CHEMICAL CHARACTERIZATION OF BOTTOM SEDIMENTS FROM RIBEIRA DE IGUAPE RIVER, PARANÁ AND SÃO PAULO STATES, BRAZIL, BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

During several decades the Alto Vale of Ribeira region (SP-PR) suffered under lead mining activities in the region. Although in 1996 all such activities ceased, the mining activities left behind a huge amount of environmental liabilities mainly in the hydrographic basin of Ribeira de Iguape river. In the present study the chemical characterization of bottom sediments was undertaken and the concentration of the major (Ca, Fe, K and Na), trace (As, Ba, Br, Co, Cs, Hf, Rb, Sb, Ta, Th, U, Zn) and rare earth elements (La, Ce, Eu, Nd, Sm, Lu, Tb, Yb and Sc) by instrumental neutron activation analysis (INAA) were determined. The validation of the analytical methodology was performed by means of certified reference materials analyses and Z-score criterion was used. Eight points were sampled at the Ribeira de Iguape river and its majoritaries from Adrianópolis (Pr) (site 01) to Registro (SP) (site 08). Granulometric analyses and textural classification were undertaken in the sediment samples. The results obtained by using INAA were compared to UCC (Upper Continental Crust) reference values. The environmental tools of Enrichment Factor (EF) and Geochemical Index (*GI*) were used to assess the degree of metal contamination in the sediment samples. Samples from site 5 (Betari river – Iporanga, SP) presented high values for As, Sb and Zn and greater *IGeo* (3.1 – 5.5) and EF (>7.0) values for these elements classifying this point as highly polluted for these elements as well as a strong anthropogenic contribution. Site 7 (Ribeira river – Eldorado, SP) was considered moderately polluted for As, Br and Sb. The high concentration levels of some metals and metalloids reflect the contribution of mining activities from the past in the region. From the results it can be seen that although mining activities no longer exist since 1996, the deleterious effects in the environment are still present and strong.

1. INTRODUCTION

The area of this study is located in the Ribeira Valley (Figure 1) and corresponds to the hydrographic basin of the Ribeira de Iguape River and its tributaries. To the north and to the

east it boarders the basins of the Tiete and Paranapanema rivers, in the south, with the basins of the Iguassu River and to the west with the Atlantic Ocean [1]

Figure 1: Map of the Ribeira valley, SP - PR, Brazil

The watershed region of the Ribeira do Iguape River, Paranaguá-Iguape-Cananéia estuarine complex and the various river basins located in this region and the Atlantic Ocean is known as the Ribeira Valley (Figure 2).

This region occupies an area of 2,830,666 hectares (28,206 km^2) in the southern state of Sao Paulo and east of the state of Paraná, with 1,119,133 hectares in the state of Parana and 1,711,533 hectares in the state of São Paulo, representing respectively 39.5% and 60.5% in relation to the total area of the basin [1]. The Ribeira do Iguape River is the main source of Iguape-Cananéia-Paranaguá estuarine complex freshwater known as Lagamar. Lagamar is of great environmental importance that extends for 200 km of coastline from north of the Ecological Station Juréia-Itatins in São Paulo to Pontal Sul, Parana State. It is a very complex ecosystem, which includes a set of lagoons, inlets, bays, estuaries, salt marshes and islands [2].

The Ribeira de Iguape river is formed by the rivers Acungui and Ribeirão Grande, in Paraná state, northwest of the Metropolitan Region of Curitiba, at an altitude of approximately 1,000 meters. It keeps the name of Ribeira river up to the nearby town of Eldorado, in São Paulo State. It has a total length of approximately 470 km, being approximately 120 km in Paraná lands. Its mouth is located in the municipality of Iguape, at Barra da Ribeira. However, since the conclusion of the Valo Grande channel, part of its waters do not flow directly to the sea, but rather to the Mar Pequeno or to Iguape, between the mainland and Ilha Comprida [1]. Valo Grande is the "channel of interconnection between Ribeira de Iguape river and Mar Pequeno", built between 1827 and 1852, to facilitate the access to the port of Iguape. The main tributaries of the Rio Ribeira de Iguape are Juquiá, São Lourenço and Jacupiranga rivers.
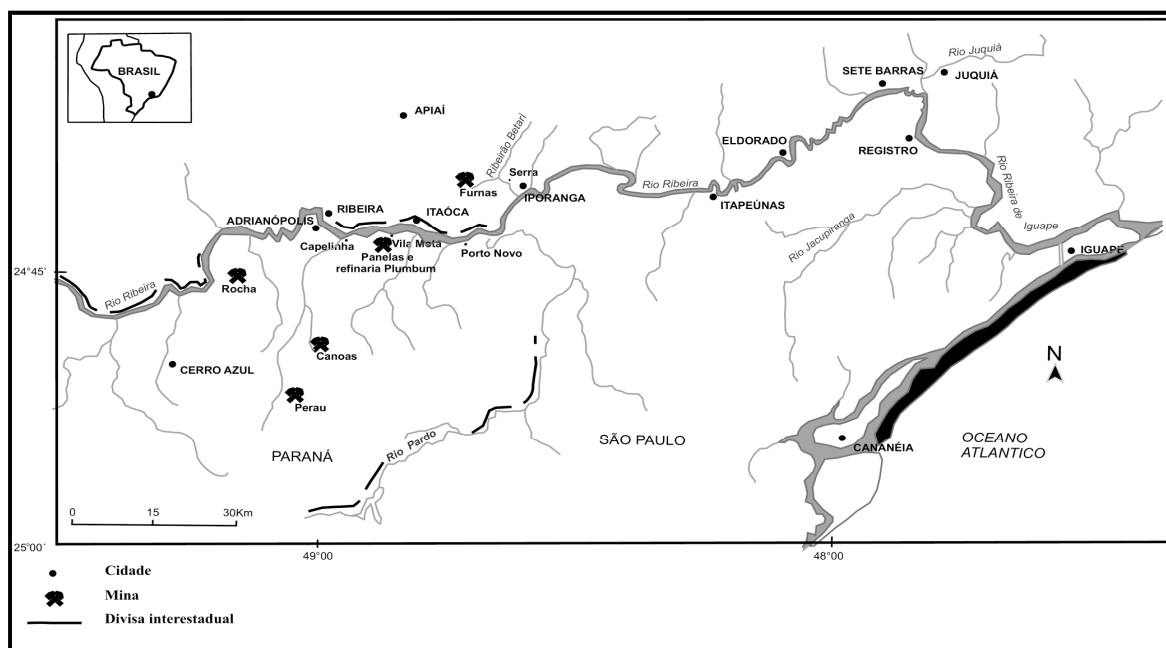
Figure 2. Ribeira de Iguape hydrographic river basin

São Paulo state is divided, according to the State Law n°. 9,034 /1994 [3] which established the National Policy of Water Resources, in 22 Units for Water Resources Management (UGRHIs). These UGRHIs are structured within the concept of river basin. The portion of the Ribeira de Iguape river basin located in São Paulo state corresponds to UGRHI 11, managed by CETESB – the Environmental Company of São Paulo State. CETESB maintains an environmental monitoring program, with the purpose of subsidizing the diagnosis and control of the quality of surface waters and sediments of this aquatic system, evaluating their compliance with environmental legislation, performing physico-chemical, biological, toxicological and ecotoxicological tests and inorganic and organic compound determinations [4].

Recent years have seen an increase of research on metals present in sediments, not as a sink or a location of deposition of metal species, but as an active agent playing a key role in the interaction of these species with aquatic life biota. Therefore, the analysis of sediments from rivers, lakes and oceans has become important in environmental assessments. The definition of chemical and physical characteristics of the sediment provides adequate parameters to assess the degree of contamination of the watershed and the impact of contaminated sediments on aquatic biota [4]. In this context, it is only possible to assess the toxic effect of metals in aquatic ecosystems through an integrated assessment, using data from the analysis of water, sediment and biomarkers.

The present study is part of a larger project entitled "Availability of metals Cd and Pb and metalloid As in the Ribeira do Iguape river hydrographic basin and its tributaries: an environmental contamination assessment". Within this context the chemical characterization of sediments is important not only to evaluate the concentration of toxic metals Cd and Pb and metalloid As but other elements such as trace and rare earth elements, as well.

Among the activities that cause environmental impact mining is extremely important to the economic and social development of many countries. The extraction and processing of ores when practiced without responsibility and without sustainable development principles has created serious environmental problems such as: deforestation, erosion, sedimentation, and production of huge amounts of mining waste products containing high levels of heavy metals which in turns dispersed into the environment contaminating air, water and soil, putting at risk not only the local biota but human health as well.

During virtually the entire 20th century, the Ribeira Valley region suffered constant environmental degradation resulting from intense exploration and refining of ores from lead, zinc and silver mines that were processed in the region, in a rudimentary manner, and without any control over environmental impacts. In 1996, all these activities were interrupted. However, they left the banks of the river unprotected and subject to environmental liabilities. These consisted of ore tailings with high levels of heavy metals, generating impacts on water quality and sediments of the Ribeira do Iguape River and its basin.

In the studies carried out by CETESB [26], from 1981, it has been found that the main sources of metals that contributed to the contamination of the Ribeira de Iguape River were located in the ribeirão Rocha, where the ore was extracted crude by Rocha mining (Paraná state), between the towns of Ribeira and Itaóca, where the Plumbum Refinery (located on the shore of Ribeira de Iguape River – Paraná State) processed the treatment of this ore. The contribution of metals also happened in ribeirão Furnas, where the CAF (Companhia Argentífera Furnas) operated, in the state of São Paulo, who performed the extraction and primary processing of lead ore.

Lopes Jr. et al. [5], conducted a study of low density multielemental geochemical mapping in the region of the High Ribeira Valley, covering the entire length of the river basin of the Ribeira de Iguape river. The aim of this study was to evaluate the quality of fluvial sediments of the region in terms of its chemical composition and to assist in the definition of areas with problems, present and future, to the environment, focusing on biota and human health.

This study contributed to the generation of important data about exposure to lead (Pb) and arsenic (As) of ecosystems and human groupings at the Top and Middle Vale do Ribeira (SP - PR). In 2003 the mining region of Furnas, Moraes et al [6], performed chemical analysis in fishes of Ribeirão Furnas and observed that two species catfish (bagres) and catfishes (cascudos) were contaminated with Pb. These species of demersal fish, who seek their food in clayey sediments, suffer strong impact, since these sediment fractions concentrated high levels of Pb. Although Pb is virtually absent from the waters of the Ribeira river and its main tributaries as observed by monitoring performed during the study, the same cannot be said of the sediments of the bad of the Ribeira river and tributaries that have Pb mines in their catchment areas.

The present study aimed to chemically characterize the bottom sediment samples from the Ribeira de Iguape River and its tributaries, regarding the occurrence of major (Ca, Fe, K and Na), trace (As, Ba, Br, Co, Cs, Hf, Rb, Sb, Sc, Ta, Th, U, Zn) and rare earths (La, Ce, Nd, Sm, Lu, Tb, Yb) elements by INAA. The results obtained were compared with the reference values of UCC (Upper Continental Crust) and evaluated by tools of enrichment factor (EF) and geoaccumulation index (*GI*), used to characterize the degree of sediments contamination by metal and trace elements.[7,8]

2. MATERIALS AND METHODS

2.1. Sampling and sample preparation

2.1.1. Sampling

Water and sediment samples were collected in 08 (eight) sampling points in the Ribeira do Iguape River and tributaries, during May/2011 (points 03, 05, 06, 07 and 08) and in September/2011 (points 01, 02 and 04), under technical, operational and logistic support from the CETESB Sampling Sector. The sampling was carried out in two periods due to the extensive area studied. The sampling points were established based on studies carried out in the region, by CETESB, between 1996 and 1998 by Eysink et al [9]. Table 1 shows the sampling points and their geographical positions. Water samples were collected in a simple way with the aid of a stainless steel bucket, transferring 250 mL volume collected in a polyethylene bottle, preserved with HNO_3. The sediment samples were collected using a Van Veen dragger and placed in stainless steel tray and transferred to 500 mL wide mouth polyethylene bottles, filled to their entire volume. The samples were kept refrigerated in a cooler with ice and sent to the laboratory. The materials used in the collection are appropriate for each type of matrix, subject to the analytical standards and quality standards for cleanliness and preservation for trace and metal element determinations. Field measurements such as physico-chemical parameters, redox potential (Eh) and pH of the sediment samples with appropriate equipment were also performed (Table 2). Sampling points are shown in Figure 3.

Table 1. Sampling points from Ribeira de Iguape river and tributaries

| Sampling points	Identification	Geographical position (GPS)	Depth (m)
Point 1	Ribeira River, downstream of the confluence of Ribeirão Rocha in Adrianopolis, PR	S 24°41'13.40" W 49°06'45.10"	2.0
Point 2	Ribeira River, upstream of the refinery Plumbum, in the town of Ribeira, PR	S 24°39'34.70" W 49°00'33.30"	2.5
Point 3	Ribeira River*, Itaóca - PR, downstream Plumbum refinary	S 24°39'23.70'' W 48°49'54.80''	2.0
Point 4	Betari river, upstream of the confluence of Ribeirão Furnas, in Iporanga, SP	S 24°31'55.90" W 48°42'09.50"	0.3
Point 5	Betari River, Iporanga- SP, downstream Furnas River	S 24°33'8.93'' W 48°40'38.64''	3.0
Point 6	Ribeira do Iguape River, Iporanga - SP, downstream of the confluence of the Betari river	S 24°35'4.80'' W 48°35'25''	2.5
Point 7	Ribeira do Iguape River, Eldorado city, SP	S 24°31'34.90'' W 48°06'7.10''	2.0
Point 8	Ribeira do Iguape River, Registro - SP, downstream of the Juquiá River	S 24°26'24.50'' W 47°49'37.20''	2.5
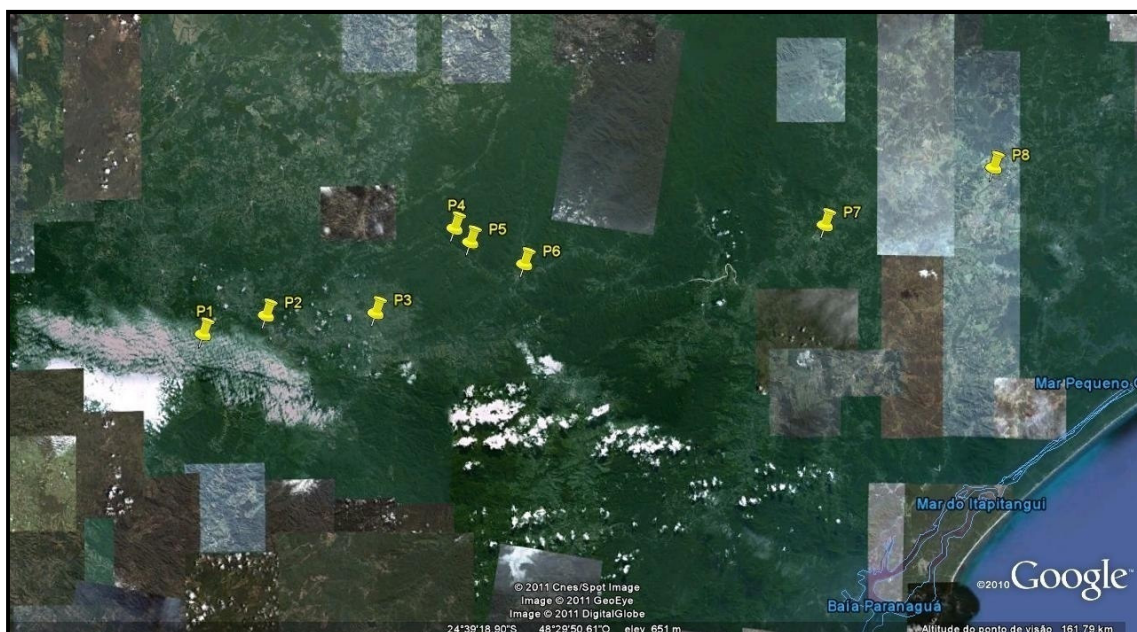
Figure 3. Location of the sampling points in the Ribeira do Iguape river and tributaries

Table 2. Sediment sample physico-chemical parameters

Sampling points	Sediments	
	pH	Eh (mV)
Point 1	7.0	-182.9
Point 2	7.2	-84.7
Point 3	7.8	70.5
Point 4	6.8	311.0
Point 5	7.5	-144.2
Point 6	7.3	187.0
Point 7	7.5	-208.0
Point 8	6.9	-90.3

2.1.2. Sample preparation

The sediment samples were previously passed a 2 mm sieve to remove the coarse fraction and dried at 40^0 C in a ventilated oven until constant weight. The dried sample was macerated

in an agate mortar and passed through a 0.074 mm sieve (200 mesh) to obtain homogeneity of the sample. In this condition the samples were ready for INAA analysis.

2.2. Analytical methodology applied

Several instrumental analytical methods are applied for the determination of metals, major, trace and rare earth elements in environmental and biological matrices. In this study Instrumental Neutron Activation Analysis (INAA) for the determination of As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Tb, Th, U, Yb and Zn in sediments was applied.

2.2.1. Instrumental Neutron Activation Analysis (INAA)

INAA is one of the most important methods among those available for the analysis of trace elements. In the case of comparative INAA, samples are irradiated together with a standard, whose composition is as similar as possible, under the same conditions. After irradiation, the sample and standard are measured on the same detector, which allows the unknown concentrations of elements of interest to be directly calculated from the counting rates of the sample and the standard [10,11].

2.2.1.1. Experimental procedure

For the multielemental analysis, approximately 150 mg of sediment (in duplicate) and reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Single and multi-element synthetic standards were prepared by pipetting convenient aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman N^o41 filter paper. Sediment samples, reference materials and synthetic standards were irradiated for 8 hours, under a thermal neutron flux of 1 to 5x 10^{12} n cm^{-2} s^{-1} in the IEA-R1 nuclear research reactor at IPEN. Two series of counting were made: the first, after one week decay and the second, after 15-20 days, Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co, respectively. The elements determined by using this methodology were As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U, Zn and the rare earths Ce, Eu, La, Lu, Nd, Sm, Tb and Yb. The analysis of the data was made by using in-house gamma ray software, VISPECT program to identify the gamma-ray peaks and by an ESPECTRO program to calculate the concentrations. The uncertainties of the results were calculated by error propagation. The precision and accuracy of the method was verified by using the Z score according to Bode [14] for Soil 5 (IAEA), Lake Sediment SL1 (IAEA) and BEN Basalt-IWG-GIT reference materials analyses. Details of the analytical methodology is described at Larizzatti et al [13].

2.2.1.2 Acceptance of the results obtained by INAA - Z-score criterion

For validation of the results obtained by INAA, Z-score criterion is frequently used. [12] The calculation of the standardized difference, or Z value, of an analytical result is given by equation 1:

$$Z_i = \frac{C_i - C_{ref}}{\sqrt{\sigma^2_i + \sigma^2_{ref}}}$$ (1)

where:
C_i: concentration of element i in the CRM analysis,
C_{ref}: certified or consensus value of concentration for element i,
σ_i: uncertainty of the concentration of element i in the CRM analysis;
σ_{ref}: uncertainty of the consensus value for element i.

According to Bode [14], the use of Z value for approval of results considers that if $|Z| \leq 3$, the result of concentration of an individual element in the reference material that is being analyzed must be within 99% of the confidence interval of the expected value.

3.   RESULTS AND DISCUSSION

3.1. Grain size sediment analyzes

The granulometric analysis of the sediment samples was performed by CETESB (Limeira) according to the 7473 and 1664-B Standard Methods [15]. The results are presented in Table 3. The granulometric classification was based on the following criteria: silt (particles from 0.004 to 0.063mm), Clay (< 0.004 mm) and sand (> 0.063mm). The textural characterization of sediments follows the Flemming classification [16].

In general, the sediment samples showed a high content of sand, in all sampled points, ranging from 36.3 to 91.5 %. Points 1, 7 and 8 presented a composition of highly silty sand, while point 3 presented a composition of extremely sandy silty mud. The remaining points (4, 5 and 6) showed moderate silt sand.

Quinaglia [17] cites Murdroch & Macknight [18] stating that many studies point to a correlation between the concentration of metals and the particle size of the sediment, suggesting higher concentrations in finer particles. However, Quinaglia [17] also points out that other fractions are also used with different purposes and that comparisons of results in different sizes of particles may be questionable, since the distribution of metals is variable. In this study, by granulometric classification we would expect a greater concentration of metals in points 1, 3, 7 and 8, however, this correlation was not observed. This relationship may not be due to the composition of the sediments sampled which are predominantly sandy.

Table 3: Granulometric analysis results for the sediment samples

Sample	Sand (%)	Silt (%)	Clay (%)	Textural classification [16]
Point 1	50.43	32.86	16.72	Highly silt sand
Point 2	74.92	19.64	5.45	Moderate silt sand
Point 3	49.14	41.88	8.99	Extremely silty sandy Mud
Point 4	91.54	7.00	1.47	Moderate silt sand
Point 5	79.40	17.55	3.05	Moderate silt sand
Point 6	78.09	19.04	2.87	Moderate silt sand
Point 7	49.81	39.47	10.73	Highly silt sand
Point 8	36.30	47.61	16.09	Highly silt sand

3.2 Acceptance of the results obtained by INAA - Z-score criterion

Figures 4, 5 and 6 shows Z-score values for the reference materials analyzed Soil-5, SL-1 and BEN- Basalt, respectively. In this study all the results showed values within the interval $|Z| \leq 3$, proving the precision and accuracy of the INAA analytical technique.
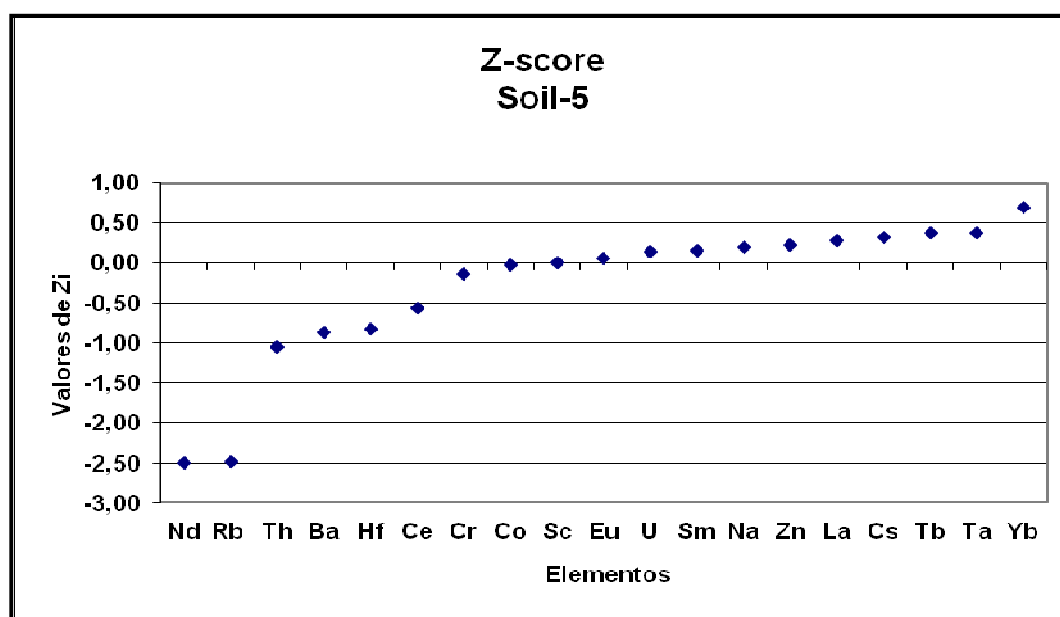

Figure 4: Z-score values obtained for the Soil-5 analyzed by INAA
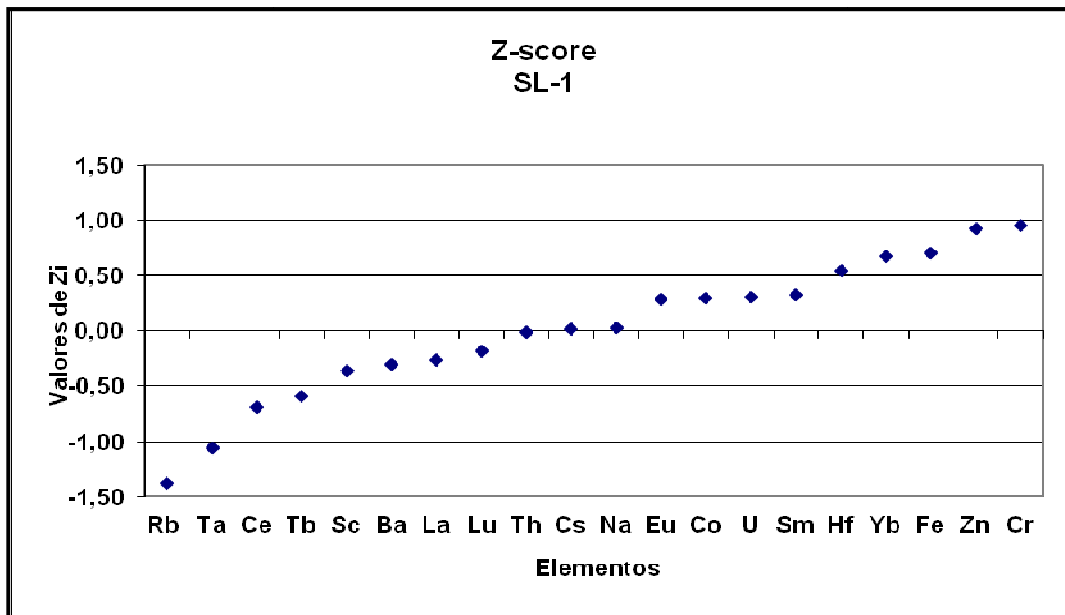
Figure 5: Z-score values obtained for the SL-1 analyzed by INAA
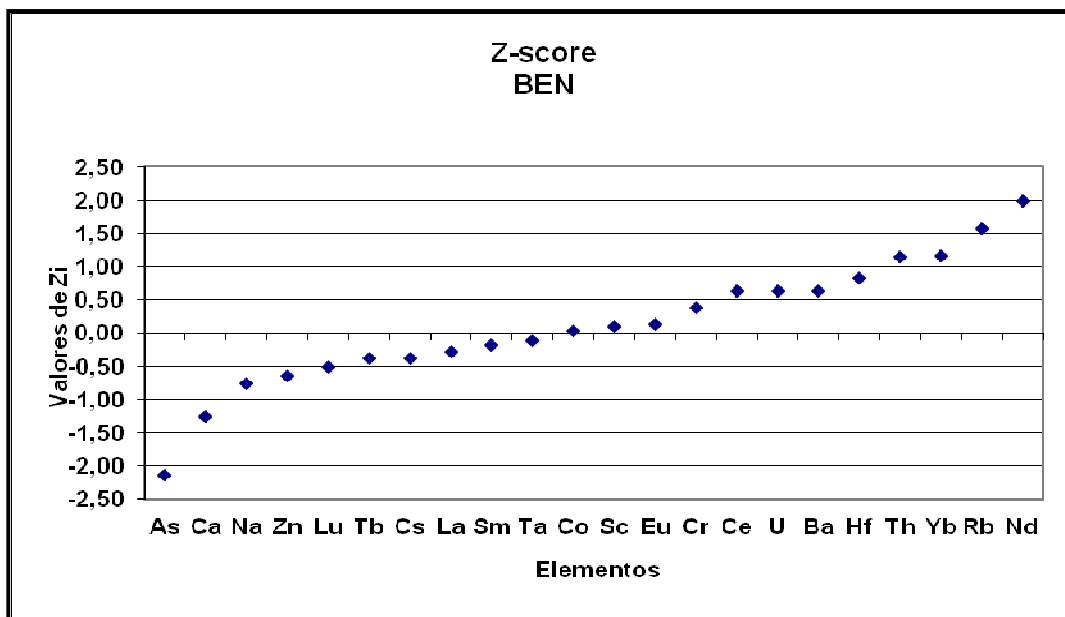
Figure 6: Z-score values obtained for the BEN-basalt analyzed by INAA

3.3. Results for the sediment analysis by INAA

Table 4 presents the results obtained for the sediment by INAA. As can be observed, the elements, Br, Co, Cr, Fe, Hf, Lu, In, Nd, Sb, Sc, Tb, Yb and Zn showed values higher than the values of UCC (Upper Continental Crust) in all sampling points. At point 5 the values of As, Na, Sb, and Zn are extremely high, with greater attention to As and Zn. Ca presented a value higher than the UCC value only in point 2. Ce presented a value lower than UCC value

only in point 4. Eu presents values exceeding the UCC value in practically all points, with the exception of point 5. The values of La were lower than the UCC value only in points 4 and 5. Rb was lower than UCC values in practically all points, with the exception of point 8. Sm presented a value lower than UCC value, only at point 6. Ta showed values lower than UCC value only in points 4 and 5.

Table 4: Results for the elements determined by INAA (mg kg^{-1}): mean (duplicate), standard deviation, and UCC values [19]

Elements	Sampling points								UCC
	PTO 01	PTO 02	PTO 03	PTO 04	PTO 05	PTO 06	PTO 07	PTO 08	
As	5.6 ± 0.7	4.4 ± 0.6	6.2 ± 0.4	3.0 ± 0.4	**139 ± 4.3**	9.0 ± 0.6	9.2 ± 0.3	8.7 ± 0.3	**2**
Ba	773 ± 59	876 ± 33	1121 ± 32	516 ± 32	444 ± 14	807 ± 43	774 ± 29	773 ± 29	**668**
Br	7.4 ± 1.8	3.5 ± 0.4	3.7 ± 0.2	5.9 ± 0.1	3.3 ± 0.2	2.4 ± 0.7	6.1 ± 0.3	5.1 ± 0.3	**1.60**
Ca (%)	2.2 ± 0.1	3.8 ± 0.1	2.4 ± 0.1	0.8 ± 0.1	2.1 ± 0.1	2.1 ± 0.1	1.5 ± 0.0	1.5 ± 0.0	**2.95**
Ce	144.7 ± 8.0	129.6 ± 5.0	111.7 ±3.3	61.0 ± 2.4	67.0±2.0	109.3 ±4.3	115.8±35	144.4 ±4.4	**65.70**
Co	18.2 ± 0.4	17.0 ± 0.3	18.5 ± 0.3	35.8 ± 0.6	21.3 ± 0.3	20.3 ± 0.3	20.6 ± 0.3	22.3 ± 0.3	**11.60**
Cr	72.9 ± 3.9	71.3 ± 2.3	67.5 ± 1.9	65.1 ± 2.5	57.5 ± 1.9	73.0 ± 2.4	83.0 ± 3.1	85.5 ± 2.7	**35**
Cs	3.8 ± 0.3	2.6 ± 0.2	3.4 ± 0.2	3.0 ± 0.2	3.3 ± 0.2	4.6 ± 0.2	5.2 ± 0.2	6.3 ± 0.3	**5.80**
Eu	2.05 ± 0.24	1.72 ± 0.09	1.52±0.05	1.05 ± 0.06	0.94 ±0.04	1.59 ±0.08	1.50 ± 0.04	1.84 ±0.05	**0.95**
Fe (%)	5.13 ± 0.06	5.78 ± 0.06	4.54±0.03	7.96 ± 0.07	4.72 ±0.03	4.86±0.04	5.01± 0.04	5.33 ±0.04	**3.09**
Hf	36.1 ± 1.3	49.3 ± 1.3	16.2 ± 0.4	9.1 ± 0.2	6.9 ± 0.2	17.3 ± 0.4	14.9 ± 0.3	19.1 ± 0.5	**5.80**
K (%)	-	1.9 ± 0.2	2.2 ± 0.2	-	1.2 ± 0.1	-	2.2 ± 0.3	2.3 ± 0.4	**2.87**
La	70.3 ± 1.4	63.0 ± 1.1	55.6 ± 0.6	29.3 ± 0.4	32.1 ± 0.3	52.3 ± 0.8	56.2 ± 0.7	69.2 ± 0.9	**32.30**
Lu	0.5 ± 0.1	0.5 ± 0.0	0.36±0.02	0.4 ± 0.0	0.35 ±0.02	0.4 ± 0.0	0.42 ± 0.02	0.55±0.03	**0.27**
Na	6726 ± 231	8395 ± 166	8035±119	3848 ± 103	3184 ± 48	8559 ±205	7012 ± 110	5678 ± 89	**25700**
Nd	48 ± 3	57 ± 3	49 ± 5	27 ± 2	27 ± 3	35 ± 2	33 ± 1	45 ± 4	**25.90**
Rb	86 ± 7	68 ± 2	104 ± 3	54 ± 3	62 ± 2	108 ± 6	108 ± 3	123 ± 4	**110**
Sb	0.87 ± 0.09	0.61 ± 0.06	0.8 ± 0.1	0.47 ± 0.04	6.7 ± 0.4	1.00 ±0.03	1.2 ± 0.1	1.2 ± 0.1	**0.31**
Sc	14.2 ± 0.6	13.5 ± 0.3	12.5 ± 0.2	24.1 ± 0.6	13.0 ± 0.2	13.6 ± 0.4	15.0 ± 0.3	16.7 ± 0.3	**7**
Sm	8.7 ± 0.3	9.2 ± 0.3	7.7 ± 0.1	5.0 ± 0.1	5.4 ± 0.1	4.1 ± 0.1	8.3 ± 0.1	9.8 ± 0.2	**4.70**
Ta	1.7 ± 0.1	2.3 ± 0.1	1.7 ± 0.2	0.4 ± 0.1	1.1 ± 0.1	2.3 ± 0.4	1.7 ± 0.1	1.7 ± 0.1	**1.50**
Tb	1.3 ± 0.3	0.9 ± 0.1	0.8 ± 0.1	0.8 ± 0.1	0.7 ± 0.1	1.0 ± 0.2	0.8 ± 0.1	1.4 ± 0.1	**0.50**
Th	15.7 ± 0.6	14.1 ± 0.4	11.8 ± 0.2	7.2 ± 0.2	7.5 ± 0.2	14.2 ± 0.4	15.1 ± 0.3	16.9 ± 0.4	**10.30**
U	2.8 ± 0.4	3.8 ± 0.2	2.4 ± 0.1	1.7 ± 0.3	1.6 ± 0.1	3.2 ± 0.3	3.1 ± 0.2	4.2 ± 0.2	**2.50**
Yb	3.5 ± 0.3	3.5 ± 0.2	2.1 ± 0.1	2.1 ± 0.1	2.1 ± 0.1	2.7 ± 0.2	2.3 ± 0.1	3.4 ± 0.2	**1.50**
Zn	108 ± 6	91 ± 3	91 ± 3	99 ± 4	**692 ± 20**	127 ± 5	123 ± 5	122 ± 3	**52**

Most of studies developed in the Ribeira de Iguape river sediments focused on the assessment of metals that are related to the mining activities in the area such as As, Cd, Cr, Cu, Pb and Zn [5,9,20].

The objective of the present study focused on metals Cr, Sb, Fe and Zn and metalloid As in sediments as well as some other trace and rare earth elements (REE) in order to characterize the chemical composition of the sediments in the studied area.

Although our study's objectives were to characterize chemical composition of the sediments in this area it has been well established that Pb occurs in the sediments mainly as results of contamination through mining activities.

Moraes in 1997 [20] verified that the isotopic ratio of sediments collected in this area, from Ribeira city until Mar Pequeno, was a fingerprint of the galena's Pb mining quarry showing that Pb contamination was indeed result of this mining activity. In the same study Moraes [20] also concluded that solid suspensions in water acted as transport and deposition agents of metals along the course of the Ribeira de Iguape River. This could possibly explain the high concentrations of As, Sb and Zn at stations 6, 7 and 8, once station 5 presented the higher concentration levels for these elements.

Guimarães and Sígolo [27], performed studies aiming to verify the contribution of slag produced by Plumbum mining, composed mainly of Zn, Pb and Cu in the contamination of the Ribeira de Iguape river. To achieve such objectives samples of slag and sediments in suspension (compartment considered in the literature as being important in transport and accumulation of contaminants) were analyzed. The analysis of the slag showed a density of $3,877 g.cm^{-3}$ and composition rich in Fe, Si, Ca; secondarily were detected lower concentrations of Al, Mn, S, K, P, Ti, Ba, Zn, Pb, Cu, and Cr. The authors concluded that an important part of heavy metals, such as Pb, Cu, and Zn, released as waste at the Ribeira de Iguape River during the ore smelting in the region of Alto Ribeira Valley, are deposited in sediments. Part of these metals is being mobilized along the sediment in suspension and migrating along the course of the river to its mouth, proved by the presence of slag in these sediments and high levels of several heavy metals determined in the study.

3.4. Enrichment Factor (EF)

The Enrichment factor (**EF**), defined as a double ratio normalized to a reference element (**RE**), is an index used as a tool to evaluate the extent of metal pollution in a given environment [21] and calculated by equation 2:

$$EF = ([M]/[RE]_{sed})/ ([M]/[RE]_{ref}) \tag{2}$$

Fe, Al and Sc are generally used as reference elements for normalization purposes [7]. In the present study Sc was chosen as a reference element and UCC values as reference values for sediments [19]. According to Zhang and Liu [22], if 0.5<EF<1.5, the elemental concentration is probably due entirely to crustal or natural weathering origins; values above 1.5 indicate anthropogenic contributions. The higher the EF value, the more severe the anthropogenic contribution.

Table 5 shows the results obtained for the EF calculated using the UCC values as reference values. There is still no regional reference value for comparison in Brazil and as such the UCC values are commonly used.

EF > 1.5 selected in Table 5 indicates sediments more enriched for the elements As, Br, Hf, Sb and Zn. The highest values of EF (EF > 7.0) were found in the sediment at point 5 for As, Sb, and Zn. In this case, there seems to be a strong anthropogenic contribution to these elements. Values between 0.5 < EF < 1.5 were found for the elements Ba, Br, Co, Cr, Fe, Th, U and Zn (with the exception of point 5) and REE (Ce, Eu, La, Lu, Nd, Sm, Tb, Yb) indicating that these elements are originating from the earth's crust and are not enriched. The other elements (Ca, Cs, Na, Rb and Ta) presented EF < 0.5, for the majority of sampling points and are impoverished in relation to UCC values.

3.5. Geoaccumulation index (GI)

Geoacumulation index has been used since the 1960s and has been widely used in studies of trace metals in Europe [23]. It was used for the first time for bottom sediments [24] and since then has been applied, with much success, for soil [23,25] and sediments contamination assessments [7,8].

Geoacumulation Index (GI) was calculated for the sediment concentration results obtained by INAA, adopting the same reference values used for the EF calculations (UCC values). The Equation 3, Muller [24] and Rezaee [8] is used for GI calculation.

$$Igeo = \log_2\left(\frac{C_{am}}{1,5C_{ref}}\right)$$

(3)

where
C_{am} = concentration of the element of interest in the sample
C_{ref} = reference concentration of the element of interest

The classification of the contamination levels from GI values is: < 0, basal level; from 0 to 1, not polluted; from 1 to 2, moderated polluted; from 2 to 3, moderated to polluted; from 3 to 4, polluted to lightly polluted; from 4 to 5, very polluted and >5, highly polluted. Table 6 presents the GI values for the INAA data.

Evaluating Table 6 results and its relation with the level of sediment contamination described above, based on GI values, we can infer that point 1 is moderately polluted by Br and Hf. Point 2 is moderately polluted by Hf. Point 3 is moderately polluted by Br and Sc. Point 4 is moderately polluted by As. Point 5 (Betari river, Iporanga, SP) is considered polluted to lightly polluted for Sb and Zn and highly polluted by As. Point 6 is moderately polluted by As. Point 7 is moderately polluted by As, Br and Sb. Point 8 is moderately polluted by As, Br, Hf and Sb.

Table 5: EF values calculated for sediment samples using UCC as reference values

Elements	Sampling points							
	01	**02**	**03**	**04**	**05**	**06**	**07**	**08**
As	1.4	1.1	1.7	0.4	37.4	2.6	2.1	1.8
Ba	0.6	0.7	0.9	0.2	0.4	0.7	0.5	0.5
Br	2.3	1.1	1.3	1.1	1.1	0.6	1.8	1.3
Ca (%)	0.3	0.3	0.5	0.1	0.4	0.4	0.2	0.2
Ce	1.1	1.0	1.0	0.3	0.5	0.8	0.8	0.9
Co	0.8	0.8	0.9	0.9	1.0	0.9	0.8	0.8
Cr	1.0	1.1	1.1	0.5	0.9	1.2	1.0	1.0
Cs	0.3	0.2	0.3	0.2	0.3	0.4	0.4	0.5
Eu	1.1	0.9	0.9	0.3	0.5	0.7	0.7	0.8
Fe (%)	0.8	1.0	0.8	0.7	0.8	0.8	0.8	0.7
Hf	3.1	4.4	1.6	0.5	0.6	1.3	1.2	1.4
La	1.1	1.0	1.0	0.3	0.5	0.8	0.8	0.9
Lu	0.8	1.0	0.7	0.4	0.7	0.8	0.7	0.9
Na (%)	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1
Nd	0.9	1.1	1.0	0.3	0.6	1.2	0.6	0.7
Rb	0.4	0.3	0.2	0.1	0.1	0.6	0.1	0.2
Sb	1.4	1.0	1.4	0.4	11.6	1.6	1.8	1.6
Sc	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sm	0.9	1.0	0.9	0.3	0.6	0.8	0.8	0.9
Ta	0.6	0.8	0.6	0.1	0.4	0.5	0.5	0.5
Tb	1.2	0.9	0.9	0.5	0.7	0.8	0.8	1.1
Th	0.8	0.7	0.6	0.2	0.4	0.7	0.7	0.7
U	0.6	0.8	0.5	0.2	0.3	0.6	0.6	0.7
Yb	1.1	1.2	0.8	0.4	0.8	0.8	0.7	1.0
Zn	1.0	0.9	1.0	0.6	7.2	1.2	1.1	1.0

Table 6: GI values for the sediment samples in the sampling points

Elements	Sampling points							
	01	**02**	**03**	**04**	**05**	**06**	**07**	**08**
As	0.89	0.54	-0.02	1.04	5.53	1.58	1.61	1.53
Ba	-0.37	-0.19	-0.96	0.16	-1.18	-0.31	-0.37	-0.37
Br	1.63	0.53	1.31	0.61	0.44	0.01	1.34	1.09
Ca(%)	-1.52	-1.17	-1.55	-0.87	-1.07	-2.46	-1.57	-1.53
Ce	0.55	0.40	-0.69	0.18	-0.56	0.15	0.23	0.55
Co	0.06	-0.03	1.04	0.09	0.29	0.22	0.25	0.36
Cr	0.47	0.44	0.31	0.36	0.13	0.66	0.57	0.70
Cs	-1.19	-1.74	-1.53	-1.34	-1.38	-0.92	-0.75	-0.47
Eu	0.53	0.27	-0.45	0.09	-0.60	0.16	0.07	0.37
Fe(%)	0.15	0.32	0.78	-0.03	0.03	0.07	0.11	0.20
Hf	2.05	2.50	0.06	0.89	-0.33	0.99	0.78	1.14
La	0.54	0.38	-0.72	0.20	-0.59	-0.08	0.21	0.51
Lu	0.17	0.42	-0.06	-0.18	-0.21	-0.11	0.06	0.44
Na(%)	-2.52	-2.20	-3.32	-3.43	-3.46	-2.17	-3.19	-2.81
Nd	0.29	0.54	-0.53	0.32	-0.53	0.46	-0.24	0.22
Rb	-0.93	-1.28	-1.60	-1.77	-2.61	-0.61	-2.33	-1.86
Sb	0.90	0.38	0.00	0.79	3.85	0.87	1.33	1.36
Sc	0.43	0.36	1.20	0.25	0.31	0.23	0.52	0.67
Sm	0.31	0.38	-0.48	0.12	-0.39	-0.07	0.23	0.48
Ta	-0.39	0.00	-2.41	-0.39	-1.05	-0.85	-0.40	-0.40
Tb	0.75	0.28	0.15	0.17	-0.15	-0.12	0.17	0.86
Th	0.03	-0.13	-1.10	-0.39	-1.05	-0.31	-0.03	0.13
U	-0.41	0.02	-1.15	-0.62	-1.23	-0.53	-0.26	0.16
Yb	0.63	0.65	-0.07	-0.11	-0.08	-0.01	0.03	0.61
Zn	0.47	0.23	0.34	0.22	3.15	0.48	0.66	0.64

4. CONCLUSIONS

The analytical technique used in this study (INAA) showed sensitivity, precision and accuracy suitable for the determination of some metals and trace elements in sediments.

The results obtained by INAA for **As, Sb** and **Zn** showed very high concentrations in all sampling points, mainly at point 05 and much higher than UCC reference values. These elements could be probably related to Pb past mining activities at this point. The REE (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) and Br, Co, Cr, Hf, Fe, Sc, Th and U showed enrichment in relation to UCC values, in all sampling points mainly at points 07 and 08. The other elements analyzed, in general, presented concentration values at the same order of magnitude or lower than UCC values.

EF, an index used as a tool to assess the extent of pollution caused by metals and trace elements in a given environment, showed values FE>1.5 for **As** in points 3, 5, 6, 7 and 8; for **Sb**, points 5 to 8; **Hf**, in points 1, 2 and 3 and finally **Zn**, in point 5 (EF= 7.2). The majority of the elements analyzed by INAA presented **0.5<EF<1.5,** indicating that the elemental

concentration in the sediments is probably due to crustal origin or natural weathering. Point 5 presented the highest EF for the elements **As, Sb** and **Zn**. The high content of **Sb** in point 5 may be related to the sulfides associated with calcareous minerals that were exploited in this region.

Based on the GI values, we can infer that point 1 is moderately polluted by **Br** and **Hf**. Point 2 is moderately polluted by **Hf**. Point 3 is moderately polluted by **Br** and **Sc**. Point 4 is moderately polluted by **As**. Point 5 (Betari river, Iporanga, SP) is polluted to highly polluted by **Sb** and **Zn** and highly polluted by **As**. Point 6 is moderately polluted by **As**. Point 7 (Ribeira river, Eldorado city, SP) is moderately polluted by **As**, **Br** and **Sb**. Point 8 (Ribeira de Iguape river, Registro city, SP) is moderately polluted by **As**, **Br**, **Hf** and **Sb**.

The high levels of metals and other elements reflect the contribution of mining activities that occurred in the Higher Ribeira Valley region, associated with the local geology. Even today, these elements are still deposited in the bottom sediments of the Ribeira de Iguape River and its tributaries. Although the mining operations have ceased in 1996, the deleterious effects to the environment are still present.

ACKNOWLEDGMENTS

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