Publicado em 2002 na Revista de Pesquisa e Desenvolvimento, 4(3):137-142

A PRELIMINARY STUDY ON THE BEHAVIOUR OF TRACE ELEMENTS IN SEDIMENT CORES FROM ILHA GRANDE (RIO DE JANEIRO) BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

The present work aims to identify atmospheric and marine inputs of 9 metals (Ba, Co, Cr, Cs, Fe, Hf, Rb, Sc, Zn), 8 rare earths (La, Ce, Nd, Sm, Eu, Tb, Yb e Lu), 2 actinides (U, Th) and 3 non-metals (As, Sb, Se) in sediment cores from a remote area, the Biological Reserve of Praia do Sul, Ilha Grande, Rio de Janeiro, Brazil. The sediment cores were sampled in a peat bog (out of the tidal reach) and in a mangrove, downstream of the peat bog. The analytical technique employed was Instrumental Neutron Activation Analysis. The samples were irradiated for 16 hours at a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} at the IEA-R1 reactor of IPEN. The measurements of the induced gamma-ray activity were carried out by high resolution gamma spectrometry, with an hyperpure Ge detector. A preliminary sediment dating with Po-210 was also carried out by applying radiochemical procedures and measurements were done in an Alfa spectrometer The results indicate that the peat bog core present a slight surface enrichment that can be attributed to atmospheric inputs. Increasing concentrations of metals with age is probably due to history of soil occupation. In the mangrove core, no significant increase in concentration could be detected in the surface sediments (except for Zn) confirming the suitability of the peat bog core as a tracer for atmospheric inputs

I. INTRODUCTION

Although heavy metals are rather chemically stable elements, their high toxicity pulled researchers to track the paths they should reach humans. Amidst the paths that were identified, the atmosphere had shown to spread elements through significant areas, overcoming global frontiers. For instance, some authors have measured metallic fallout in Greenland ices [1] and also in Alpine lake sediments [2]. These pollutants were estimated to be originated partly from geogenic sources but an important contribution was identified as industrial [3, 4].

Although in this very remote regions, the contamination with metals are barely detectable, in some areas the atmospheric spreading of metals became a real pollution problem. Lindqvist et al. [5] studied mercury contamination in Swedish lakes and observed that the pollution originated from the north-industrialized Germany was reaching alarming concentrations that would affect biota of the lakes. In some lakes fishing had to be prohibited.

In Amazonian region, the atmospheric contamination by mercury was also shown to be significant as determined by degassing experiments in the French Guyana [6]. The atmospheric spreading of the mercury used in gold mining was attributed to contaminate the Tucuruí dam (water, sediments and mainly fish), an area where no significant gold mining activity was reported [7].

The identification and quantification of metallic atmospheric inputs always constituted a challenge for environmental scientists. The most obvious approach is the direct measurement of the atmospheric fallout, that can be carried out through rain water [8] and particles [9] analyses. Although direct measurements are very precise procedures, the natural variability requires long term monitoring, that are very costly and do not permit depicting the historical evolution of the contamination. Furthermore, in this kind of study it is difficult to distinguish between natural and antropogenic fallout.

An alternative to direct measurements is the study of remote sedimentary records. In these procedures it has to be assumed that no direct metal input is present, except

atmospheric. Therefore, some conditions have to be fulfilled in order to consider an area suitable for atmospheric input studies: 1) no external of any kind can be present in the drainage basin (that should preferably be a pristine area); 2) It must be a continuously sedimentary environment (preferably permanently submerged), and 3) although sedimentary, no tidal marine inputs can be present. Altitude lake sediments and peat bogs have shown to be suitable environments for the study of atmospheric inputs [10-12]

The aim of the present work was to determine the atmospheric inputs of 9 metals (Ba, Co, Cr, Cs, Fe, Hf, Rb, Sc, Zn), 8 rare earths (La, Ce, Nd, Sm, Eu, Tb, Yb e Lu), 2 actinides (U, Th) and 3 non-metals (As, Sb, Se) in a Po-210 dated sediment core from a remote peat bog, located in the Biological Reserve of Praia do Sul, Ilha Grande, Rio de Janeiro, Brazil. The comparison of the peat bog core with an estuarine core would permit the distinction between atmospheric and non atmospheric inputs in the region.

II. MATERIAL AND METHODS

Study Area

The Ilha Grande is a coastal island located in the center of Ribeira Bay, which is a semi enclosed bay of the Southeast coast of Rio de Janeiro State, Brazil (Figure 1). It is a particularly important environment where background levels could be established for the region (e.g.: [13]). In spite of the quite natural condition, which characterizes the island as a suitable environment for remote area studies, the island is subjected to atmospheric inputs derived from the mega-urban centers of São Paulo and Rio de Janeiro [14, 8].

The studied marsh (figure 1) was chosen for its depositional and natural conditions. It is located in a Law protected Biological Reserve (Praia do Sul), in the southernmost basin of the Ilha Grande. The environment is characterised by a dense humid tropical forest cover (Mata Atlântica), aged of circa 150 years. The region suffered from forest burnings since the indian occupation, 3000 or 4000 years BP. The primitive agriculture remained and was intensified during the Portuguese occupation until the early 19th century, when the land was definitively exhausted and abandoned [15]. Based on the preceding author, Silva-Filho et al [16] summarised the occupation of the region in a time scale scheme.

The chemical characteristics of the studied marsh were described by de Paula et al. [13] who measured average alkalinity of 0.56 meq L^{-1}, conductivity of 133 µS cm^{-1}, pH of 6.0

Sampling and Analytical Procedures

The sediment core T4 was collected in a peat bog area. The sampling location is covered with vegetation and has an extremely difficult accessibility. Core 5 was collected in a mangrove area in the margin of the Leste Lagoon (Figure 1). The core was collected with an Acrylic tube and sliced *in situ* with a plastic spatula. The samples were stored in plastic Zip-lock bags and refrigerated at 4°C until the laboratory.

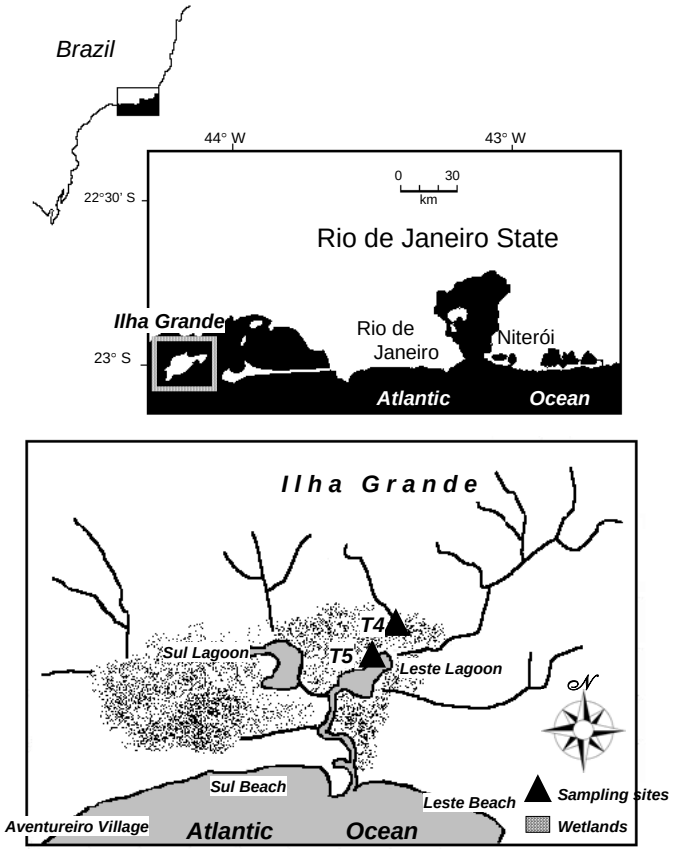

Figure 1: Sampling sites

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^2 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 hours at a thermal neutron flux of 10^{13} n cm^{-2} s^{-1}, 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 a 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 ^{60}Co. Two series of counting 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 VISPECT 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 material *Buffalo River Sediment* (NIST SRM 2704).

Preliminary results on dating of the layers were carried out with Po-210. Radiochemical extractions with $HNO_3/HClO_4$ were performed in 0.5 - 1.0 g of the sample. Po-210 was spontaneously deposited in steel discs that were measured by alpha spectrometry [17]

III. RESULTS AND DISCUSSION

The figures 2a and 2b present the concentration profiles of selected elements against time in years before present (Years BP) of core 4 and figures 3a and 3b present the same elements for core 5. The choice of the elements was based on a cluster analysis of both cores, that yielded the gathering as presented in Tables 1 and 2. Representatives of each group were selected and some important elements, such as As (as pollutants) and Fe, due its geochemical importance (redox sensible element), also were included.

TABLE 1. Results of the Cluster Analysis for core 4 (the bold symbols represent the selected elements)

1	2	3	4	5
La, **Rb**, Nd	Sm, **Th** Sc, **Cr**, Hf	Cs, **U**, Yb, Ta, **Fe**, Co, Tb, **As**, Lu, Sb	**Ce**, **Zn**	**Ba**

TABLE 2. Results of the Cluster Analysis for core 5 (the bold symbols represent the selected elements)

1	2	3	4	5	6
La, Nd	Sm, **U**, **Th**, Sc, **Cr**, Eu, Yb, Tb, Cs, Ta, Lu, Sb, **Fe**, Co, **As**, Hf	**Rb**	**Zn**	**Ce**	**Ba**

Even though all the profiles present a general trend of increasing concentrations with depth, it is possible to identify in most of the polluting elements (Zn, As, Cr and Fe) but also La and Ce, a steep increase in concentrations starting at the last 15 years. The increase in concentration observed also could be attributed to geochemical processes at the interface of the sediments. The thick of the layers corresponding to the first 15 years does not exceed 1 cm depth.

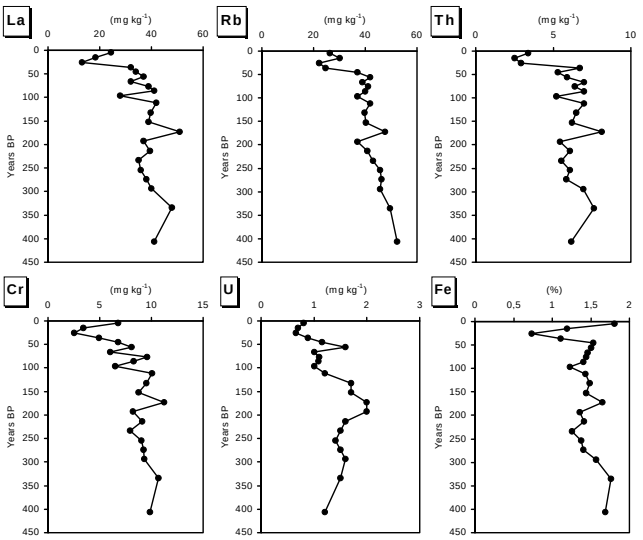

Figure 2a. Concentration profiles of La, Rb, Th, Cr, U and Fe in core 4

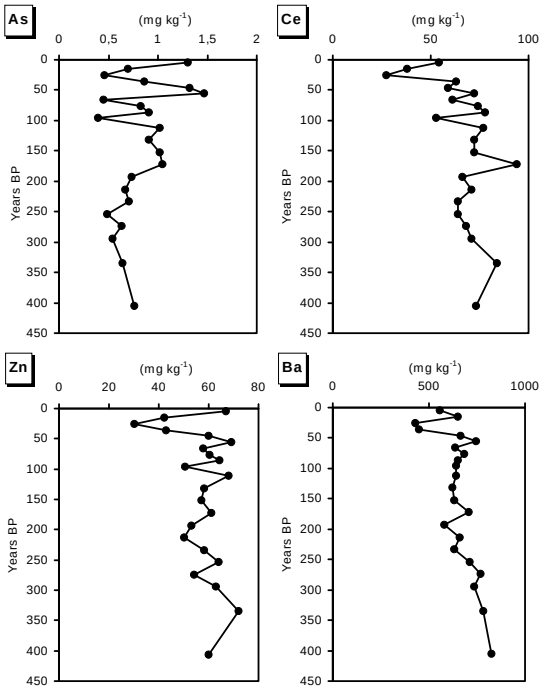

Figure 2b. Concentration profiles of As, Ce, Zn and Ba in core 4

It is worth note that the increase in concentrations with age should be attributed to the changes in the drainage basin soil use. When indians (Caiçaras) occupied the region, their practices were semi-nomad and based on burning forest, cultivation during a maximum of 5 years and moving elsewhere after this time. The group would come back to the same land 10 or 15 years later, when forest was partly regenerated [15, 18]. In the seventeenth century, Portuguese occupation intensified soil use with the same primitive procedures, but reducing the lag for forest

recovery [18]. This model is coherent with our results, showing that the increase in concentrations observed 400 years BP should be attributed to intense Portuguese soil exploitation. As the soil gets leached, eroded and impoverished, the elemental contributions to the peat bog decrease, as it can be observed between 400 Years BP and 150 Years BP. After Oliveira et al. [15], in the 19th century the region is completely abandoned and the recovery of the forest further increases the depletion of elements in core 4.

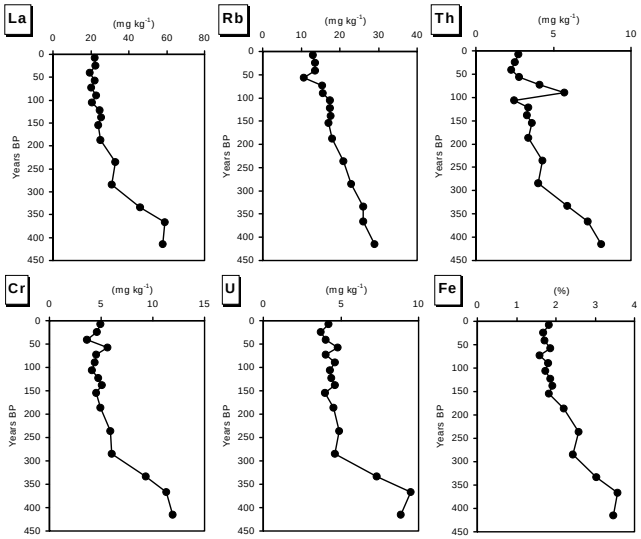

Figure 3a. Concentration profiles of La, Rb, Th, Cr, U and Fe in core 5

Core 5 is located in the mangrove area, under the influence of the marine tides and therefore is subjected to marine inputs. It is interesting to note that the increase in concentrations corresponding to the last 15 years is not clear anymore. Instead, it can be observed a more supported increase in concentrations of Zn from the fifties to date. This enrichment, observable only for Zn, is attributed to the elevated inputs sourced in the industries present in the neighboring Sepetiba Bay. Recent works report concentrations of up to 2894 mg kg^{-1} of Zn in the sediments [19] that would easily reach the south shore of the Ilha Grande associated with particulate matter. Cd is another element that enters the Sepetiba Bay (associated with Zn) and would yield the same type of profile, but unfortunately, measurements of this metal were not possible with the applied analytical technique

The same enrichment observed in the older sediments of core 4, appears in the core 5, but now the curves seem more smoothed, indicating that although this core is not suitable to track atmospheric inputs, it confirms the sedimentation model as it was established for core 4

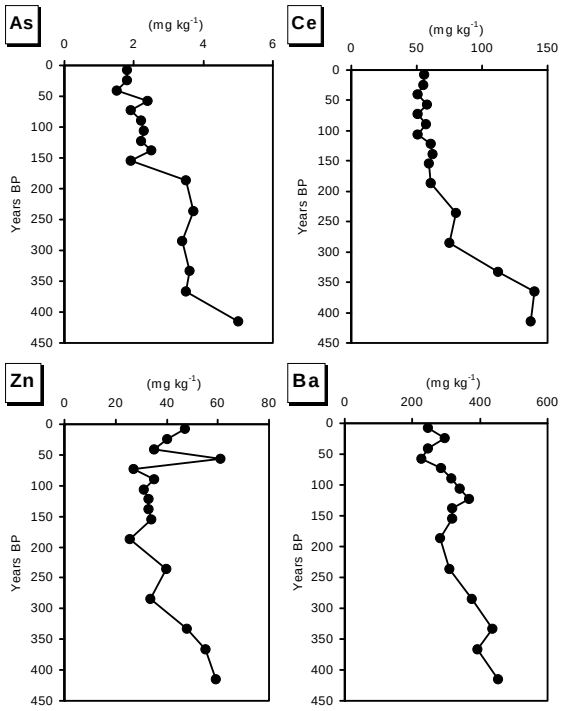

Figure 3b. Concentration profiles of As, Ce, Zn and Ba in core 5.

IV. CONCLUSIONS

In the present work, it was possible to identify a very recent increase in metallic concentrations of a core collected in a peat bog of the Ilha Grande. The results of sediment dating should still be taken with care, because, at the present stage of the research, only Po-210 could be measured and due to its short half-life, the confidence in precision is limited.

Measurements of Al that would permit normalization of the results are being carried out and the results would permit suitable calculations of precise deposition rates, an extremely valuable information to understand the atmospheric contributions for the whole region

V. AKNOWLEDGEMENTS

The authors are grateful to Mr. Carlos Athayde from FEEMA - Angra do Reis, who authorized the collection of samples in the Biological Reserve of Praia do Sul and borrowed the house seat for a three unforgettable days in that piece of paradise on earth. We sincerely hope this work will help the maintenance of the Reserve. We also owe thanks for the FEEMA staff in the Island, that kindly guided us in the forest up to the peat bogs where the cores were collected.

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