

METAL, TRACE AND RARE EARTH ELEMENT ASSESSMENT IN A SEDIMENTARY PROFILE FROM ITUPARARANGA RESERVOIR, SÃO PAULO STATE, BRAZIL, BY NAA

Sharlley A. Silva¹, Heloise A. R. Henrique¹, Déborah I. T. Fávaro²

¹ Setor de Química Inorgânica - ELAI - Companhia Ambiental do Estado de São Paulo
Av. Professor Frederico Hermann Jr. 345
05459-900, São Paulo, SP
shasilva@sp.gov.br

² Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP), Laboratório de Análise por Ativação
Neutrônica (LAN) – Centro do Reator de Pesquisa (CRPq)
Av. Professor Lineu Prestes 2242,
05508-000 São Paulo, SP
defavaro@ipen.br

ABSTRACT

In the present study the preliminary results for 2 sediment cores from the Itupararanga Reservoir are presented. Instrumental neutron activation analysis was also applied to the sediment samples to determine the total concentration of some metal, trace and rare earth elements. The results obtained were compared to the reference values NASC (North American Shale Composite). The enrichment factor (EF) was applied to the results obtained by using NASC (North American Shale Composite) and the concentration values of the last layer of this profile as reference values for sediment contamination index assessment. The EF calculated with the NASC values presented enrichment for As, Ce, Fe, La, Th and U in the two profiles Nd, Sm Hf and Tb, only present enrichment in the 2nd campaign. However, with respect to the base of the profile there was no element with enrichment. For semi metal As and for metals Cr and Zn the concentration values were compared to the oriented values from Environmental Canada (TEL and PEL). As and Cr presented values between TEL and PEL and Zn, values below TEL. The distribution pattern of light and heavy REEs was also verified in relation to the normalization of PAAS (Pos Archean Australian Shale).

1. INTRODUCTION

A research project has being developed by CETESB (Environmental Company of São Paulo State), and IPEN in important water supply reservoirs in São Paulo State, in order to do a wide evaluation of rare earth element, toxic metal and trace element contents in sediment samples. In the present study the preliminary results for the Itupararanga reservoir, are presented. This reservoir, was constructed for electric energy generation in 1912, is located at upper Sorocaba River, major tributary of the Tietê River in what is known as the High Tietê River Basin. The Sorocaba River is formed by the Sorocamirim, Sorocabuçu and Una rivers in the Votorantim – SP. [1]

The environment of the Itupararanga Reservoir is being strongly affected by negative anthropogenic influences, especially when considering that a part of the drainage area of Itupararanga dam is located in the Metropolitan Region of Sao Paulo (MRSP). 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 [2].

As chemicals or substances are released into the environment through natural processes or human activities, they may enter aquatic ecosystems and partition into the particulate phase and these particles may be deposited into the bed sediments where the contaminants, such as heavy metals may accumulate overtime. Then sediments may therefore act as long-term reservoirs of chemicals to the aquatic environmental and to organisms living in or having direct contact with them. Sediment quality guidelines provide scientific benchmarks, or reference points, for evaluating the potential for observing adverse biological effects in aquatic systems [3]

In addition to the more intense use of metals, in recent years rare earth elements (REE) have been gaining space, because the emission of these elements in the environment that can be related to industrial processes that include production of cathode ray tubes, used in the manufacture of household appliances to laser sources. The most relevant studies taking into account REE concentrations in the planet are in the geochemistry area, and are due to the fact that these elements are sensitive indicators of magmatic differentiation, thus aiding in the studies of Earth's geochemical evolution. [4].

A study carried out in China [5], studied the geochemistry of REEs in stream sediments of the Yangtze River. Samples of water, particulate matter and sediments from 8 different locations were analyzed by INAA. The standard of REEs distribution normalized by the chondrites showed enrichment in La, Ce and Pr and depleted in Eu. However, in the NASC (North American Shale Composite) normalization both sediments and particulate material, showed relative enrichment of the La, Ce and Pr and depletion in the Tb, Dy, Ho, Er, Tm, Yb and Lu. REEs were relatively enriched in the fine fractions of the sediments.

Instrumental neutron activation analysis (INAA) has been widely applied for soil and sediment analysis at LAN [6-8]. This analytical technique allows the determination of 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 purpose of this study was to assess the concentration of some metals, trace and REEs in sediment samples from the Itupararanga Reservoir by INAA, and thus, evaluate the pollution impacts on its aquatic system. The enrichment factor (EF) was assessed for sediment contamination index using NASC (North American Shale Composite) as reference values [9]. For semi metal As and for metals Cr and Zn the concentration values were compared to the oriented values from Environmental Canada (TEL and PEL) and adopted by CETESB [3]. The REEs distribution patterns were also verified in relation to the normalization of PAAS (Pos Archean Australian Shale). [9] About REEs concentration in the sediment cores analyzed, they will initiate a REEs concentration data bank

in water supply reservoirs. This databank maybe can be used in the future to establish legal limits for CETESB.

2. MATERIAL AND METHODS

2.1. Sampling and sample preparation

In this study one geo-referenced sampling point was used and sediment core samples were collected near the dam (point 1), in two sampling campaigns (August/2014 and February/2015). The reservoir and point 1 location are presented in Figure 1. Two sediment cores were collected using an 80 cm core sampler, sliced every 2.5 cm, totalizing 26 and 22 samples, respectively, 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.



Figure 1: Sampling point location in the Itupararanga Reservoir

2.2. Multielemental determination by Instrumental Neutron Activation Analysis (INAA)

2.2.1. 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. Sediment samples, reference materials and synthetic standards were irradiated for a daily cycle (6-7 hs), under a thermal neutron flux of 1 to 5×10^{12} n cm⁻² 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 1.21 keV and 2.23 keV for ⁵⁷Co and ⁶⁰Co, respectively.

The elements determined 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 using an in-house gamma ray software, VERSAO 2 program to identify the gamma-ray peaks and by an EXCELL spreadsheet to calculate the concentrations. The uncertainties of the results were calculated by error propagation and considering the uncertainties in all steps of the analytical procedure, mainly errors in the statistical counting. The methodology validation was verified by means of certified reference material analyses. Soil 7 (IAEA), Lake Sediment SL1 (IAEA) and BEN Basalt-IWG-GIT were used for this purpose.

3. RESULTS AND DISCUSSION

3.1 INAA results

The precision and accuracy of the INAA analytical methodology were verified by reference material analysis and Z value calculation was. 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. For used this purpose were the certified reference material Soil 7 (IAEA), Lake Sediment SL1 (IAEA) and BEN Basalt-IWG-GIT. 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.

Figures 2 and 3 present the concentration distribution of the elements analyzed according to depth, in both sampling campaigns. Regarding concentration levels we could observe small concentration variation along the cores for most of the elements analyzed.

3.2 Comparison with TEL and PEL oriented values

For semi metal As and for metals Cr and Zn the concentration values were compared to the oriented values from Environmental Canada (TEL and PEL) [3] as guiding values and used for CETESB as reference in monitoring the state of São Paulo, presented in Figure 4. The results for the Aug 2014 sampling campaign showed As concentration levels between TEL and PEL oriented values, as were Cr and Zn. For these elements, the sediments from point 1 (Aug 2014), can be classified as regular for As ($>11.5 < 17.0$ mg kg⁻¹), good for Cr ($\geq 37.3-63.7$ mg kg⁻¹) and very good for Zn (< 123 mg kg⁻¹). For the Feb 2015 sampling campaign results, for As and Cr, all the values were in between TEL and PEL values. For Zn, the results did not exceed the TEL Level.

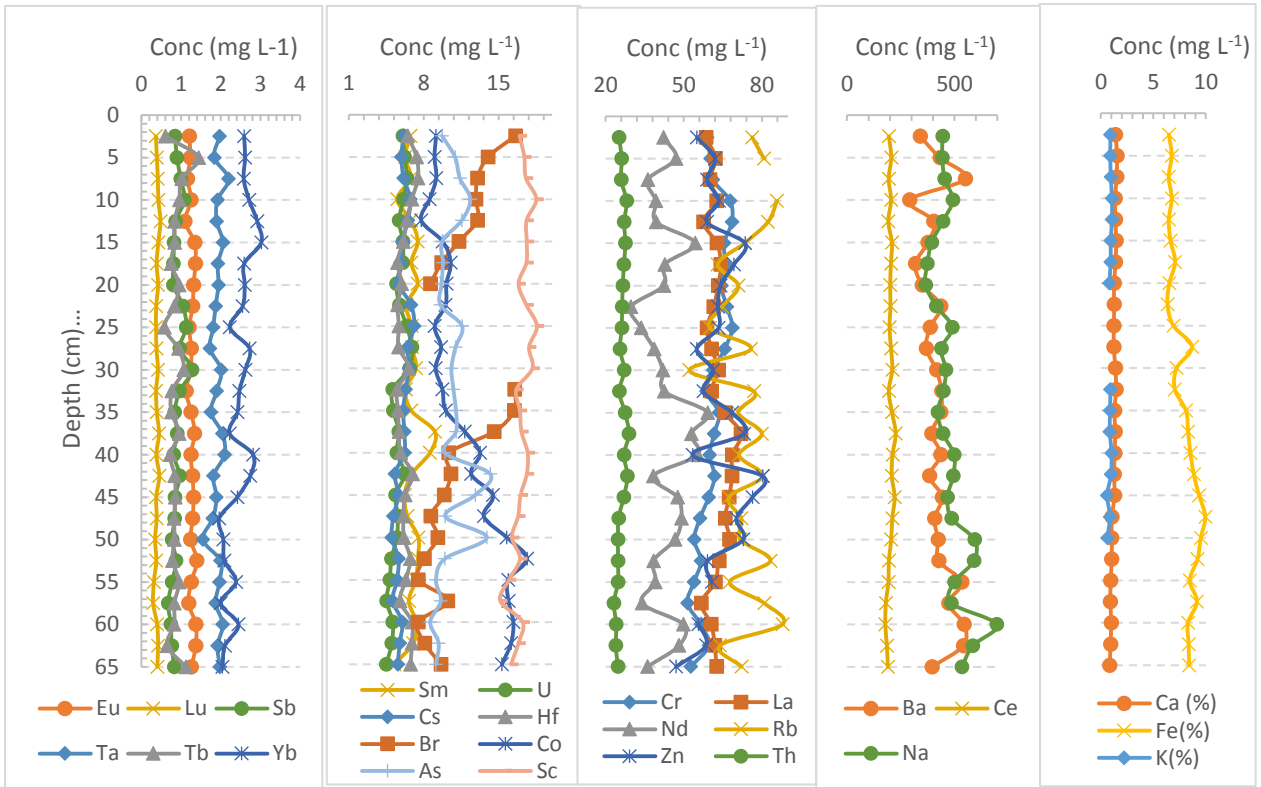


Figure 2: Results (mg kg⁻¹) for the elements analyzed by INAA in the sediment samples, sampling in Ago/2014

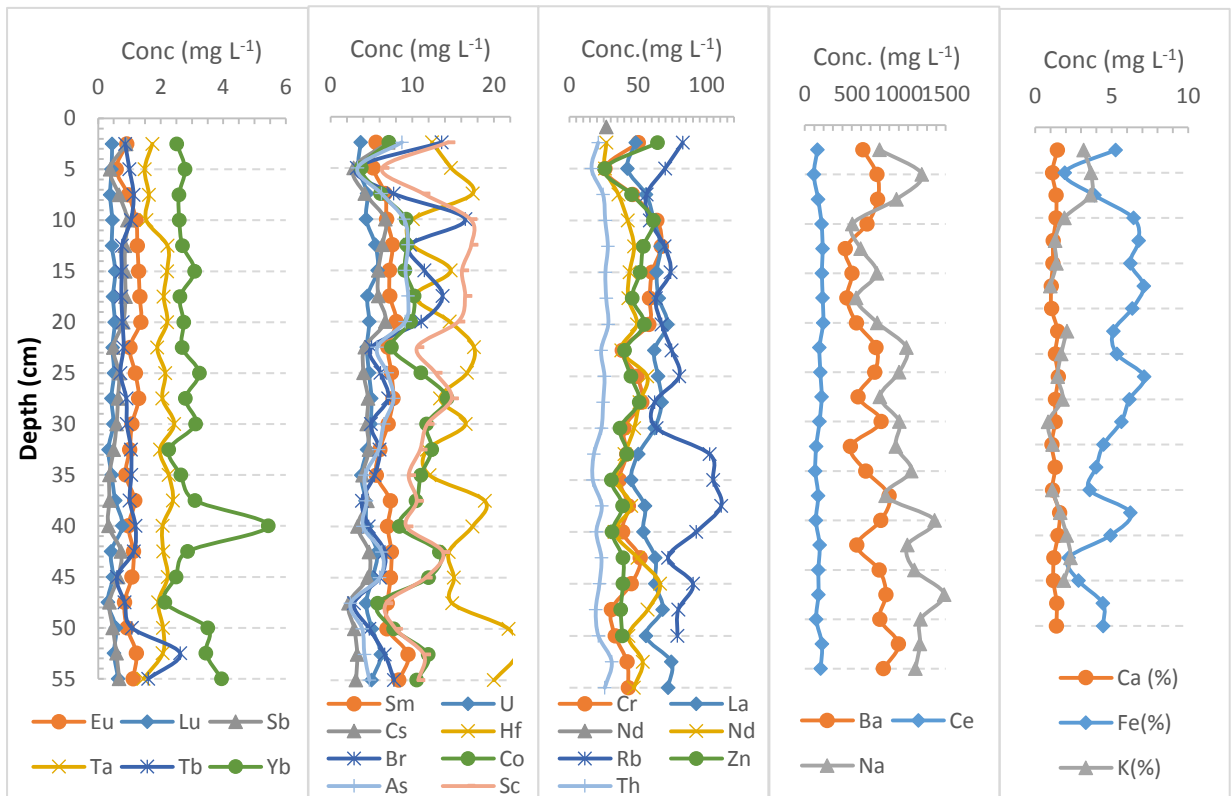


Figure 3: Results (mg kg⁻¹) for the elements analyzed by INAA in the sediment samples, sampling in Feb/2015.

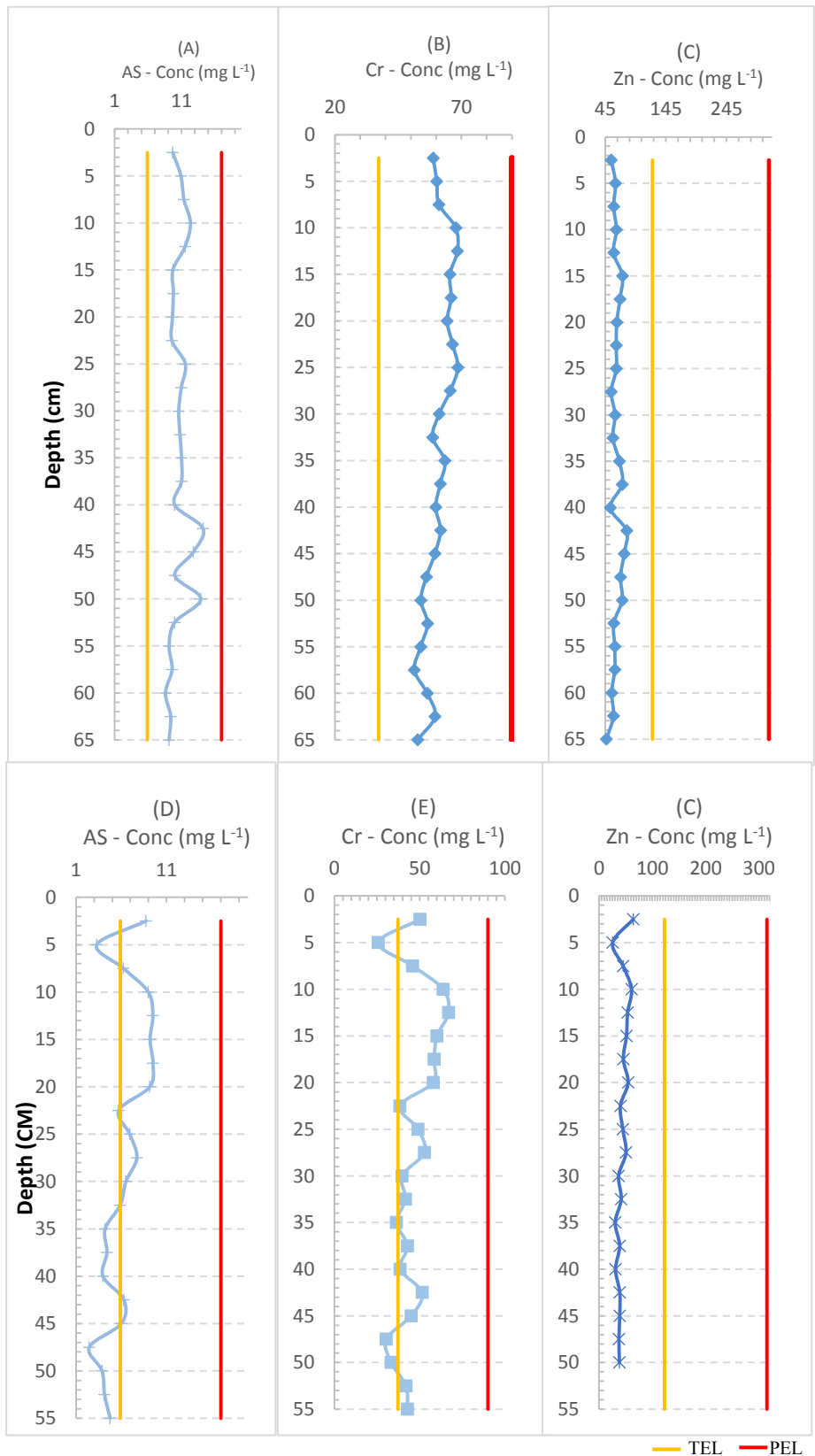


Figure 4: Results (mg kg⁻¹) for the elements As, Cr and Zn compared to the oriented values from Environmental Canada (TEL and PEL). (A), (B) and (C) corresponds to sampling Aug/2014 and (D), (E) and (F) Corresponds to sampling Feb/2015.

3.3 Enrichment Factor Calculation

Enrichment Factor (EF), an index used as a tool to evaluate the extent of metal pollution [11-13], can be defined as a double normalized ratio to a reference element (RE) and calculated by the equation:

$$EF = ([M]/[RE]_{sed}) / ([M]/[RE]_{ref}) \quad (1)$$

Fe, Al and Sc are generally used as reference elements for normalization purposes [7] and in the present study Sc was chosen as a reference element. NASC values [9] and the elemental concentration in the base of the profile, fraction 65cm and 50cm respectively, were used as reference values for EF calculations. These values from the base of the core (bottom of the core) were considered as background or basal values for the reservoir. At present, there are still no regional reference values for comparison in Brazil thus NASC is commonly used for this purpose. According to Zhang and Liu [13], by convention if $0.5 < EF < 1.5$, then this indicates 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. Higher the EF value, more severe the anthropogenic contribution. Table 1 presents the calculated EF values, in which highlight elements have an **EF > 1.5**.

For the August/2014 sampling campaign the EF calculated for sediments using NASC as a reference value, showed an **EF > 1.5** for the elements As, Ce, Fe, Nd, Ta, Th and U. It appears that for these elements there is an anthropogenic contribution in the Ituparanga Reservoir, mainly for As ($EF > 4$). However when the levels of the base of the profile were used, values $0.5 < EF < 1.5$ were found for almost all elements, except for Ca in the first fractions of the profile, indicating that the elemental concentrations are probably due to crustal or natural weathering origins.

For the February/2015 sampling campaign, when NASC was used as reference values the results showed **EF > 1.5** for the elements As, Ba, Ce, Fe, Hf, La, Lu, Nd, Sm, Ta, Tb, Th, U and Yb. However, when the base levels of the profile were used all elements results showed **$0.5 < EF < 1.5$** pointing to the fact that the elemental concentration found are probably due to natural weathering origins. The difference observed for the reference values used suggests the need for regional basal values in order to obtain further reliable information on contamination status of an aquatic environment, in this case Ituparanga Reservoir.

Table 1: EF values calculated by using NASC values [9], in both campaigns

Depth (cm)	P1- Agust/2014										P1- February/2015										
	EF (NASC)								EF (base)		EF (NASC)										
	As	Ce	Fe	La	Nd	Ta	Th	U	Ca	Sm	As	Ba	Ce	Fe	Hf	La	Nd	Ta	Tb	Th	U
2.5	4.3	2.4	1.4	1.6	1.4	1.6	1.9	2.0	1.6	1.2	4.6	1.0	1.9	1.4	2.1	1.6	1.0	1.6	1.1	1.8	1.4
5.0	4.7	2.4	1.5	1.7	1.5	1.4	1.9	2.0	1.7	1.1	3.9	2.9	3.1	1.1	5.6	3.1	2.2	3.2	2.8	3.2	3.0
7.5	4.7	2.3	1.4	1.6	1.1	1.7	1.8	2.0	1.6	1.2	4.1	1.6	2.6	1.3	3.7	2.3	1.7	2.0	1.8	2.7	2.2
10.0	5.0	2.3	1.4	1.6	1.2	1.4	1.9	1.8	1.4	0.9	3.9	0.9	2.1	1.4	1.4	1.7	1.4	1.2	1.1	1.9	1.4
12.5	4.9	2.2	1.4	1.5	1.2	1.5	1.9	1.8	1.5	1.2	4.1	0.6	2.3	1.5	1.4	1.8	1.5	1.8	0.8	2.0	1.8
15.0	4.0	2.4	1.4	1.7	1.7	1.6	2.0	1.9	1.6	1.3	4.3	0.7	2.3	1.4	2.2	1.9	1.5	1.9	0.8	2.0	2.0
17.5	4.1	2.4	1.5	1.7	1.3	1.5	1.9	1.9	1.5	1.2	4.3	0.6	2.4	1.6	1.5	1.9	1.4	1.7	0.8	2.0	1.5
20.0	4.3	2.4	1.5	1.8	1.4	1.6	2.0	1.8	1.4	1.4	4.4	0.8	2.6	1.5	2.2	2.1	1.7	1.9	0.9	2.3	1.7
22.5	4.1	2.4	1.4	1.6	0.9	1.4	1.9	1.8	1.4	1.1	4.0	1.7	3.0	1.8	3.9	2.7	1.9	2.4	1.4	2.7	2.3
25.0	4.7	2.2	1.4	1.5	1.0	1.3	1.8	1.9	1.3	1.1	4.1	1.4	2.7	1.6	3.1	2.4	2.4	2.3	1.0	2.5	2.0
27.5	4.6	2.4	1.8	1.6	1.2	1.3	1.8	2.1	1.3	1.2	3.9	0.9	2.5	1.8	2.2	2.1	1.9	1.9	1.1	2.1	1.9
30.0	4.4	2.4	1.5	1.6	1.3	1.5	1.9	2.0	1.5	1.2	4.1	1.6	2.7	1.9	3.3	2.5	2.2	2.8	1.4	2.5	2.3
32.5	4.9	2.4	1.6	1.7	1.4	1.6	1.9	1.7	1.7	1.2	4.0	1.0	2.3	1.9	2.6	2.1	2.0	2.5	1.7	2.0	2.3
35.0	4.9	2.5	1.8	1.8	1.9	1.4	2.0	1.7	1.5	1.2	3.3	1.6	2.4	1.7	3.0	2.2	1.9	3.2	2.0	2.2	2.2
37.5	4.8	2.7	1.8	2.0	1.7	1.6	2.1	1.8	1.5	1.6	3.1	2.0	2.8	1.4	4.3	2.4	2.3	3.1	1.7	2.8	2.3
40.0	4.2	2.5	1.8	1.8	1.7	1.6	1.9	1.7	1.4	1.5	3.2	2.1	2.6	1.4	4.5	2.7	1.9	3.0	2.3	2.6	2.7
42.5	6.1	2.4	1.9	1.8	1.2	1.4	2.0	2.0	1.4	1.2	3.4	1.0	2.4	1.7	2.5	2.1	2.0	2.1	1.5	2.1	2.3
45.0	5.6	2.7	2.1	1.9	1.5	1.5	2.0	1.7	1.5	1.1	3.9	1.6	2.6	1.6	3.1	2.5	3.1	2.6	0.9	2.3	2.5
47.5	4.5	2.6	2.2	1.8	1.6	1.5	1.9	1.8	1.2	1.2	2.7	3.0	4.4	1.2	5.2	4.7	4.6	3.9	2.2	3.5	3.6
50.0	6.4	2.6	2.2	1.9	1.6	1.3	1.9	1.9	1.2	1.4	3.6	2.4	3.1	1.3	6.5	3.3	2.9	3.5	2.4	3.3	3.5
52.5	4.4	2.4	2.0	1.8	1.2	1.6	1.8	1.6	1.2	1.4	--	--	--	--	--	--	--	--	--	--	--
55.0	4.3	2.5	2.0	1.8	1.3	1.7	1.9	1.7	1.1	1.4	--	--	--	--	--	--	--	--	--	--	--
57.5	4.7	2.5	2.3	1.8	1.2	1.7	1.9	1.7	1.1	1.3	--	--	--	--	--	--	--	--	--	--	--
60.0	3.7	2.1	1.8	1.6	1.6	1.6	1.7	1.6	1.1	1.3	--	--	--	--	--	--	--	--	--	--	--
62.5	4.2	2.3	1.9	1.7	1.6	1.6	1.8	1.7	1.0	1.3	--	--	--	--	--	--	--	--	--	--	--
65.0	4.2	2.4	2.0	1.8	1.2	1.7	1.9	1.5	1.0	1.0	--	--	--	--	--	--	--	--	--	--	--

3.4 Distribution pattern of the Rare Earth Elements (REEs)

In order to eliminate the “zigzag” REE distribution pattern and identify any individual REE anomalies, the measured concentrations of REE are commonly normalized to different data sets. The “shales” (NASC and PAAS) are commonly utilized in environmental studies [14]. In Figures 5 and 6 show the distribution patterns obtained for RREs concentration in the samples collected in August/2014 and February/2015, respectively, using the Post-Archean Australian Shale values (PAAS) for normalization [15]. It can be seen from Figure 5 and 6, a positive anomaly for Ce in the two profiles, but more pronounced in the first campaign (Ago 2014).

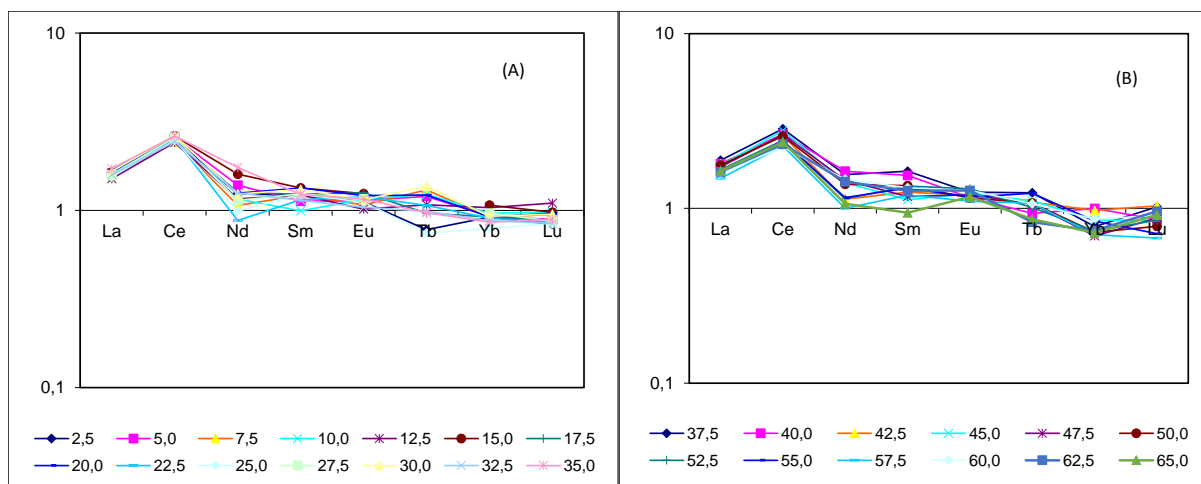


Figure 5: REE distribution patterns normalized to PAAS (August/2014)

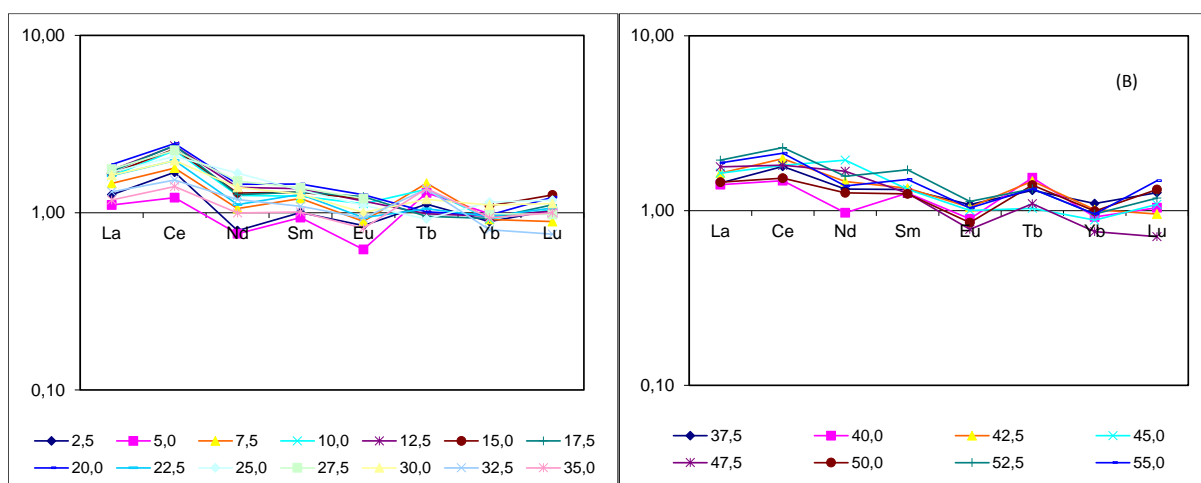


Figure 6: REE distribution patterns normalized to PAAS (February/2015)

4. 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 results obtained by INAA it can be observed that sediments showed $EF > 1.5$ for the elements As, Ce, Fe, La, Nd, Ta, Th and U when NASC was used as reference values. However, when values from the base of the sediment profile was used, $0.5 < EF < 1.5$ were found indicating that the elemental concentrations are probably due to crustal or natural weathering origins without any contamination for the elements analyzed. This behavior can be observed in both sediment profiles of the reservoir. The differences observed for the reference values used suggest the need for regional basal values in order to obtain more reliable information on contamination status of the Itupararanga Reservoir.

The present study contributes to a data bank results for REEs concentration in sediment profiles for the Itupararanga Reservoir. When REEs concentrations were used for distribution pattern according to PAAS normalization, a positive anomaly for Ce was observed, in both profiles.

Based on the results for the elements analyzed, by using different criteria of pollution assessment, the Itupararanga Reservoir can be considered a not polluted aquatic body.

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