

## METAL, TRACE AND RARE EARTH ELEMENT ASSESSMENT IN A SEDIMENTARY PROFILE FROM PROMISSÃO RESERVOIR, SÃO PAULO STATE, BRAZIL, BY INAA

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### ABSTRACT

In the present study the preliminary results for the Promissão reservoir, situated in the Lower Tietê region covering a little more than 1% of the SP state population, is characterized by intense agro pastoral activities. Its operations for generating electrical energy started in 1975. It is located at Tietê River and its hydrographic basin has a drainage area of 530 km<sup>2</sup>. The total extension of the reservoir is 110 km along the Tietê River, with a medium depth of 20 m. A core sampler was used and a 33 cm sediment core was collected from the dam in January 2013, sliced at every 2.5 cm, totaling 13 samples. 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 elements (Ce, Eu, La, Lu, Nd, Sm, Tb, and Yb). The enrichment factor (EF) was applied to the results obtained by using North American Shale Composite, Upper Continental Crust and the concentration values of the last layer of this profile as reference values for sediment contamination index assessment. When the results for As, Cr, and Zn were compared to threshold effect level (TEL) and probable effect level (PEL) oriented values, sediments from 0–10 cm exceeded the TEL values for **As** (5.9 mg kg<sup>-1</sup>), all samples exceeded the PEL values for **Cr** (90 mg kg<sup>-1</sup>), and all samples had much lower values than TEL values for **Zn** (123 mg kg<sup>-1</sup>).

### 1. INTRODUCTION

A research project is being developed by the Environmental Company of São Paulo State (CETESB), Campinas State University (UNICAMP), and Institute of Nuclear and Energy Research (IPEN) in important water supply reservoirs in São Paulo State, in order to conduct a more detailed assessment of rare earth element (REE), toxic metal, and trace element contents in sediment samples. In this paper, the preliminary results for the Promissão reservoir, also known as Mario Lopes Leão reservoir, are presented.

In addition to the intensive use of metal concentration for studying contamination in sediments, in recent years, another class of elements has become important—the REEs. The issue of higher concentration of such elements in the environment may be related to industrial processes ranging from the production of cathode ray tubes used in the production of household appliances and petroleum-cracking catalysts to laser sources. The most relevant papers that take into account the REE concentrations on the planet are in the geochemistry field, due to the fact that these elements are sensitive indicators of magmatic differentiation and therefore are valuable in geochemical evolution studies of the Earth [1].

Zhang et al [2] studied water, suspended matter, and sediment samples from eight locations along the Yangtze River, in China. The concentration and speciation (exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual forms) of REEs were determined by instrumental neutron activation analysis (INAA).

Olmez & Sholkovitz [3] studied the REE composition of sediment cores in California showing that with their unique signature and source, the REEs may be new tracers for anthropogenic inputs in coastal environments and for oil-refined petroleum products in aquatic sediments.

More recently, REE determination in environmental samples such as aquatic plants, mollusks, and sediments was observed in a study conducted in the Netherlands [4].

In a study, Rezaee et al [5] presented results for sediment surface from river mouths and polluted marine environments for REE contents by using INAA. Results of total concentration were used to establish baseline data in an environmental pollution assessment and to develop the correlations between the Ce/Ce\* anomalies and the distribution patterns of some light rare earth elements (LREEs) and heavy rare earth elements (HREEs). The chondrite-normalized REE pattern from each examined site was used to explain the sedimentation patterns by anthropogenic activities and by natural processes.

As already known, INAA has been widely applied for sediment analysis in lakes and reservoirs at LAN/IPEN [6-9], allowing 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 RREs (Ce, Eu, La, Lu, Nd, Sm, Tb, and Yb).

The purpose of this study was to assess the concentration of all these elements in sediment samples from the Promissão reservoir by INAA, and thus evaluate the effect of pollution on its aquatic system. The results obtained were compared to North American Shale Composite (NASC) and Upper Continental Crust (UCC) reference values. The enrichment factor (EF) and geoaccumulation index (*I<sub>geo</sub>*) were assessed for sediment contamination index. The distribution patterns of REEs in sediments were also verified. Statistical tools of cluster analyses were applied to the data.

The results for REE concentration in the sediment profile will be used to initiate a sediment REE concentration data bank in water supply reservoirs. This databank may be used in the future for CETESB to establish legal limits.

## 2. MATERIAL AND METHODS

### 2.1. Study area

Promissão reservoir, situated in the Lower Tietê region, which includes a little more than 1% of the São Paulo State population is characterized by intense agro pastoral activities [1]. Its operations for generating electrical energy started in 1975. It is located at the Tietê River and its hydrographic basin includes an area of 51.8 thousand km<sup>2</sup> with a drainage area of 530km<sup>2</sup> and accumulation volume of 2x10<sup>9</sup>m<sup>3</sup>. It bathes the cities of Promissão, Guaiçara, Pongai, Pirajuí, Ibitinga, Borborema, Novo Horizonte, Sales Adolfo José Bonifácio and Iacanga. The total extension of the reservoir is 110 km along the Tietê River, with a medium depth of 20m [10]. Figure 1 shows the location of the Promissão reservoir along the Tietê River Basin.

### 2.2. Sampling and sample preparation

In this study, one geo-referenced sampling point (point 1) was used and a sediment core sample was collected in January/2013 in the dam. The location of the sampling point is presented in Figure 1. The sediment core (33 cm long) was sliced at every 2.5 cm *in situ* giving a total of 13 sediment samples. The sediment samples were dried at 40°C 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 Promissão 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 and reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Sediment samples and reference materials 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  $^{57}\text{Co}$  and  $^{60}\text{Co}$ , 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 5 (IAEA), IAEA-SL-1 (Trace and Minor Elements in Lake Sediment) and GEOSTANDARD BE-N (Basalt-IWG-GIT). Details of the analytical methodology is described at Larizzatti et al [6].

## 3. RESULTS AND DISCUSSION

### 3.1 INAA results

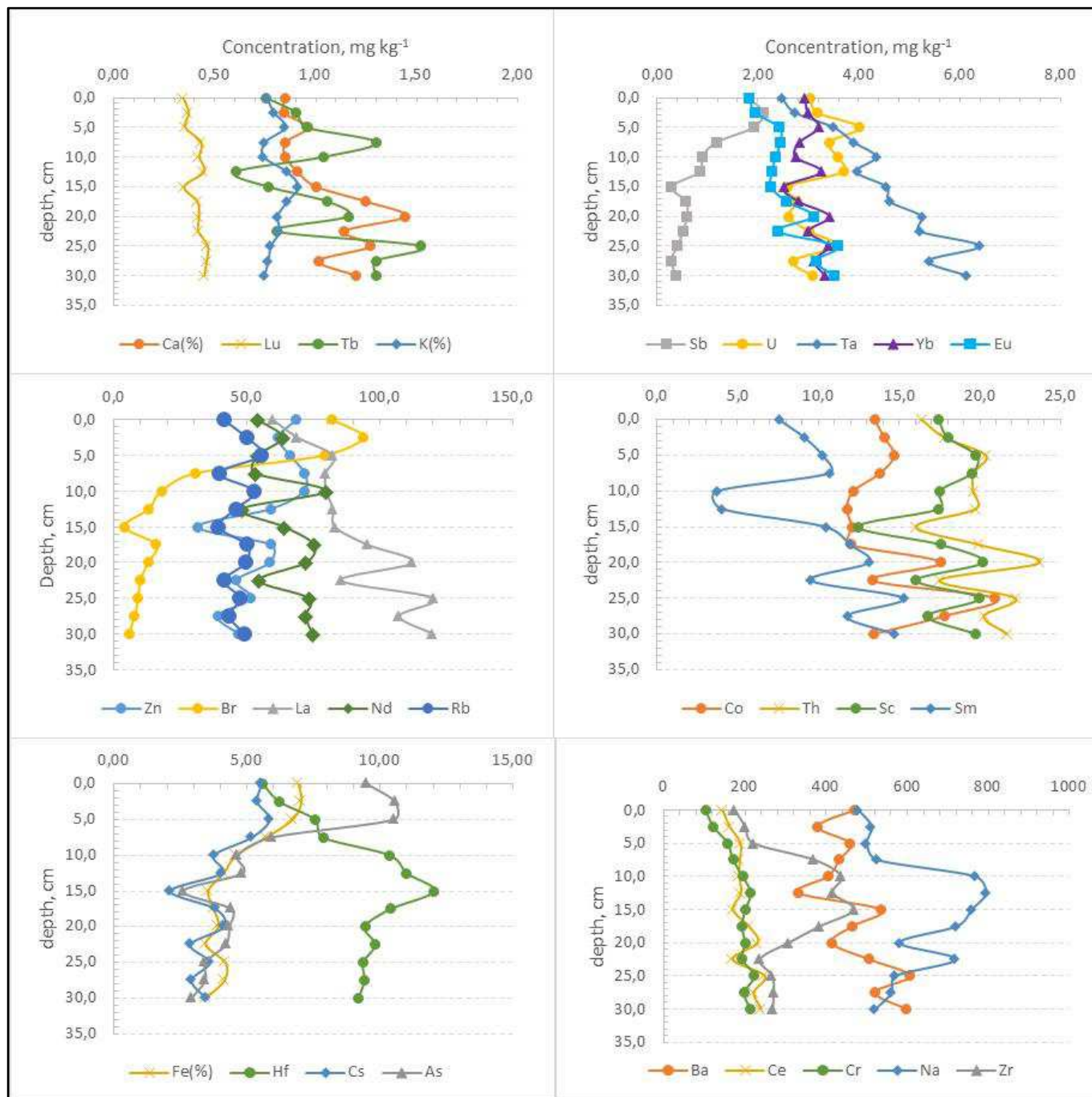
The precision and accuracy of the INAA analytical methodology were verified by reference material analysis. Z value calculation was made according to Bode [11]. If  $|Z| < 3$ , the individual result of the control sample (reference material) lies on the 99% confidence interval of the target value. For 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 2, shows the results obtained by INAA grouped by concentration level. There are three groups of elements according to their behavior in relation to depth: a) elements with decreasing concentration levels according to depth: As, Br, Fe, Sb and Zn; increasing of concentration according to depth: Ba, Ca, Ce, Cr, Eu, Hf, La, Lu, Nd, Rb, Sc, Sm, Ta, Tb, Th and Zr; c) small concentration fluctuations according to depth but not a significant variation between the top and bottom of the sediment profile: Co, Cs, K, Na, U and Yb.

As, Br, Fe, Sb and Zn presented a decreasing in concentration according to the depth that may be an indication of anthropogenic contribution over time.

The average values found for the Lower Tietê region (including the Promissão reservoir) in a Nascimento & Mozeto study [12], where the purpose was to establish regional reference values for bottom sediments in the Tietê River basin, were: As,  $18 \pm 8$ ; Co,  $24 \pm 6$ ; Cr,  $189 \pm 49$ ; Th,  $19 \pm 4$ ; U,  $4.2 \pm 1.5$  and Zn,  $63 \pm 9$   $\text{mg kg}^{-1}$ . All these values were much higher than

the values obtained in the present study for the 0-5 cm bottom sediment samples (As,  $10.0 \pm 0.7$ ; Co,  $13.8 \pm 0.4$ ; Cr,  $113 \pm 13$ ; Th,  $17 \pm 1$ ; U,  $3.1 \pm 0.1$  and Zn,  $65 \pm 5 \text{ mg kg}^{-1}$ ), except for Zn.



**Figure 2: Concentration ( $\text{mg kg}^{-1}$ ) x depth (cm) for the elements analyzed by INAA in the sediment samples**

For quality sediment evaluation, CETESB (Companhia Ambiental do Estado de São Paulo) adopted TEL and PEL oriented values, established by the Canadian Council of the Ministry of the Environment (CCME) [13] for the total concentration of arsenic, metals and organic compounds, in order to assess possible deleterious effects on the biota. TEL (Threshold Effect-Level) indicates the concentration below which there is a rare occurrence of adverse effects to biota and Probable Effect Level (PEL) indicates the concentration above which there is frequent occurrence of adverse effects to biota. When the results for As, Cr and Zn were compared to TEL and PEL oriented values, sediments from 0-10 cm surpassed the TEL values for **As** ( $5.9 \text{ mg kg}^{-1}$ ). For **Cr**, all samples in the profile exceeded the PEL value ( $90 \text{ mg kg}^{-1}$ ) and for **Zn**, all the results were much lower than TEL value ( $123 \text{ mg kg}^{-1}$ ), mainly the deeper layers.

### 3.2 Enrichment Factor (EF)

For the estimation of anthropogenic inputs, it is more useful to calculate the non-dimensional enrichment factor by normalizing metal concentrations to Sc. EF, an index used as a tool to evaluate the extent of metal pollution [14,15] is defined as a double normalized ratio to a reference element (NASC, UCC) [16,17] and calculated by the equation:

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

Fe, Al and Sc are generally used as reference elements for normalization purposes [14] and in the present study, Sc was chosen as a reference element. UCC, NASC and the elemental concentrations in the base of the sediment profile, in this study PR-13 sample, were used as reference values for EF calculations. These values from the base of the sediment profile 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 [18], 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.

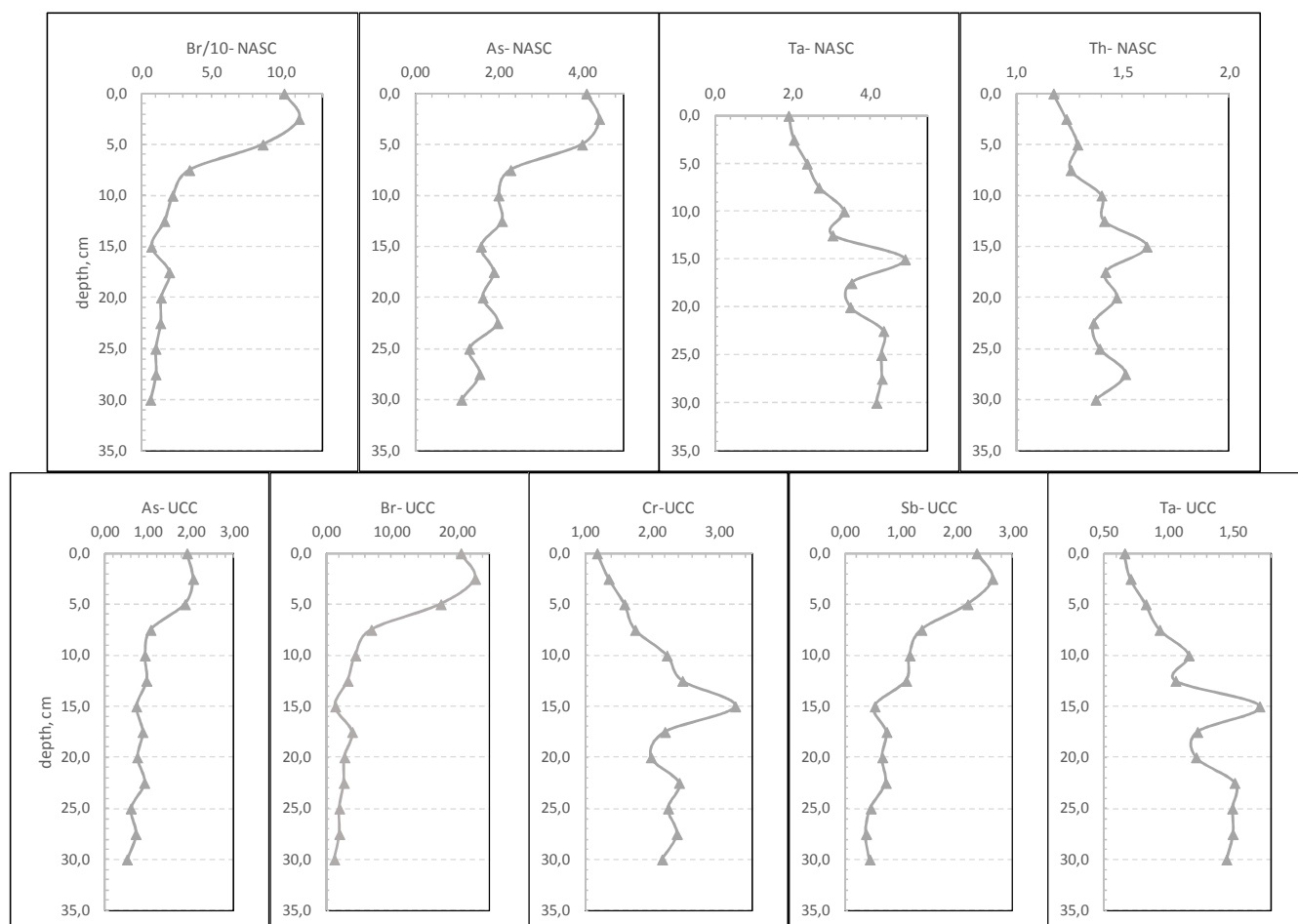
According to the Chaudhry [19],  $EF < 1$  indicates no enrichment,  $< 3$  is minor; 3-5 is moderate; 5-10 is moderately severe; 10-25 is severe; 25-50 is very severe and  $> 50$  is extremely severe. Figure 3 presents the EF values, only for the elements that showed an  $EF > 1.5$ : a) NASC, b) UCC and c) concentration in the base of the sediment profile (PR-13 sample), used as reference values, respectively.

It can be observed that the EF calculated for sediments using NASC as a reference value, showed  $EF > 1.5$  for the elements As, Br, Ta and Th. The elements As and Br, presented higher EF values at the top of the profile while Ta, Th and some REEs (Ce, Eu, La, Nd and

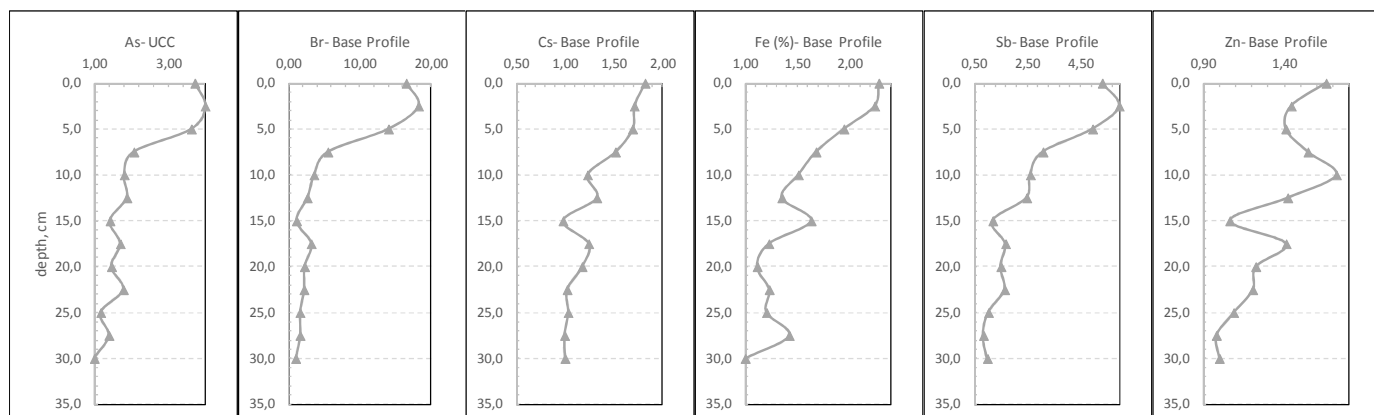
Sm), higher values at the bottom of the sediment profile. According to the Chaudhry classification [19], minor enrichment ( $<3$ ) for Th and REEs, moderate (3-5) for As and Ta and extremely severe for Br ( $>50$ ).

For UCC as a reference value, the elements As, Br and Sb presented a higher EF value at the top of the profile and elements Cr and Ta, higher EF in the bottom of the profile. REEs presented an  $EF < 1.5$  for all of them. According to the Chaudhry classification, minor enrichment ( $<3$ ) for As, Cr, Sb and Ta and severe for Br (10-25).

However when the levels of the base of the profile were used as reference values As, Br, Cs, Fe, Sb and Zn showed an  $EF > 1.5$  with higher values at the top of the profile. Again REEs presented an  $EF < 1.5$  for all of them. According to the Chaudhry classification [19], minor enrichment ( $<3$ ) for Cs, Fe and Zn, moderate (3-5) for As and Sb and severe for Br (10-25). It appears that only for the elements As, Br and Sb there is an anthropogenic contribution in the Promissão reservoir according to the EF criteria. 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 and according to the Chaudhry classification ( $<1$ ), no enrichment.



**Figure 3: EF values using UCC, NASC and base of the sediment profile as reference values**



**Figure 3: EF values using UCC, NASC and base of the sediment profile as reference values**

### 3.3 Geoaccumulation Index (*I<sub>geo</sub>*)

Muller [20] introduced *I<sub>geo</sub>* to assess heavy metal pollution in sediments. The *I<sub>geo</sub>* is calculated according to the equation:

$$I_{geo} = \log_2 (C_n/1.5B_n) \quad (2)$$

where  $C_n$  is the measured concentration of a metal in sediments and  $B_n$  is the geochemical background value in the average shale of element n, and 1.5 is the background matrix correction due to terrigenous effects [20].

Muller [20] has distinguished seven classes of geoaccumulation index: 1)  $I_{geo} < 0$ , basal level; 2) from  $0 \leq I_{geo} < 1$ , unpolluted to moderately polluted; 3)  $1 \leq I_{geo} < 2$ , moderately polluted; 4)  $2 \leq I_{geo} < 3$ , moderately to strongly polluted; 5)  $3 \leq I_{geo} < 4$ , strongly polluted; 6)  $4 \leq I_{geo} < 5$ , strongly to extremely polluted and 7)  $I_{geo} > 5$ , extremely polluted.

The results obtained for *I<sub>geo</sub>* values using NASC, UCC and base of sediment profile concentrations as geochemical background values are presented in Table 1. The *I<sub>geo</sub>* results confirm the EF results, giving a sediment classification of moderately polluted for As, Cr and Sb ( $1 \leq I_{geo} < 2$ ) and extremely polluted for Br ( $I_{geo} > 5$ ) (NASC and UCC as reference values) and strongly polluted ( $3 \leq I_{geo} < 4$ ), when the base of the sediment profile concentration value was used.



**Table 1: *Igeo* values using NASC, UCC and base of the sediment profile as geochemical background values**

Depth (cm)		NASC		UCC					Base of the sediment profile		
		As	Br	As	Br	Cr	Sb	Ta	As	Br	Sb
2.5	PR1-01	1.66	6.31	1.66	5.10	0.97	1.97	0.14	1.12	3.28	1.65
5	PR1-02	1.82	6.50	1.82	5.29	1.22	2.18	0.28	1.28	3.47	1.86
7.5	PR1-03	1.81	6.25	1.81	5.04	1.58	2.05	0.64	1.27	3.23	1.73
10	PR1-04	0.98	4.89	0.98	3.68	1.70	1.35	0.79	0.44	1.86	1.03
12.5	PR1-05	0.63	4.11	0.63	2.89	1.89	0.95	0.95	0.09	1.08	0.63
15	PR1-06	0.69	3.66	0.69	2.45	2.03	0.87	0.81	0.15	0.63	0.55
17.5	PR1-07	-0.20	1.93	-0.20	0.72	1.94	-0.67	1.01	-0.74	-1.10	-0.98
20	PR1-08	0.55	3.94	0.55	2.73	1.87	0.32	1.04	0.01	0.91	0.00
22.5	PR1-09	0.53	3.63	0.53	2.42	1.93	0.36	1.22	-0.01	0.61	0.04
25	PR1-10	0.49	3.26	0.49	2.04	1.88	0.16	1.21	-0.05	0.23	-0.16
27.5	PR1-11	0.20	3.14	0.20	1.93	2.09	-0.19	1.51	-0.34	0.11	-0.51
30	PR1-12	0.20	2.90	0.20	1.69	1.92	-0.73	1.26	-0.34	-0.13	-1.05
35	PR1-13	-0.04	2.44	-0.04	1.23	2.02	-0.27	1.45	-0.58	-0.58	-0.58

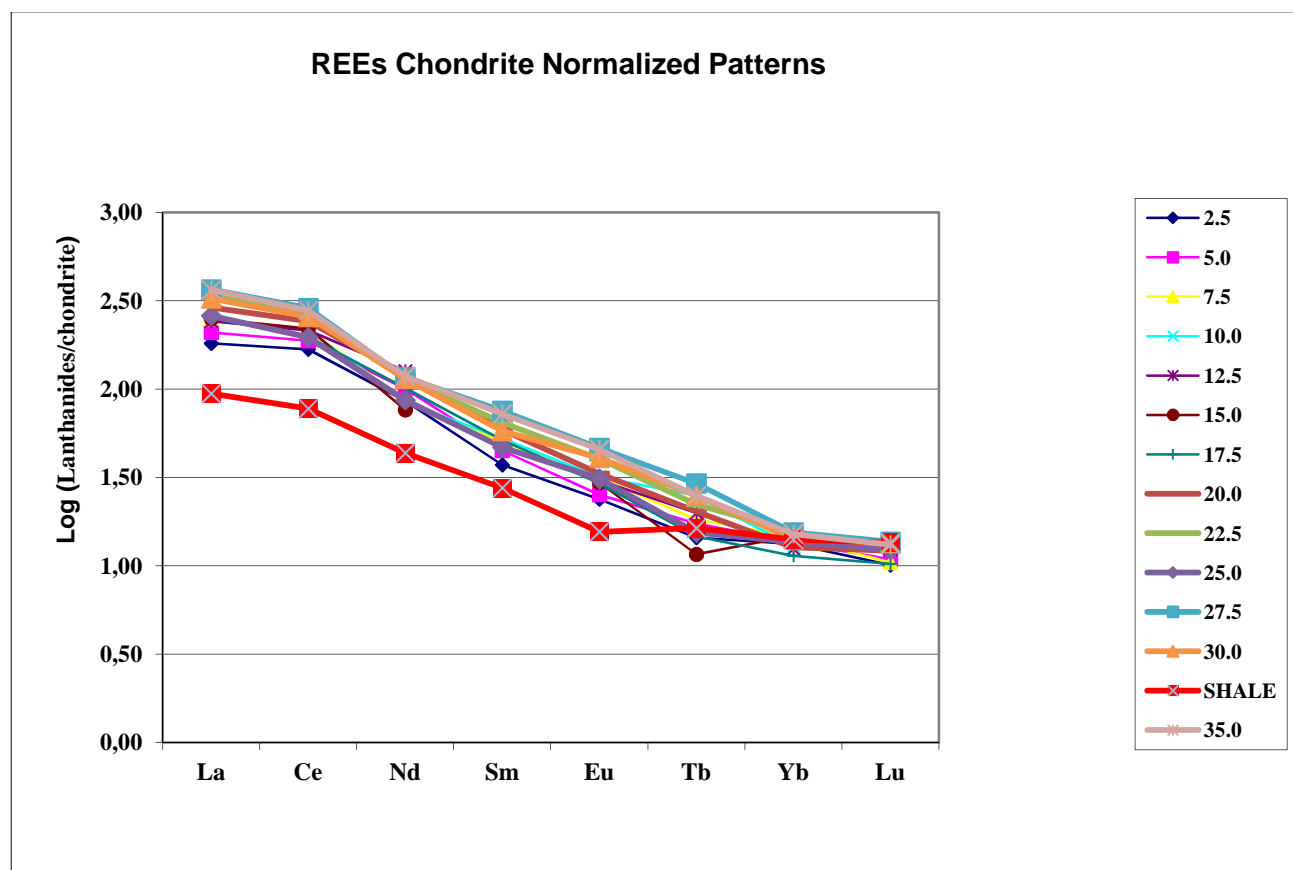
*Igeo*>1.5 - highlighted

### 3.4 Distribution patterns of REEs in the sediment profile

To study the distribution patterns of Rare Earth Elements (REEs), chondrite-normalization is widely applied. [4] The contents of REEs in chondrite proposed by Haskin et al [21] are often cited.

The signature or pattern of the REEs is usually described by normalizing the individual REE concentrations of a sample to those of the crustal abundance of the earth. An average REE composition of shale is used for this normalization [16, 22].

The normalization of REE concentrations with respect to a geological “reference” value is a useful tool to obtain a comparison among information of “contamination” sources.[23] The results obtained and the NASC reference levels were normalized in relation to chondrite values [24] as reference values (Figure 4). An enrichment of the light REE (LREE) (La to Sm) and for the middle REE (MREE) (Eu and Tb), and the same pattern for Yb and Lu (heavy –HREE) just as in the NASC values, were observed. This shows that sediments may be comparable to shale because they show the same contour as the curve of shale, and may soon be subject to the same geochemical processes in the environment.



**Figure 4: Chondrite-normalized curves showing the distribution patterns of REEs in sediments**

### 3.5 Multivariate statistical Analysis

Cluster Analysis for the chemical data (without RREs) was performed using Ward's method and Euclidian distances (Figure 5). The purpose of this analysis was to verify possible similarities between core samples (Figure 5a) and elements (Figure 5b). Two groups were identified (Figure 5a and b):

Group 1, formed by 2 sub-groups:

- sub-group A: samples Pr-09, 11, 12 and 13, grouped by K, Na and Hf;
- sub-group B: samples Pr-05, 06, 07, 08 and 10, grouped by Th, Sc, Rb and Ta, Cr, Ca, Co and Ba.

Group 2, formed by 2 sub-groups:

- sub-group A: samples Pr-03 and 04, separated by U, Zn and Cs;
- sub-group B: sample Pr-01 and 02, separated by Fe, Br, Sb and As.

Cluster Analysis was also performed for the REEs using Ward's method and Euclidian distances (Figure 6). Two main groups were again identified (Figure 6a and b):

Group 1, formed by 2 sub-groups:

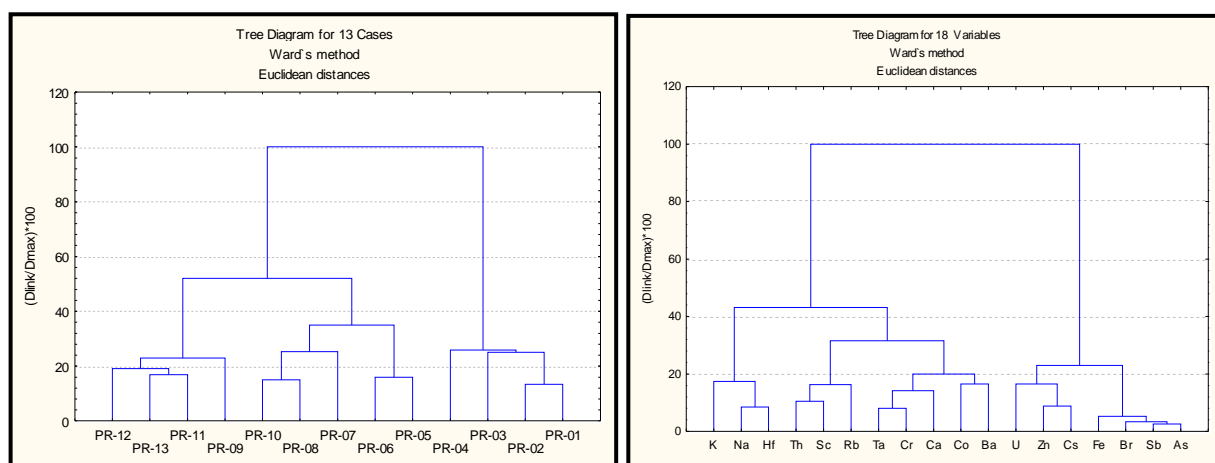
- sub-group A: samples Pr-11 and 13, for Tb and Sm;

- sub-group B: and Pr-09 and 12, for Nd;

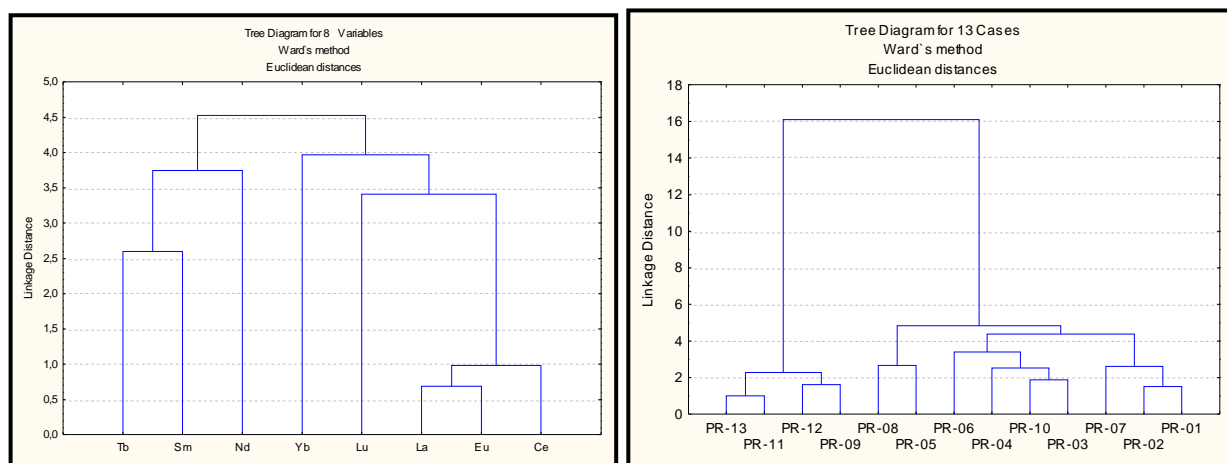
Group 2, formed by three sub-groups:

- sub-group A: samples Pr-05 and 08 formed by Yb;
- sub-group B: samples Pr-03,04, 06 and 10, formed by Lu;
- sub-group C: samples Pr-01, 02 and 07, separated by La, Eu and Ce

The Cluster analysis confirmed that sediment samples were grouped according to the obtained metal and trace concentrations in the sediment samples. In addition, these results confirmed those obtained from the EF and Igeo contamination indexes.



**Figure 5: Cluster Analysis for the chemical data: a) core samples b) elements**



**Figure 6: Cluster Analysis for the REE: a) elements b) core samples**

### 3. CONCLUSIONS

The determination of some metals, trace, and rare earth elements by INAA proved to be highly appropriate and thus can be an important tool for sediment monitoring, because its sensitivity, precision, and accuracy are extremely reliable.

Analyzing the results obtained by INAA it can be seen that As, Br, Fe, Sb, and Zn presented a decrease in concentration according to depth, indicating a possible anthropogenic contribution.

When the results for As, Cr, and Zn were compared to TEL and PEL oriented values, sediments from 0–10 cm surpassed the TEL values for **As** ( $5.9 \text{ mg kg}^{-1}$ ). For **Cr**, all samples in the profile exceeded the PEL value ( $90 \text{ mg kg}^{-1}$ ), and for **Zn**, all the results were much lower than the TEL value ( $123 \text{ mg kg}^{-1}$ ), mainly in the deeper layers.

When EF for sediments was calculated using NASC as a reference value, an  $EF > 1.5$  was found for the elements As, Br, Ta, Th, and some REEs (Ce, Eu, La, Nd, and Sm). The elements As and Br, presented higher EF values at the top of the profile, while Ta, Th, and some REEs (Ce, Eu, La, Nd, and Sm) showed higher values at the bottom of the sediment profile.

When EF was calculated using UCC as a reference value, the elements As, Br, and Sb presented a higher EF value at the top of the profile and Cr and Ta showed a higher EF in the bottom of the profile. REEs presented an  $EF < 1.5$  for all of them.

However, when the concentration levels at the base of the sediment profile were used as reference values, As, Br, Cs, Fe, Sb, and Zn showed an  $EF > 1.5$  with higher values at the top of the profile. Again REEs presented an  $EF < 1.5$  for all of them.

The *Igeo* results confirmed the EF results, giving a sediment classification of moderately polluted for As, Cr, and Sb ( $1 \leq Igeo < 2$ ) and extremely polluted for Br ( $Igeo > 5$ ) (NASC and UCC as reference values) and strongly polluted ( $3 \leq Igeo < 4$ ), when the base of the sediment profile concentration value was used.

When REE results and NASC values were normalized in relation to chondrite values as reference values, an enrichment as in the NASC values were observed for the LREEs (La to Sm), MREEs (Eu and Tb), and the same pattern for HREEs (Yb and Lu). This shows that these sediments may be comparable to shale and may be subject to the same geochemical processes in the environment.

As a conclusion of the present study, the sediment samples from Promissão reservoir can be classified as moderately polluted for As, Cr, and Sb and extremely polluted for Br, by using sediment contamination index assessment tools.

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