

MICRO AND MACROCONSTITUENTS OF SEDIMENT CORES FROM ITUPARARANGA RESERVOIR SOROCABA/SP, BY INAA

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ABSTRACT

The Itupararanga reservoir was constructed by LIGHT for generating electrical energy, starting its operations in 1912. It is formed by the Sorocaba river dam. The reservoir finds itself in an area of strong environmental pressures. The waters of the Itupararanga reservoir are currently also used to supply approximately 63% of the basin of Sorocaba, in addition to power generation and recreation areas of nearby cities. Since 2003 it keeps receiving alerts from CETESB (Environmental Company of São Paulo State) that continues today. In this study four geo-referenced sampling points were used and bottom sediment samples were collected, were collected using a 60 cm core sampler, sliced at every 10 cm. The sediment samples were dried at 40^oC, ground in an agate mortar, sieved (200 mesh) and again homogenized. Instrumental neutron activation analysis was applied to the sediment samples in order to determine some major elements (Fe, K and Na) and trace (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Tb, Th, U and Zn) and rare earth (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) metals. The validation of the analytical methodology was performed by the analysis of certified reference materials. The results obtained were compared to NASC (North American Shale Composite) and UCC (Upper Continental Crust) reference values. The enrichment factors (EF) was assessed for sediment contamination index. Statistical tools of Factorial and Cluster analyses were applied to the data.

1. INTRODUCTION

The Itupararanga reservoir was constructed by LIGHT for electric energy generation in 1912. This reservoir is located at the upper Sorocaba river, major tributary of the Tietê river in what is known as the lower basin of the Tietê basin. The Sorocaba river is formed by the Sorocamirim, Sorocabuçu and Una rivers in the Votorantim-SP county [1].

The basin of the Itupararanga reservoir suffers strong environmental pressures, especially when considering that a part of the drainage area of Itupararanga dam is located in the Metropolitan Region of Sao Paulo (RMSP). Furthermore, the rivers that form the basin of the Upper Sorocaba also suffer severe environmental impacts throughout their course due to diffuse pollution from agricultural production and organic load, when crossing small villages and cities [2]. The waters from the Itupararanga dam are used for multiple purposes, such as

water supply for more than half of the region's population, power generation, regulation of water flow of the Sorocaba River Basin and recreational activities for nearby cities. Despite having an excellent spring, the dam is suffering serious environmental risks due to improper use and nearby irregular occupation.

The sedimentary column of aquatic environments, especially their organic fraction, trade nutrients with the overlying water column. In general, sediments are not just a warehouse for products that are found in the water column, but represent a recycling compartment that some biological pathways involving compounds, physicochemical, chemical and transport processes [3]. With the use of sediment analysis from these aquatic systems, it is possible to assess toxic metal contamination [4], understand transport phenomena that occur in these complex systems and trace the history of pollution [5].

Instrumental neutron activation analysis (INAA) has been widely applied for soil and sediment analysis at LAN [6-8], allowing the determination of several elements such as Zn, As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, Sb, Se, Ta, Th, U, W, Zr and rare earth elements (REE). ICP OES metal determinations mainly for Cd, Cr, Cu, Hg, Pb and Ni is commonly used for soil, sediments and environmental samples.

The purpose of this study was to assess the concentration of some heavy metals and trace elements in sediment samples from the Itupararanga reservoir by INAA, and thus, evaluate the pollution impacts on its aquatic system. The results obtained were compared to NASC (North American Shale Composite) and UCC (Upper Continental Crust) reference values. The enrichment factor (EF) was assessed for sediment contamination index. Factorial and Cluster analyses statistical tools were applied to the data.

2. MATERIAL AND METHODS

2.1. Sampling and sample preparation

In this study four geo-referenced sampling points were used and sediment core samples were collected: Sorocaba river headwaters (point 1), the middle of the reservoir (point 2), near a big housing condominium (point 3) and near the dam (point 4). These points are presented in Table 1. The sediment cores were collected using a 60 cm core sampler, sliced every 10 cm, totalizing 6 samples for each core. The sediment samples were dried at 40⁰C in a ventilated oven until constant weight. After this step, sediment samples were ground in an agate mortar, sieved (200 mesh) and again homogenized before analysis. Instrumental neutron activation analysis was applied to the sediment samples in order to determine some major (Fe, K and Na), trace (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Tb, Th, U and Zn) and rare earth (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) elements. The validation of the analytical methodology was performed by certified reference material analyses.

Table 1: Sampling point location in the Itupararanga reservoir.

Samplings Points	Location	Geographical Position (GPS)	Depth (m)
P-01	Upstream from Sorocaba River	S 23°37'17.80'' W 047°13'525''	6.5
P-02	Near village stream	S 23°37'14.10'' W 047°18'313''	14
P-03	Dowstream from Village	S 23°36'5.50'' W 047°20'188''	16
P-04	2 Km from the dam	S 23°37'56,8'' W 047°23'105''	17



Figure 1: Sampling point locations in the Itupararanga reservoir.

2.2 Granulometric analysis

The granulometric analysis of the sediment samples was performed at CETESB (Limeira) according to CETESB standard L6.160 [9]. 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).

2.3 Total Organic Carbon (TOC), Total Nitrogen (TNK) and Organic Matter Content

TOC was determined according to Gaudette et al method [10]. TNK refers to total Kjeldahl nitrogen and was determined according to the Standards Methods (1998) [11]. The organic matter content was calculated from the TOC % according to the equation:

$$\text{OM}(\%) = \text{TOC} * 1.8 \quad (1)$$

This calculation considers that OM contains 58% of carbon.

2.3 Multielemental determination by Instrumental Neutron Activation Analysis (INAA)

2.3.1 INAA- Experimental Procedure

For the multielemental analysis, approximately 150 mg of sediment (duplicate samples) 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°41 filter paper. Sediment samples, reference materials and synthetic standards were irradiated for 8 hours, under a thermal neutron flux of 1 to $5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ at 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 analyzed 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 undertaken by using an 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 methodology validation was verified by measuring reference material Soil 7 (IAEA), Lake Sediment SL1 (IAEA) and BEN Basalt-IWG-GIT. Details of the analytical methodology is described at Larizzatti et al [6].

3. RESULTS AND DISCUSSION

Table 2 presents the results obtained for granulometric analysis, Total Organic Carbon (TOC), Total Nitrogen Kjeldahl (TNK) and Organic Matter Content (OM) for the sediment samples. Figure 2 shows the granulometric composition of the sediment samples. The high concentration of sand fraction at point 1, classified as silty sand, suggests the possibility of lower concentrations of some elements in the sediment at this point of sampling. On the other hand, the high levels of silt+clay found at points 2, 3 and 4, suggest higher concentration levels for some metals in the sediments.

Regarding TNK, TOC and OM levels we could observe that there was a decrease of N concentration, TOC and OM contents from P1-10 to P1-20. At point 2 there was a small variation in the fractions, except for P2-20. Points 3 and 4 presented an accentuated decrease

from the top to the base of the profile for N, TOC and OM concentrations. At point 3, an increase in concentration was observed in the last fraction (P3-60).

The OM and TOC values found in the present study can be seen as high values, but Bottino [12] analyzing superficial sediment samples from Itapararanga reservoir along the 4 seasons, found OM values ranging from 2.0 to 26% and TNK from 270 to 4,648 $\mu\text{g g}^{-1}$.

The molar ratio TOC/TNK is an indication of organic matter source for an ecosystem. The molar ratio C/N with values from 10 to 1,000 is considered from terrigenous origin; 6.6 is autoctone origin and values from 6.6 and 10.0 terrigenous and aquatic origin of organic matter. In the present study this ratio varied from 3.9 (P3-60) to 19.2 (P1-10), with superficial sediment samples showing higher values than the basal fractions.

The precision and accuracy of the INAA analytical methodology were verified by reference material analysis and Z value calculation was made according to Bode [13]. If $|Z| < 3$, the individual result of the control sample (reference material) lies on the 99% confidence interval of the target value. For the reference materials analyzed in the present study all results were in the interval range of $|Z| < 3$, indicating good precision and accuracy of the INAA technique. Figure 3 presents the results obtained by INAA in the reference materials SL 01 (Lake Sediment, IAEA) and BEN (Basalt-IWG-GIT) and Figure 4, shows the results obtained by INAA grouped by concentration level.

Table 2: Granulometric composition, TNK, TOC and OM content of the sediment samples

Point	Sample	Sand (%)	Silt (%)	Clay (%)	Textural classification	TNK (mg L^{-1})	TOC (%)	Organic matter content (%)	TOC/TNK
Pt 01	P 1-10	26.15	31.89	41.96	Clay Sandy	1,715	3.30	5.94	19.2
	P 1-20	60.10	20.14	19.76	Silty Clay	1,281	1.68	3.02	13.1
	P2-10	0.18	15.40	84.42	Silty Clay	2,482	3.69	6.64	14.9
Pt 02	P2-20	0.05	24.78	75.16	Silty Clay	4,116	4.41	7.94	10.7
	P2-30	0.05	23.47	76.47	Silty Clay	2,928	3.20	5.76	10.9
	P2-40	1.82	42.05	56.12	Silty Clay	2,691	3.52	6.34	13.1
	P2-50	0.35	53.29	46.36	Silty Clay	2,956	3.12	5.62	10.6
	P3-10	1.81	28.98	69.21	Silty Clay	8,307	7.93	14.27	9.6
Pt 03	P3-20	0.10	21.39	78.51	Silty Clay	5,855	4.69	8.44	8.0
	P3-30	0.36	36.17	63.46	Silty Clay	3,190	3.45	6.21	10.8
	P3-40	1.01	47.93	51.06	Silty Clay	3,334	2.11	3.80	6.3
	P3-50	0.30	35.02	64.68	Silty Clay	3,913	2.13	3.83	5.4
	P3-60	0.23	43.56	56.21	Silty Clay	6,596	2.57	4.63	3.9
	P4-10	13.47	42.33	44.20	Silty Clay	6,939	7.48	13.46	10.8
Pt 04	P4-20	0.95	29.96	69.09	Silty Clay	4,140	3.42	6.16	8.3
	P4-30	1.30	61.07	37.62	Silty Clay	4,718	2.82	5.08	6.0
	P4-40	0.68	40.90	58.43	Silty Clay	2,867	2.50	4.50	8.7
	P4-50	0.16	32.09	67.75	Silty Clay	3,508	2.20	3.96	6.3
	P4-60	0.24	34.52	65.25	Silty Clay	3,215	2.06	3.71	6.4

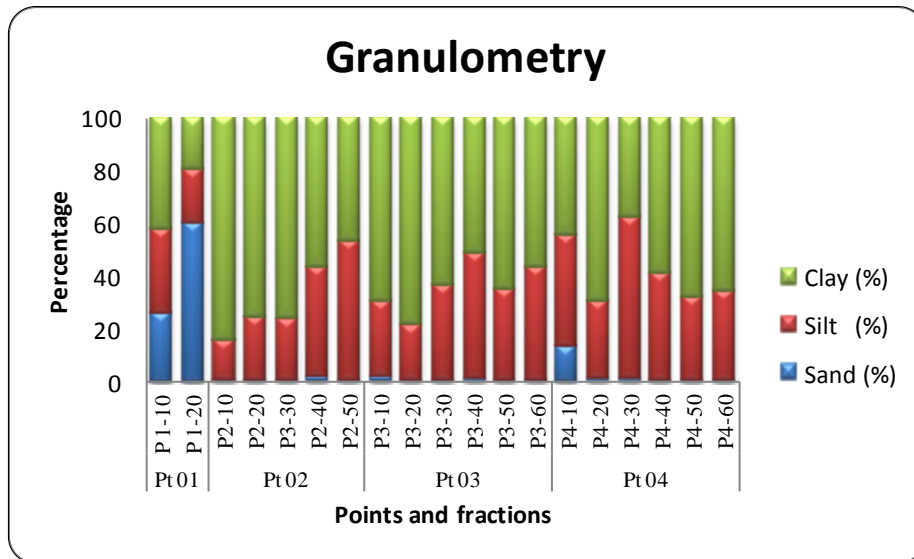


Figure 2: % of clay, silt and sand in each fraction of the sediment samples, in each sampling point.

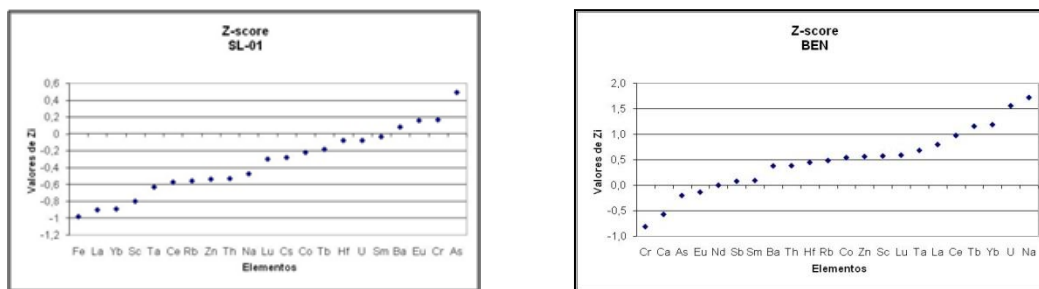


Figure 3: Z-core obtained for INAA. in the reference materials SL-01 and BEN- basalt.

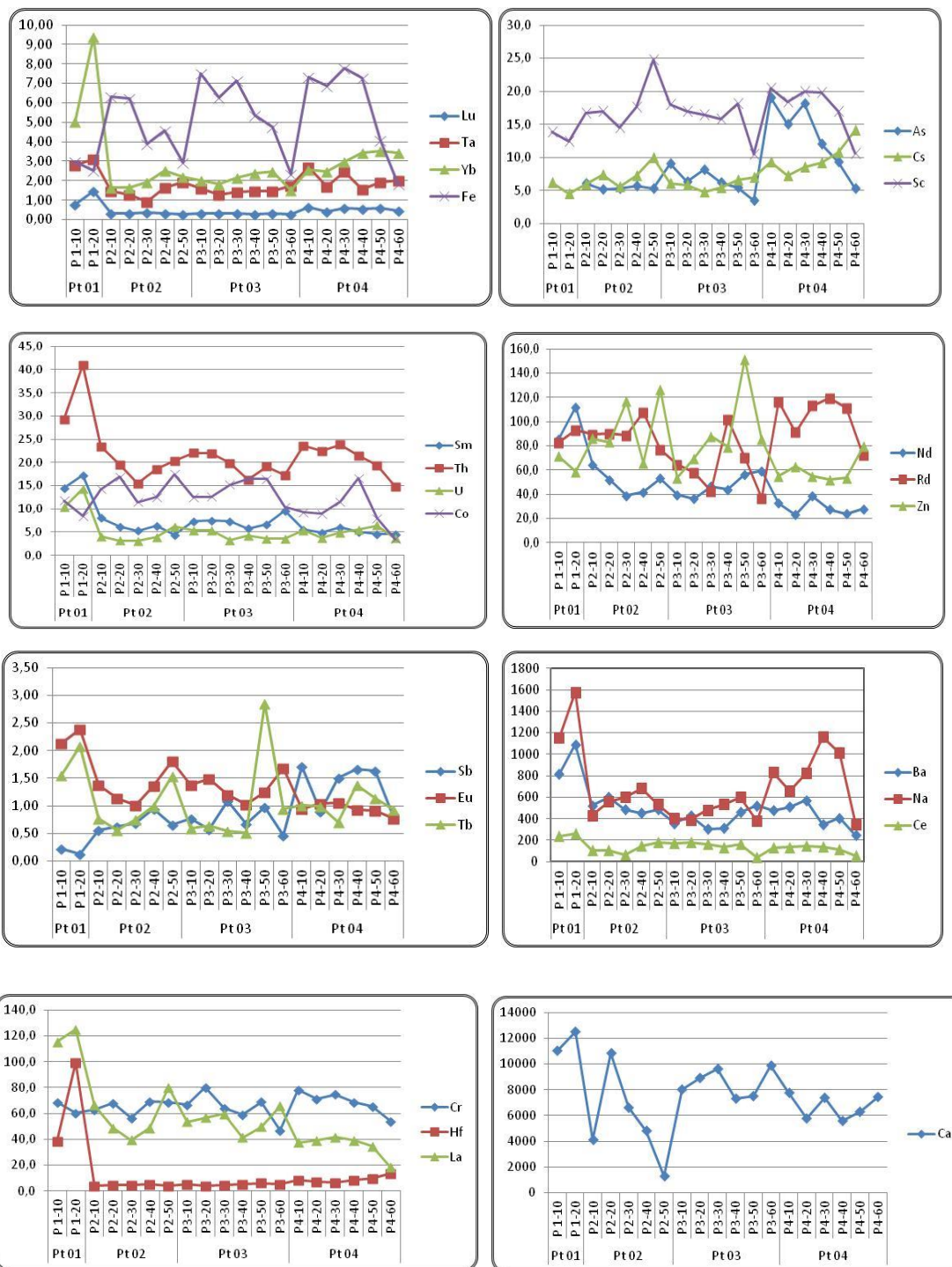


Figure 4: Results (mg kg^{-1}) for the elements analyzed by INAA in the sediment samples

Enrichment Factor (EF). is an index used as a tool to evaluate the extent of metal pollution [14,15] and is defined as a double normalized ratio to a reference element (RE) and calculated by the equation:

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

Fe, Al and Sc are generally used as reference elements for normalization purposes [13] and in the present study Sc was chosen as a reference element. UCC, NASC [15,16] and the elemental concentration in the base of the profile of point 03 (P3-60) were used as reference values for EF calculation. These values from point 3 were considered as background or basal values for the region. At present, there are still no regional reference values for comparison in Brazil and as such UCC and NASC are commonly used. According to Zhang and Liu [16], by convention if $0.5 < EF < 1.5$, then this is an indication that trace metals are entirely provided from crustal contribution (e.g. weathering products); values above 1.5 indicate that an important proportion of trace metals is delivered from non-crustal materials, for example, anthropogenic contributions. The higher the EF value, the more severe the anthropogenic contribution. Table 3 presents the calculated EF values, which only shows the elements that had $EF > 1.5$.

It can be observed that the EF calculated for sediments from point 1 using UCC as a reference value, showed $EF > 1.5$ for the elements Ce, Hf, La, Lu, Nd, Sb, Ta, Tb, Th and U being the higher EF value found for Hf (9.7). However, when NASC values were used all these elements plus Ba, Cs, Eu, La, Lu and Yb presented $EF > 1.5$ with Hf again presenting the highest value (26.2). When the concentration levels of the base of the profile (point 3) were used all elements except elements Cs, Fe and Sb, presented $EF > 1.5$. Point 2 presented $EF < 1.5$ for all elements analyzed when UCC values were used; $EF > 1.5$ for the elements As, Ce, Cs, La, Nd, Sb, Th, U and Zn for NASC values and Ce, Fe and Rb for the base of the profile as reference values. Point 3: for UCC values $EF > 1.5$ was found for As and Ta; for NASC values, As, Ce, Cs, Fe, La, Nd, Sb, Sm, Th and U. For the base of the profile, $EF > 1.5$ was found for Ce, Fe, Rb and Tb. Point 4: for UCC reference only As and Rb showed an $EF > 1.5$. For NASC reference values As, Ce, Cs, Sb, Tb, Th showed $EF > 1.5$ and for the last slice (P4-60), Yb and Zn as well. When the levels of base of the profile were used As, Ce, Fe, Na, Rb and Sb showed an $EF > 1.5$. It appears that for these elements there is an anthropogenic contribution in the Itupararanga reservoir. For most elements analyzed by INAA the EF was $0.5 < EF < 1.5$ indicating that the elemental concentrations are probably due to crustal or natural weathering origins.

When comparing the EF results for the different reference values (UCC, NASC and base of the profile) we can observe a variation of the elements which present an $EF > 1.5$. For example, As in point 4 presented lower EF when UCC and base of the profile were used as reference values instead of NASC values.

Table 3: EF values using UCC, NASC and base of the profile (point 3) as reference values

	Point Sample	Pt 01		Pt 02					Pt 03					Pt 04						
		P1-10	P1-20	P2-10	P2-20	P2-30	P2-40	P2-50	P3-10	P3-20	P3-30	P3-40	P3-50	P3-60	P4-10	P4-20	P4-30	P4-40	P4-50	P4-60
Standard	As	--	--	1.3	1.1	1.3	1.1	0.7	1.8	1.3	1.7	1.4	1.0	1.2	3.3	2.9	3.2	2.1	1.9	1.8
	Ce	1.8	2.3	0.7	0.6	0.5	0.9	0.8	1.0	1.1	1.0	0.9	1.0	0.4	0.7	0.8	0.8	0.8	0.7	0.6
	Cs	0.5	0.4	0.4	0.5	0.5	0.5	0.5	0.4	0.4	0.3	0.4	0.43	0.8	0.5	0.5	0.5	0.6	0.8	1.6
	Hf	3.4	9.7	0.3	0.3	0.4	0.4	0.2	0.3	0.3	0.3	0.4	0.4	0.6	0.5	0.5	0.4	0.5	0.7	1.5
	La	1.8	2.2	0.9	0.6	0.6	0.6	0.7	0.6	0.7	0.8	0.6	0.6	1.4	0.4	0.5	0.5	0.4	0.4	0.4
	Lu	1.4	3.1	0.5	0.5	0.6	0.5	0.3	0.5	0.5	0.5	0.4	0.5	0.6	0.8	0.6	0.8	0.7	0.9	1.1
	Nd	1.7	2.4	1.0	0.8	0.7	0.6	0.6	0.6	0.6	0.8	0.8	0.8	1.5	0.4	0.3	0.5	0.4	0.4	0.7
	Rb	0.4	0.2	0.8	0.8	1.1	1.2	0.6	1.0	0.8	1.5	1.0	1.2	1.0	1.9	1.1	1.7	1.9	2.2	1.6
	Sb	1.6	2.1	0.7	0.5	0.5	0.3	0.6	0.7	0.7	0.5	0.6	1.4	0.4	0.4	0.4	0.4	0.4	0.4	0.6
	Ta	1.6	2.4	0.6	0.5	0.7	0.8	0.9	0.5	0.5	0.5	0.5	2.2	1.3	0.7	0.8	0.5	1.0	0.9	1.2
UCC	Tb	1.4	2.2	1.0	0.8	0.7	0.7	0.6	0.8	0.9	0.8	0.7	0.7	1.1	0.8	0.8	0.8	0.7	0.8	0.9
	Th	2.1	3.2	0.7	0.5	0.6	0.6	0.7	0.8	0.9	0.6	0.7	0.6	0.9	0.7	0.6	0.7	0.8	1.1	0.9
	U	1.7	3.5	0.5	0.5	0.6	0.7	0.4	0.5	0.5	0.6	0.7	0.6	0.7	0.6	0.6	0.7	0.8	1.0	1.5
	As	--	--	3.4	2.8	3.4	3.0	2.0	4.7	3.5	4.6	3.7	2.8	3.1	8.8	7.7	8.6	5.7	5.2	4.7
	Ba	1.6	2.4	0.9	1.0	0.9	0.7	0.5	0.5	0.7	0.5	0.5	0.7	1.4	0.6	0.8	0.8	0.5	0.7	0.6
	Ce	4.6	5.7	1.7	1.6	1.2	2.3	2.0	2.6	2.8	2.6	2.3	2.4	1.1	1.7	1.9	2.0	1.9	1.8	1.4
	Cs	2.1	1.7	1.7	2.0	1.8	1.9	1.9	1.6	1.6	1.4	1.6	1.7	3.1	2.1	1.9	2.0	2.2	2.0	6.3
Standard	Eu	1.9	2.4	1.0	0.8	0.9	0.9	0.9	0.9	1.1	0.9	0.8	0.9	2.0	0.6	0.7	0.6	0.6	0.7	0.9
	Fe	0.8	0.7	1.4	1.4	1.0	1.0	0.4	1.5	1.4	1.6	1.3	1.0	0.8	1.3	1.4	1.4	1.4	0.9	0.6
	Hf	9.1	26.2	0.7	0.9	1.0	0.9	0.5	0.9	0.7	0.9	1.1	1.1	1.5	1.3	1.2	1.0	1.4	1.9	4.1
	La	4.4	5.4	2.1	1.5	1.4	1.5	1.7	1.6	1.8	1.9	1.4	1.5	3.3	1.0	1.1	1.1	1.1	1.1	0.9
	Lu	2.5	5.4	0.9	0.8	1.1	0.9	0.5	0.8	0.8	0.9	0.8	0.9	1.1	1.4	1.1	1.3	1.2	1.6	2.0
	Nd	3.7	5.4	2.3	1.8	1.6	1.4	1.3	1.3	1.3	1.7	1.7	1.8	2.4	0.9	0.7	1.1	0.8	0.8	1.5
	Sb	0.8	0.6	1.8	1.9	2.5	2.9	1.4	2.3	1.8	3.5	2.2	2.9	2.3	4.5	2.6	4.0	4.5	5.1	3.9
	Sm	3.2	4.2	1.5	1.1	1.1	1.1	0.5	1.2	1.3	1.4	1.1	1.1	2.7	0.8	0.8	0.9	0.8	0.8	1.3
	Ta	2.9	3.7	1.3	1.1	0.9	1.4	1.1	1.3	1.1	1.3	1.3	1.2	2.4	1.9	1.3	1.8	1.2	1.6	2.8
	Tb	2.8	4.1	1.1	0.8	1.9	1.4	1.5	0.8	0.9	0.8	0.8	3.9	2.2	1.2	1.3	0.9	1.7	1.6	2.1
UCC	Th	4.0	6.2	2.6	2.2	2.0	1.0	1.5	2.3	2.4	2.3	1.9	2.0	3.1	2.2	2.3	2.3	2.0	2.1	2.6
	U	7.0	10.9	2.3	1.8	2.0	2.1	2.4	2.8	3.0	1.9	2.5	1.9	3.1	2.5	1.9	2.3	2.6	3.6	3.2
	Yb	2.9	6.1	0.8	0.8	1.0	1.1	0.7	0.9	0.9	1.0	1.2	1.1	1.1	1.0	1.1	1.2	1.4	1.7	2.6
	Zn	1.3	1.2	1.3	1.2	2.0	0.9	1.3	0.7	1.0	1.3	1.2	2.1	2.0	0.7	0.8	0.7	0.6	0.8	1.8
	Standard profile	As			1.1	0.9	1.1	1.0	0.6	1.5	1.1	1.5	1.2	0.9	1.0	2.8	2.5	2.7	1.8	1.6
Ba		1.2	1.8	0.6	0.7	0.7	0.5	0.4	0.4	0.5	0.4	0.4	0.5	1.0	0.5	0.6	0.6	0.4	0.5	0.5
Ce		4.2	5.3	1.6	1.5	1.1	2.1	1.8	2.4	2.6	2.4	2.1	2.2	1.0	1.6	1.8	1.8	1.8	1.7	1.3
Cs		0.7	0.6	0.5	0.7	0.6	0.6	0.6	0.5	0.5	0.4	0.5	0.5	1.0	0.7	0.6	0.6	0.7	1.0	2.0
Fe		1.0	0.9	1.7	1.7	1.2	1.2	0.5	1.9	1.7	2.0	1.5	1.2	1.0	1.6	1.7	1.8	1.7	1.1	0.8
Hf		5.8	16.7	0.5	0.6	0.6	0.6	0.3	0.6	0.5	0.6	0.7	0.7	1.0	0.8	0.8	0.7	0.9	1.2	2.6
La		1.3	1.6	0.6	0.5	0.4	0.4	0.5	0.5	0.5	0.6	0.4	0.4	1.0	0.3	0.3	0.3	0.3	0.3	0.3
Lu		2.3	4.9	0.8	0.7	1	0.8	0.5	0.7	0.7	0.8	0.7	0.8	1.0	1.3	1.0	1.2	1.1	1.4	1.8
Na		2.3	3.5	0.7	0.9	1.1	1.1	0.6	0.6	0.6	0.8	0.9	0.9	1.0	1.1	1.0	1.1	1.6	1.6	0.9
Nd		1.1	1.6	0.7	0.5	0.5	0.4	0.4	0.4	0.4	0.5	0.5	0.5	1.0	0.3	0.2	0.3	0.2	0.2	0.5
Rb		1.7	2.2	1.5	1.5	1.0	1.8	0.9	1.0	1.0	0.7	1.9	1.1	1.0	1.6	1.4	1.6	1.7	1.9	2.0
Sb		0.4	0.2	0.8	0.8	1.1	1.2	0.6	1.0	0.8	1.5	1.0	1.2	1.0	1.9	1.1	1.7	1.9	2.2	1.7
Tb		1.3	1.9	0.5	0.4	0.6	0.6	0.7	0.4	0.4	0.4	0.4	1.8	1.0	0.6	0.6	0.4	0.8	0.7	1.0
Th		1.3	2.0	0.9	0.7	0.6	0.6	0.5	0.7	0.8	0.7	0.6	0.6	1.0	0.7	0.7	0.7	0.7	0.7	0.9
U		2.2	3.5	0.7	0.6	0.6	0.7	0.8	0.9	0.9	0.6	0.8	0.6	1.0	0.8	0.6	0.7	0.8	1.1	1.0
Yb	2.6	5.3	0.7	0.7	0.9	1.0	0.6	0.8	0.8	0.9	1.1	1.0	1.0	0.9	0.9	1.1	1.2	1.5	2.3	

X – EF>1.5

The results obtained by the INAA technique plus the granulometric composition, TOC and TNK results were gathered and statistical treatment applied. Factor analysis with principal components extraction and Varimax normalized rotation were performed and the results are shown in Table 4. Values > /0.6/ are marked and the extraction of principal components are presented in Table 5. Factor 1 comprises Ba, Ce, Eu, Hf, La, Lu, Na, Nd, Sm, Ta, Th, U, Yb, sand and presented a negative correlation with the silt+clay fraction; Factor 2 comprises the elements Eu and Nd and a negative correlation for As, Cs, Rb and Sb; Factor 3, presents a

positive correlation for Fe and negative correlation for Cs, TOC and TNK; Factor 4, positive correlations for Tb and Zn and Factor 5, for Cr.

Table 4: Results of Factor Analysis using Varimax rotation with values /0.6/ marked.

	Fator 1	Fator 2	Fator 3	Fator 4	Fator 5
As	-0.05661	-0.799397	0.248942	-0.331812	0.066780
Ba	0.83158	0.290877	0.233831	0.030298	-0.097697
Ca	0.43586	0.446805	-0.117888	-0.594840	0.116918
Ce	0.65876	0.141482	0.480283	0.084047	0.357575
Co	-0.35605	0.239322	0.591997	0.375026	0.381631
Cr	0.07199	-0.077312	0.111800	0.025476	0.854437
Cs	-0.07232	-0.625590	-0.631506	0.198562	0.008728
Eu	0.63833	0.627727	0.151926	0.165969	0.144907
Fe	-0.37421	-0.381717	0.610429	-0.431519	0.244491
Hf	0.94999	0.213675	0.007340	-0.058114	-0.102962
La	0.70720	0.568108	0.258662	0.135790	0.128716
Lu	0.96994	-0.103872	0.019039	-0.131676	-0.045062
Na	0.86308	-0.270616	0.176542	0.020879	0.026051
Nd	0.69938	0.626536	0.131589	0.138738	0.076277
Rb	0.27211	-0.765851	0.266510	0.093284	-0.103080
Sb	-0.25152	-0.860335	-0.007609	-0.102864	0.270966
Sc	-0.23143	-0.512616	0.561307	0.381878	0.350824
Sm	0.77487	0.568863	0.066371	-0.179420	0.069225
Ta	0.84338	-0.221716	-0.122308	-0.097189	0.151042
Tb	0.52495	0.050365	-0.141355	0.611627	0.204802
Th	0.89120	0.105684	0.330387	-0.136128	0.082750
U	0.94845	0.106922	0.111001	0.005946	0.106159
Yb	0.96841	0.008380	-0.038734	-0.022213	-0.064777
Zn	-0.30626	0.409589	-0.054983	0.731583	0.025428
Sand	0.93010	0.270260	-0.080392	-0.062623	-0.113063
Silt+Clay	-0.93004	-0.270373	0.080351	0.062542	0.113190
TOC	-0.25321	0.239087	-0.858207	0.203975	-0.097818
TNK	-0.44860	0.082258	-0.719907	-0.131404	0.120603
Expl.Var	12.07977	5.147919	3.453688	2.127048	1.497130
Prp.Totl	0.43142	0.183854	0.123346	0.075966	0.053469

Table 5: Factor Analysis with Principal Component Extraction

	Eigenvalue	% Total Variance	Cumulative Eigenvalue	Cumulative %
1	13.11	46.83	13.11	46.83
2	4.76	17.02	17.88	63.85
3	3.33	11.90	21.21	75.75
4	2.00	7.14	23.21	82.89
5	1.10	3.91	24.31	86.81

Using the same database of Factor Analysis, Cluster Analysis was performed using Ward's method and Euclidian distances (Figure 4). The purpose of this analysis was to verify possible similarities between sampling points (Figure 5) and determined elements and other parameters (Figure 6). Two groups were formed (Figure 5): group 1 formed by samples from point 1 and group 2 formed by 2 sub-groups:

- sub-group 1: point 4, with the exception of P4-10 fraction and
- sub-group 2: constituted of P4-10 sample and all samples from points 2 and 3

Group 1 presented the higher concentrations especially for Ba, Ca, Cr, Hf, Th, U, some rare earth elements (REE) (Eu, La, Lu, Nd, Sm, Yb) and the granulometric composition quite different from the other sampling points, with a predominant sand fraction (Table 2).

Group 2, sub-group 1 (Figure 5), constituted by samples from point 4 except for P4-10 that presented higher concentrations for most elements analyzed and was located in sub-group 2. Group 2, sub-group 2, consisted of P4-10 and all the samples from points 2 and 3, presenting similar concentrations for some parameters such as As, Ce, Ca, Cr, Na, Sc, Ta, Tb, Th, U, Zn and TOC.

When the same database was used for parameters as variables (Figure 6), 2 groups were also formed. Group 1 was constituted by 2 sub-groups: sub-group 1: light REE (Eu, La, Nd, Sm) and Ca; sub-group 2: REE (Ce, Lu, Yb) Ba, Hf, Na, Ta, Th, U and sand fraction. Group 2 also sub-divided in 2 sub-groups: sub-group 1: TOC, TNK and Cs, Tb and Zn; sub-group 2: silt+clay fraction, Co, Cr, Rb, Sc and semi-metals As and Sb. These results indicate a controlled element distribution mainly by granulometric fractions with OM content strictly correlated to the silt+clay content.

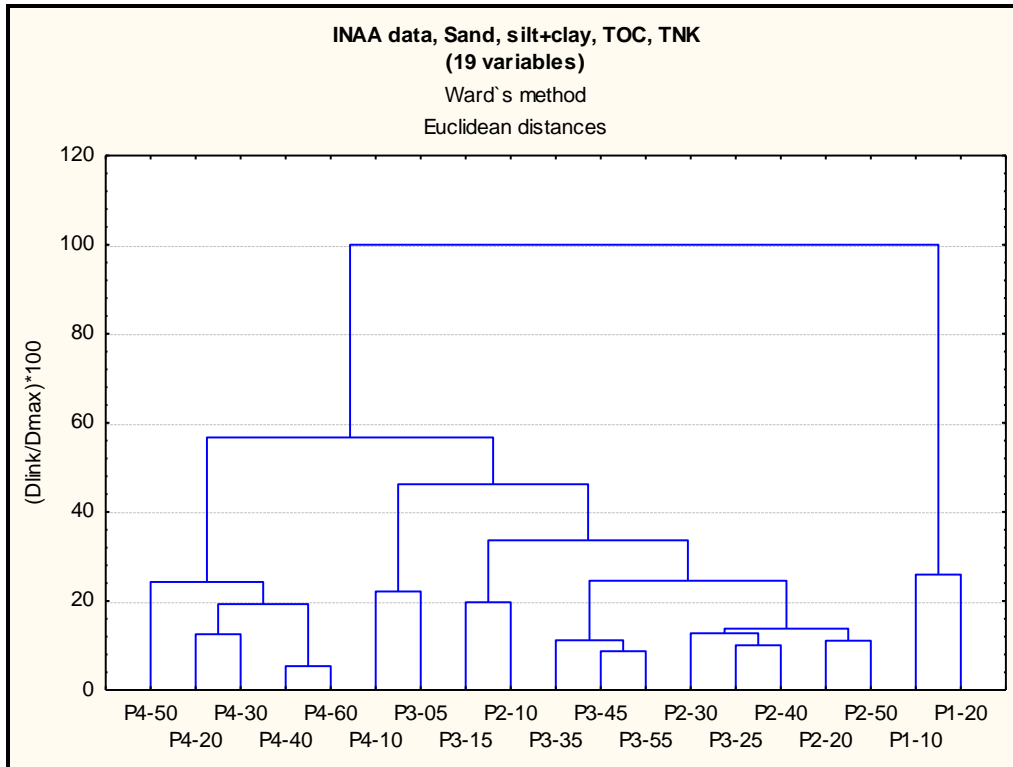


Figure 5: Dendrogram resulting from Cluster Analysis, variable: sampling points.

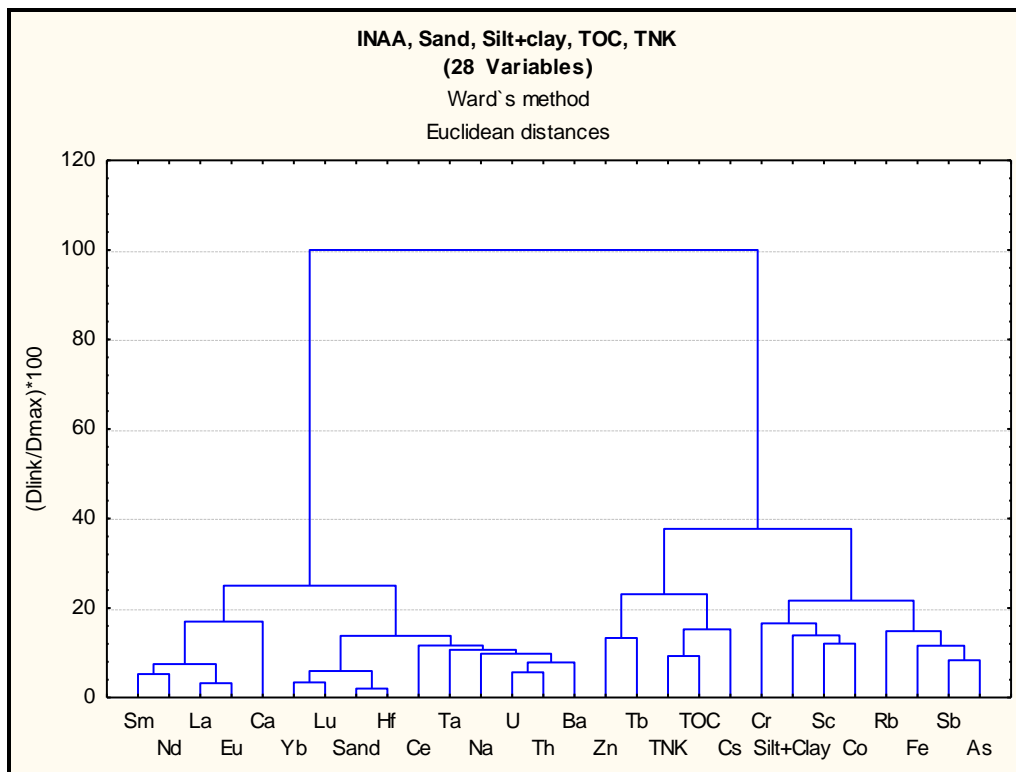


Figure 6: Dendrogram resulting from Cluster Analysis, variables: determined elements, granulometric composition, TOC, and TNK.

3. CONCLUSIONS

The determination of some metals and trace elements by Instrumental Neutron Activation Analysis (INAA) technique proved to be highly appropriate and thus can be an important tool for sediment monitoring as its sensitivity, precision and accuracy are extremely reliable.

From the granulometric analysis it appears that the sediment from Itupararanga reservoir is characterized by a silt+clay fraction in all points (except for point 1), which indicates a potential to retain metals and trace elements.

The Carbon/Nitrogen relation defined the origin of organic matter in the sediment as being terrigenous origin for points 1 and 2, terrigenous and aquatic for points 3 and 4, respectively.

From results obtained by INAA it can be observed that sediments from point 1 showed $EF > 1.5$ for the elements, Hf, Na, Ta, Th, U and ETR (Ce, La, Lu, Nd, Yb and Sm) decreasing in concentration values from the base to the surface of the profile. For most elements analyzed by INAA the EF was $0.5 < EF < 1.5$ indicating that the elemental concentrations are probably due to crustal or natural weathering origins.

When comparing the EF results for the different reference values (UCC, NASC and base of the profile) we can observe a variation of the elements which present an $EF > 1.5$. For example, As in point 4 presented an EF lower when UCC and base of the profile were used as reference values rather than NASC values.

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