ) closed diamonds correspond to granulometry corrected concentrations.

authors have chosen as background values, sediment concentrations from *uncontaminated* neighbouring areas (approximately  $60 \mu\text{g g}^{-1}$ ).

Based on the increase of zinc concentration, it is

possible to calculate an average sedimentation rate, considering that the industrial activities in the area started in the early 60s and the cores were collected in 1996. The 36 years of effluent disposal would yield

a contaminated layer of approximately 30 cm and therefore, a sedimentation rate of  $0.8 \text{ cm yr}^{-1}$ . This value agrees fairly well with the results obtained in other studies in the area that ranged between 0.8 and  $1.3 \text{ cm yr}^{-1}$  (Japenga et al., 1988; Barcellos et al., 1991). Nevertheless, no  $^{210}\text{Pb}$  dating has been done in the area, and these results must be carefully considered.

Other metals as chromium and iron, described as important contaminants in the Sepetiba Bay originated from the diversified industrial activities present in the drainage basin (Lacerda, 1983; Fiszman et al., 1984; Souza et al., 1986; Lacerda and Rezende, 1987; Lacerda et al., 1987). These industrial activities include zinc smelters, coal combustion plants, steel works, iron ore treatment plants and other small scale sources.

In our study, although total concentrations of chromium ( $8\text{--}80 \mu\text{g g}^{-1}$ ) agree with the values obtained by the above mentioned authors ( $24\text{--}121 \mu\text{g g}^{-1}$ ), the granulometry corrected profiles did not present a contaminant shape as did zinc. The little variation with depth in the core 1 is also observed for all other profiles that show ranges between 70 and  $130 \mu\text{g g}^{-1}$ . Mobility should not account for the fairly homogeneous profiles of this element, because under the reducing and alkaline conditions of the sediments it has a very low rate of diffusion (Reimann and de Caritat, 1998). It can be stated that although the existing sources are providing sediments with chromium, its contamination is not yet significant (at least in the sites we have sampled).

Similar to chromium, arsenic was expected to be enriched in the sediments as a result of the industrial activities present in the drainage basin, however it did not present any particular feature of a polluting element. Although total concentrations are higher than in other environments, it is situated within the range of the mean shale (Table 2). Cores 1, 2 and 4 (Figs. 7, 8 and 10) show homogeneous profiles of the granulometry corrected concentrations from top to bottom, showing that little variation of the inputs are detected in the period of sedimentation of these cores. Core 3 (Fig. 9) shows higher concentrations in the top centimetres (level 0–3 cm) that can be attributed to a double effect of decrease in fine grained sediments percentage (less than 20%) and enrichment in organic carbon concentrations (more than 5%). Considering that core 3 is not particularly subjected to As contam-

ination, it is not likely that this enrichment is due to any anthropogenic source.

The comparison of arsenic and iron total concentrations in core 3 (Fig. 9) show that these elements are well correlated ( $r = 0.98$ ,  $p < 0.01$ ,  $n = 16$ ), indicating that both are sensible to the redox potential (Levinson, 1980; Reimann and de Caritat, 1998).

Another possible polluting element is uranium, that in the region can be associated with the use of fertilisers or emission from the combustion of coals. The profiles of this element did not show a well-defined behaviour. In core 1 granulometry corrected concentrations of uranium presented increasing values with depth, a behaviour that did not agree with iron's that is relatively homogeneous (although not confirmed by correlation coefficient:  $r = -0.51$ ;  $p > 0.01$ ;  $n = 29$ ). Uranium is a redox sensible element (Reimann and de Caritat, 1998) that is soluble under oxidising conditions and precipitates under reducing conditions (Bareille et al., 1998), therefore uranium seems to be remobilised and leached under the oxidising conditions of the surface (mainly at low tide) while iron is supposed to precipitate. Although cores 3 and 4 also show increasing concentrations with depth, this is not as clear as for core 1. While core 4 concentrations decrease in the top layers, indicating a probable leaching, contrarily core 2 shows a more marked increase in the top 10 cm. The roots zone, as discussed in Section 3.1 may affect the behaviour of this metal that, due to a better oxygenation of the sediment will be under a mobile form that eventually would adsorb on or even be absorbed by the roots. Further work on speciation (see for example Clark et al., 1998) should be necessary to understand better the interactions of roots and uranium in the sediments. Deeper concentrations of uranium should also be influenced by ground water infiltration (see discussion below).

Iron and manganese in sediment cores are regarded as redox sensible elements that tend to precipitate at redoxiclyne depths. A general trend for iron concentrations is a steep increase from surface until the redoxiclyne (where iron precipitates) and then a slow decrease until deeper stability (Presley et al., 1972; Lacerda and Rezende, 1987). However, this behaviour, observed in submerged sediments of oxygenated waters is frequently disturbed. The redoxiclyne can be too close to the surface sediments and

Table 3

Results of the leaching experiments for establishing the leachability of bromine in some bromine enriched samples

Sample	Total concentration ( $\mu\text{g g}^{-1}$ ) <sup>a</sup>	Concentration after leaching ( $\mu\text{g g}^{-1}$ ) <sup>a</sup>	% associated with insoluble phases
Core 1 (0–3 cm)	265 ± 11	43.1 ± 0.2	13.2
Core 1 (3–6 cm)	208 ± 7	46.6 ± 0.3	22.4
Core 1 (6–9 cm)	305 ± 13	43.2 ± 0.2	14.2

<sup>a</sup>  $n = 3$ .

only a slow reduction of concentrations is observed (Wasserman et al., 1998); furthermore, other parameters like granulometry, anthropogenic inputs, biological activity and mineralogy may interfere in the profile. In this study, cores 1 and 4 (Figs. 7 and 10) show slightly increasing concentrations with depth that indicate an insufficient variation in the redox potential. On the other hand, the two peak concentrations observed in core 2 (Fig. 8) confirm the presence of two oxidising zones (UOZ and LOZ) in mangrove sediments with high root biomass. In this core, many other elements are probably co-precipitating with iron oxides, therefore showing good correlations with iron (for example zinc). Core 3 (Fig. 9) show a recurrent increase in granulometry corrected concentration of the first layer that is attributed to a strong reduction in granulometry, but also to an associated increase in oxidising conditions. In sediments with very low percentages of fine grained fraction, iron coatings on quartz grains (Carrol, 1958) may artificially increase concentrations after granulometry correction. At the level 18–21 cm, the percent of fine grained fraction was as small as 0.4% and the granulometry corrected concentration of iron was 263%, a completely unreliable value that was removed from the graphic representation (in Fig. 9). This behaviour is clearly the result of the presence of iron associated with the coarse sediments, that are erroneously attributed to be associated with the fine grained sediments in the calculations.

Total concentrations of iron in Core 3 (Fig. 9) did not show any correlation with granulometry ( $r = 0.21$ ;  $p > 0.01$ ;  $n = 16$ ), probably as a result of the low percentages of fine grained sediments (between close to 0 and 50%).

### 3.4. Rare earth elements

Cerium, europium, lanthanum, lutetium, samarium

and ytterbium present similar chemical behaviour in the environment (Reimann and de Caritat, 1998). The granulometry corrected profiles of all four cores (Figs. 7–10) confirm that rare earth elements (REE) behave similarly in the sediments of Sepetiba Bay. In core 1, concentrations tend to slightly increase until the depth of 75 cm. Then, a strong increase in concentrations is observed. Other elements like hafnium, arsenic, thorium and uranium show a similar trend. One possibility that has already been discussed in other works (Lopez-Portillo, 1989; Reay et al., 1992) is the infiltration of continental ground waters that would hardly mix with the overlying seawater due to the presence of a thick layer of fine grained and relatively impermeable sediments (in core 1, at least 50 cm). This percolation of ground water is confirmed by the behaviour of bromine, that is a typically marine element and presents a strong impoverishment in these layers. In order to confirm this process, extractions of water leachable bromine were performed on three samples (Core 1, levels 0–3, 3–6 and 6–9 cm; see Section 2) revealing that after leaching very little bromine (Table 3) is associated with insoluble phases (only an average of 17.6% of the total concentrations is insoluble).

Although studies on the ground water elemental chemistry are not available, Francisco and Cunha, 1977 observed the presence of uranium and thorium containing rocks that may also contain rare earth elements. Monazite sands have been observed in a number of sites in Sepetiba Bay, that may contain concentrations of up to 6% of Th and 0.32% of U (Leonardos and Santos, 1972). Further, the observed increase in concentrations of REE with increasing depth should be the result of upward diffusion and mixing of this ground water with seawater.

Cores 3 and 4 (Figs. 9 and 10) show a behaviour similar to core 1, with a slight downward increase in concentrations that should be attributed to ground water infiltration, but in these cores this is not

confirmed by bromine concentrations. In core 3, the very high values observed in the top layer is again attributed to a granulometry effect.

It is interesting to note that in core 1 a peak concentration appears at a depth of around 30 cm. If the Zn profile is used for dating, this depth should be associated with the early 70s, coincident with beginning of the construction of the nuclear power plant of Angra dos Reis, in the neighbouring Ribeira Bay. If we consider that most REE are used in the nuclear industry, it is reasonable to think that these peak concentrations are associated with the nuclear plant. Nevertheless, the multiple character of the industrial activities in the Sepetiba Bay area renders difficult the attribution of the responsibility of this slight contamination.

### 3.5. Other elements

Barium, hafnium and thorium are frequently considered as geogenic and are probably associated with the REE (Reimann and de Caritat, 1998). Anthropogenic sources of Th associated with fertilisers and coal combustion can also contribute to the total concentrations in the sediments. Their concentrations in the base of cores 1 and 4 (Fig. 6) significantly increase and the explanation for that behaviour may be the same as for the REE enrichments associated with the mineralised ground water infiltration. In this case, thorium reaching the core base through ground water should also come from fertilisers applied in the adjacent areas. The other cores present a general trend of decreasing concentrations with depth, the same as the REE and uranium confirming the geogenic origin of these elements.

The co-precipitation of some elements like Co and Zn (also Cu and other elements) in iron hydroxides (Jenne, 1968) would engender good correlations between these metals and iron. In the case of Zn, as discussed before, the very strong anthropogenic inputs would mask any possible co-precipitation, however, Co shows significant correlations within (for both granulometry corrected and total concentrations) all cores (correlation coefficients always very close to 1.00).

The correlation between caesium and iron and scandium and iron are significant (Figs. 3–6), yet these elements are not reported to be specially asso-

ciated (Reimann and de Caritat, 1998). Co-precipitation of caesium or scandium with iron hydroxides are neither reported, although are possible processes. Actually, the geochemistry of these two elements is poorly known and can hardly provide explanation for these correlations.

Like some other elements discussed above, rubidium has a fairly unknown geochemistry. In the cores 1 and 2 (Figs. 3 and 4) it can be well correlated with iron concentrations, but in the cores 3 and 4 it could not be related to any of the studied processes.

As discussed above, bromine (Figs. 3–6) shows a behaviour that is apparently similar to that of zinc, presenting very high concentrations in the surface that decrease downward to the bottom of the sediment core (except core 2). Bromine presents concentrations that are one or two orders of magnitude higher than that of normal shale values (Table 1). However the only source of bromine in the region is seawater that provides enough of this element to reach the observed values. The reduction in bromine concentrations with depth can be explained by early diagenesis that reduces the pore size and therefore eliminates seawater rich with this element. The infiltration of ground water already discussed above (confirmed by leaching experiments, Table 3) is also responsible for the observed fall in concentrations of bromine in the bottom of the sediments.

## 4. Concluding remarks

The advantage of a multi-element analysis like instrumental neutron activation is to produce at the same shot and without sample destruction a number of elements that for other procedures would be very long, and less precise.

At least in core 1 (probably also in cores 3 and 4), infiltration in the deeper layers of mineralised ground waters adjacent to the sampling sites enriches sediments with REE elements, uranium, thorium, hafnium, barium and arsenic.

Among the studied elements zinc is the only which is of anthropogenic origin. This was expected since a number of other studies had established the polluting character of zinc in this region. On the other hand, one of the questions posed in this work was to know whether Zn utilisation was associated with other less



studied elements. This question can be answered based on two different approaches. First, none of the studied elements did present a behaviour similar to that of zinc, i.e., very high concentrations in the top layers and (apparently) background concentrations in the bottom layers. Second, the comparison of the mean concentrations measured with natural values or shale values indicates that the studied elements are not contaminants (except zinc). Therefore, it can be concluded that the heavy contamination of zinc in Sepetiba Bay sediments is not associated to any other of the studied elements.

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