ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR – ABEN
2019 International Nuclear Atlantic Conference - INAC 2019
Santos, SP, Brazil, October 21-25, 2019

Agência Brasileira do ISBN
ISBN 978-85-99141-08-3

METAL DISTRIBUTION IN SEDIMENT CORES OF PONTE NOVA RESERVOIR, SÃO PAULO, BRAZIL

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ABSTRACT

The study of the metal distribution in sediments is very important from the point of view of environmental pollution. One of the objectives of the study of metal pollution in estuarine sediments is the historical record of anthropic activity. Ponte Nova reservoir, located in the upper basin of the Tietê River in the southern region of São Paulo State, covers an area of 25.7 km^2 and drains an area of 320 km^2. A sediment core was collected in the dam in August 2018 and in February 2019, sliced at every 2.5 cm, totalizing 13 samples in August and 17 samples in February 2019. Instrumental neutron activation analysis (INAA) was applied to the sediment samples 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. Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) was applied to determine (Cd, Cu, Mn, Ni, P and Pb). The results were evaluated by comparison to Canadian Sediment Quality Guidelines (TEL and PEL) and by the enrichment factor (EF) in relation to background values. EF>1.5 was obtained for As in both campaigns. In comparison to guidance values from Canada, Cr and Pb exceeded TEL in some superficial samples. Other elements analysed did not show enrichment factors >1.5 and the results were below TEL, indicating that there is not an important anthropogenic contribution of the analyzed elements in the reservoir.

1. INTRODUCTION

In the last decades, the study of sediment profiles has shown to be an excellent tool to establish the effects of natural and anthropic processes in depositional environments. Several studies have used sediment profiles to describe the history of different environments contamination.

Sediments are layers of relatively thin and divided materials that cover the bottom of rivers, streams, lakes, reservoirs, bays, estuaries and oceans. They usually consist of a mixture of minerals with fine, medium and coarse granulometric fractions, including clays, silts, and sand, aggregated to organic materials. Its composition may vary between sediments composed solely of minerals, or predominantly organic material. Sediments are deposits of a variety of biological, chemical and pollutant debris in the body of water [1-8].

Many contaminants can leave their signature in sediments, having as their condition their stability within the sediment column. Although most metals can be studied, the most commonly applied metals in the industry, such as Cd, Cr, Cu, Fe, Hg, Ni, Pb and Zn, are the most studied [4].

Mortatti *et al.* [9] evaluated the concentration and distribution of heavy metals in bottom sediments of the upper basin of the Tietê River. Nascimento & Mozeto [10] proposed regional reference concentrations of metals and metalloids in bottom sediments of the Tietê River basin, which, for some elements, proved to be very different from the global reference values. Favaro *et al.* [7] studied the distribution of metals in bottom sediments of various points of the Tietê River, from Salesópolis to Porto Feliz.

The reservoirs that supply the cities have been greatly influenced by urban expansion, due to the irregular occupation in its surroundings, presenting degraded areas. Several studies have presented serious problems of metal pollution in reservoirs.

Silva *et al*. [6] studied the behavior of the elements Al, Fe, Mn, Ca, Cu, Pb, Cd, Zn, Ni and Cr in sediments of three reservoirs located in the Metropolitan Region of São Paulo (SPMR), namely, Billings, Pirapora and Rasgão. Alegre *et al.*. [11] evaluated five-point sediment profiles from the Tietê River, from Salesópolis to Suzano, including a point in the Ponte Nova Reservoir, showing higher rates of metal pollution in Mogi das Cruzes and Suzano.

The São Paulo Metropolitan Region is considered the largest Brazilian urban area. According to the Brazilian Institute of Geography and Statistics (IBGE), it had about 12 million inhabitants in 2017, possessing eight water-producing systems. One of the major problems concerning the reservoirs is the quality of the water. Within the set of SPMR producer systems we will focus on the Alto Tietê system.

The Alto Tietê-UGRHI 06, according to the Integrated System of Management of Water Resources of the State of São Paulo (SigRH) comprises 34 municipalities and its main rivers are: Tietê, Pinheiros, Tamanduateí, Claro, Paraitinga, Jundiaí, Biritiba-Mirim and Taiaçupeba.

Since UGRHI 06 concentrates intense economic activities, environmental impacts on soil, water and air are of concern, so environmental monitoring is necessary to assess the quality of the environment and prevent or control possible impacts [12].

In order to evaluate the situation of the Ponte Nova Reservoir in relation to metal contamination and verify a historical record of anthropic activity, two sediment profiles were analyzed for major and trace elements.

The results were compared to guidance values and background values for a better understanding of the distribution of each element in the profile according to their geographic position and chemical behavior

2. MATERIAL AND METHODS

2.1. Study area

Ponte Nova reservoir is located at Salesópolis, in the upper basin of the Tietê River. The reservoir was built in 1972 for public water supply and controlling the river flow in São Paulo Metropolitan Region. According to Waters and Energy Department, DAEE, Ponte Nova Reservoir, supply 3.4 thousand liters per second of water. The space around the reservoir are mainly used to agricultural activities, natural pasturing and farming in the rural areas of the Mogi das Cruzes, Suzano and Itaquaquecetuba municipalities. This area shows high demographic occupation [8].The vegetation of the region covers about 1.3% of the Mata Atlântica forest. The preservation of the native forest helps to maintain the quality of water and climate, that in the region is classified as mesothermal (rainy summers and dry winters).

2.2. Sampling and sample preparation

Two sediment profiles were collected, in August/2018 and in February/2019, with the support of the Environmental Agency of the State of São Paulo (CETESB). The location of the sampling points are presented in Figure 1 (S 23 34' 30.4'', W 45 57' 23.9''). The sediment cores were sliced at every 2.5 cm *in situ* giving a total of 13 sediment samples (August/2018 profile) and 17 samples (February/2019). The sediment samples were dried at 40ºC in a stove at IPEN, sieved (< 2 mm), ground in an agate mortar, and homogenized before analysis.

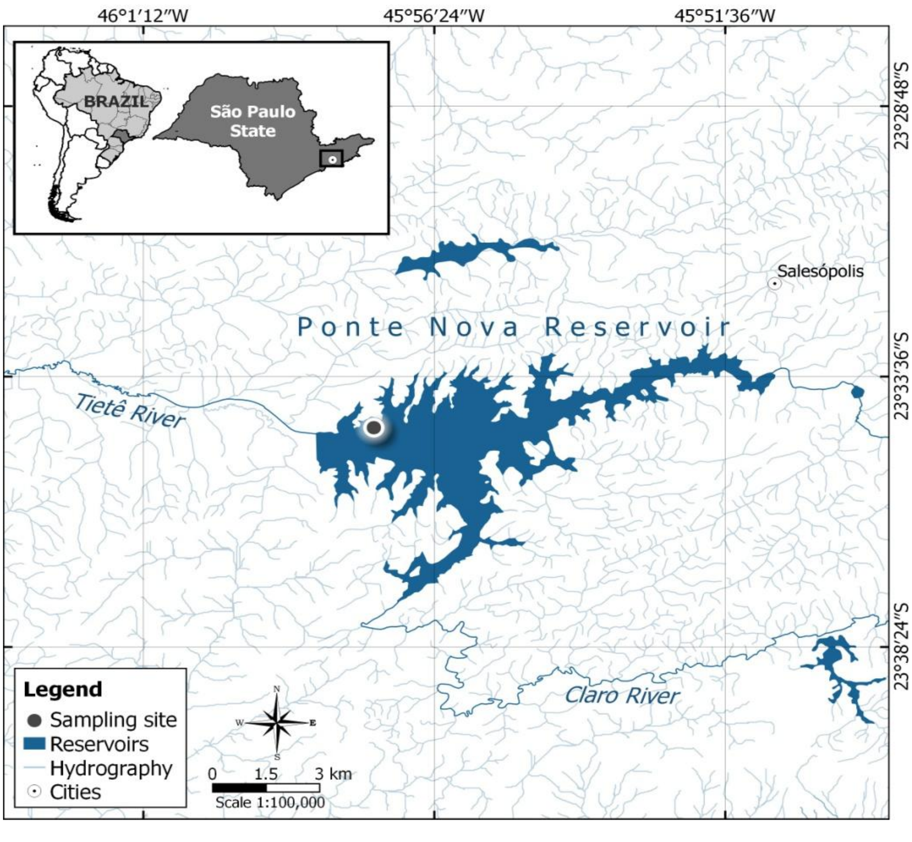

Figure 1: Sampling site located at the Ponte Nova Reservoir

2.3. Instrumental Neutron Activation Analysis (INAA)

For INAA, 100 mg of the sediment samples and the reference materials basalt BE-N and granite GSN (GIT-IWG) were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Samples and reference materials were irradiated for 8 hours, under a thermal neutron flux of 3 to 5x 10^{12} n/cm²s at the IEA-R1 nuclear research reactor at IPEN. Two series of measurements were made: the first, after one week decay and the second, after two weeks decay (15-20 days). Gamma spectrometry was performed using a GX20190 hyperpure Ge detector (Canberra). The gamma-ray spectra were processed by using an in-house gamma-ray software, VISPECT.The elements analyzed were As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb, Zn, Zr. The quality control of the results was performed by analyzing the reference material SOIL-7 (IAEA). The uncertainty of the results was propagated from the uncertainty of the parameters involved in the calculations: counting statistics; masses of samples; reference materials and uncertainty of the certified values of the reference materials.

2.4. Quality Control

The precision and accuracy of the results were verified by the analysis of the reference material (SOIL-7 IAEA). The zeta-score test was applied. If zeta-score ≤ 2, the individual result of the control sample (reference material) lies on the 95 % confidence interval of the target value. For the reference material analyzed in the present study, all results were in the interval range of $-2 \geq z \leq 2$, indicating good precision and accuracy of the INAA technique.

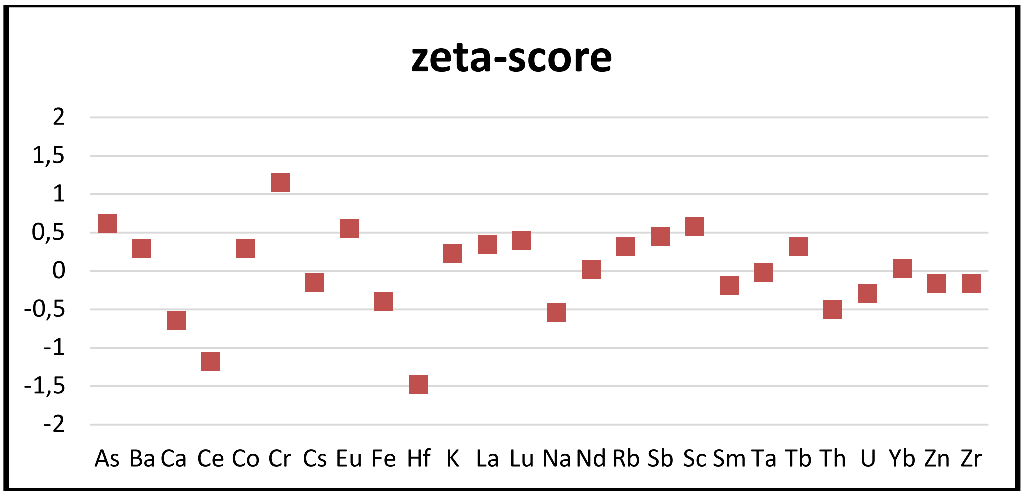

Figure 2: Control chart (zeta-values) for the analysed elements in Soil-7 (IAEA) reference material

2.5. ICP MS (*Inductively Coupled Plasma – Mass Spectrometry*)

The analyses of Cd, Co, Mn, Ni, P and Pb were performed at CETESB Laboratory of Inorganic Chemistry by ICP MS (Inductively Coupled Plasma Mass Spectrometry). The samples (1st and 2nd campaign) and the reference materials were weighed (approximately 0.5g) and subsequently transferred to teflon tubes where 10 mL of HNO_3 nitric acid (65%) were added. Samples and reference materials were digested according to EPA 3051 A [13] microwave-assisted method. After cooling, the samples were transferred by filtration to 50 mL volumetric flasks, where the content was completed using ultrapure water.

2.6 Enrichment Factor (EF)

The enrichment factor (EF) is an index used as a tool to evaluate the extent of metal pollution, defined as the double normalized ratio for a reference element (conservative or background) with the element studied and calculated by the equation:

$$EF = ([Me]/ [RE]sed) / ([Me]/ [RE]ref)$$

The elements more frequently used for this normalization are Al and Fe, but there are some studies that use Sc as conservative element [19]. In the present study, Sc was chosen as a normalize element and background values as reference values for sediments. The background values used are the concentration obtained in the last layer analysed in the sediment profile. EF values between 0.5 and 1.5 indicate that there is no pollution of anthropic origin. However, values of EF > 1.5, means that the main source of pollution is of anthropogenic origin. The higher the EF value, the higher the degree of pollution [12].

3. RESULTS AND DISCUSSION

Figure 3 and 4 presents the profiles of the analyzed elements with depth, in the first campaign (August 2018) and in the second campaign (February 2019).

The results of the first campaign showed that elements such as As, Cr, Pb, Ni and Sb presented the same behavior in both seasons, showing higher concentrations in surficial layers (0-12.5 cm) of the sediment profile. These elements are frequently associated to anthropogenic activities, suggesting anthropogenic origin of these elements.

In winter, elements usually associated to natural origin presented higher concentrations in deeper layers (22.5-32.5 cm), such as Ba, Ca, Cs, Hf, K, Lu, Na, Nd, Rb, Se, Ta, Th, U, Yb and Zr.

When the results obtained are compared with other studies in the same region, as the study of Favaro *et al.* [7] and Rocha *et al.* [8], it can be observed that higher concentrations in the first layers for Br, Co, Cr, Fe, Sc (behavior observed for the samples of August/ 2018 as February/2019), were also observed in the two cited studies.

In general, the same profiles with depth of the studied elements was observed in this study and in literature data, indicating that there was not a significant change in the situation of the reservoir in relation to metal contamination from 2014 to 2018.

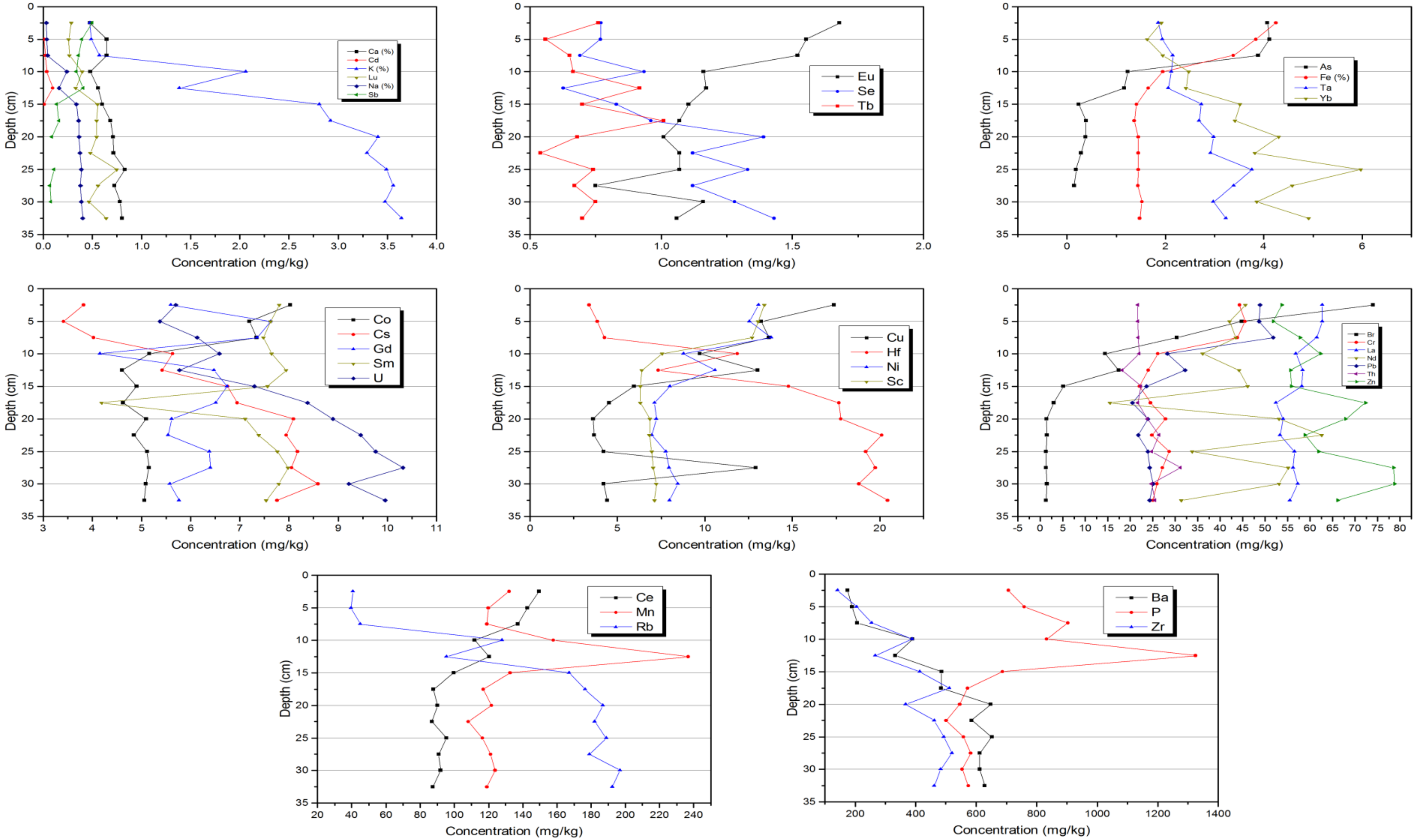

Fig 3: Element concentration profile August 2018

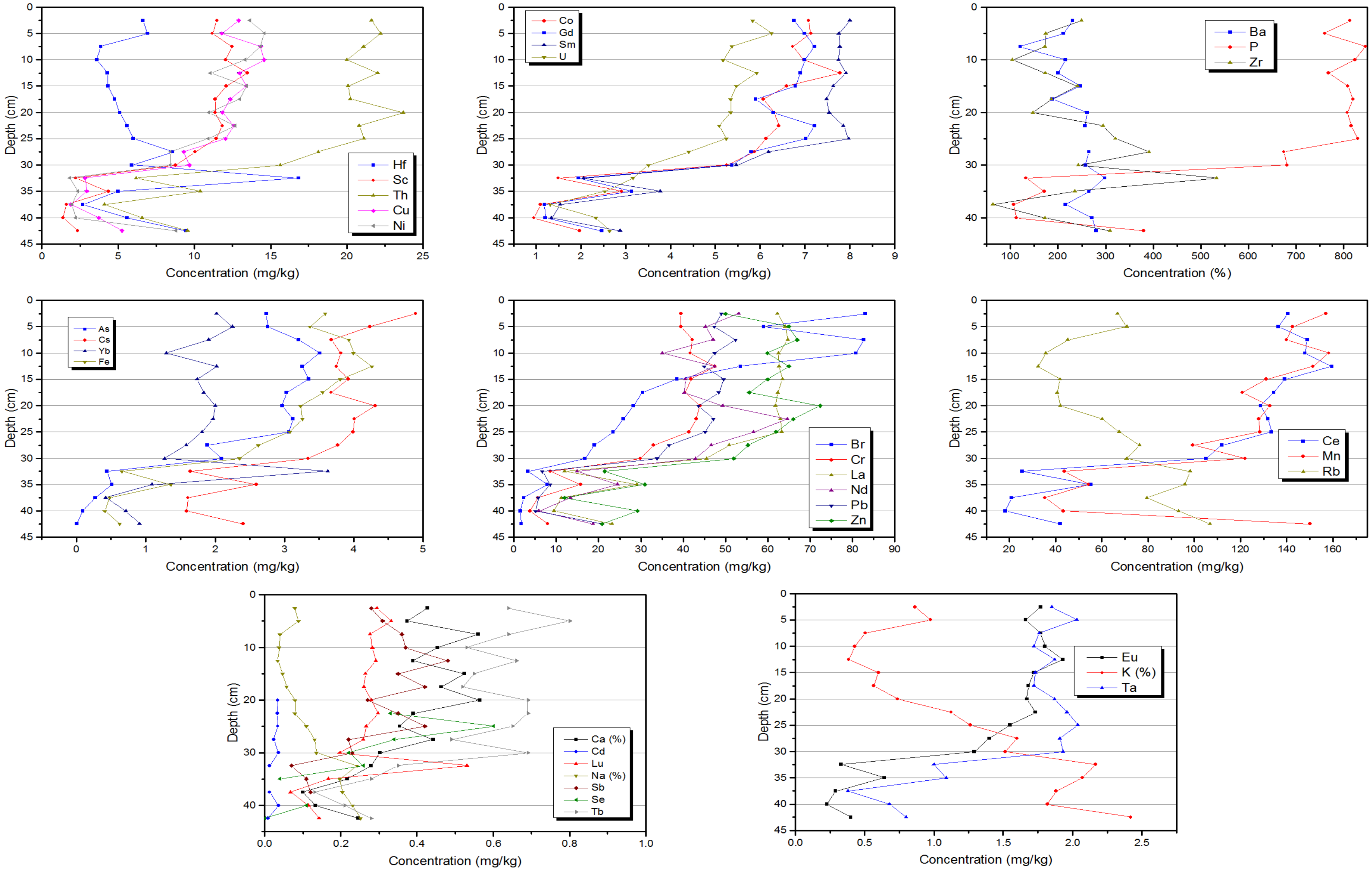

Fig 4: Element concentration profile February 2019

For the evaluation of the quality of sediments, CETESB adopted the guiding values TEL (Threshold Effect Level) and PEL (Probable Effect Level), established by the Canadian Council of the Environment Ministry CCME [18] for the total concentration of arsenic, chromium, cadmium, lead and zinc, in order to evaluate possible deleterious effects to biota. TEL indicates the concentration below which there is a rare occurrence of effects to biota and PEL indicates the concentration above which there is frequent occurrence of adverse effects to biota. Cr and Pb values in the first cuts (0-10 cm) exceeded the values of TEL, for the first campaign and in the second campaign (0-27.5 cm). For As Cd and Zn, all results were below TEL values in both campaigns (Figure 5).

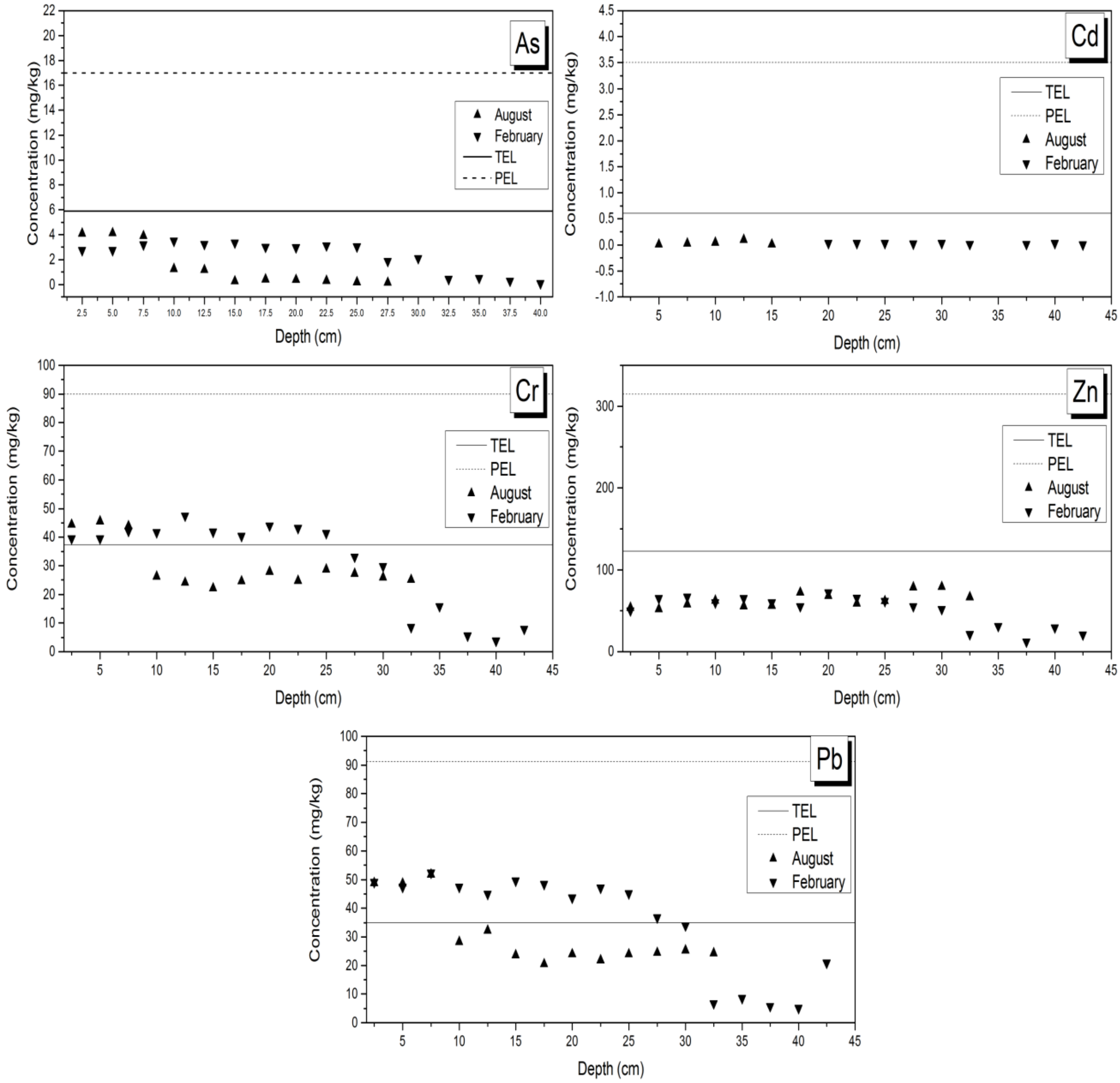

Figure 5: Results for As, Cd, Cr, Pb and Zn compared to TEL and PEL guiding values.

In this study, values of EF > 1.5 were obtained for As, Cu, Ni and Sb, for the first campaign, as can be observed in Figure 6. For the second campaign, EF>1.5 were obtained for As and Ba, and the results indicated possible anthropogenic contribution. The elements Cr, Pb and Zn presented EF<1.5 indicating that there is no anthropogenic contribution.

Sutherland [14], after justifying the absence to define a degree of pollution based on enrichment factor, proposed five categories of: EF < 2 low ; EF between 2 and 5 moderate; EF between 5 and 20 significant; EF between 20 and 40 very high and EF > 40 extremely high. According to this criterium, the degree of pollution of the elements As, Cu, Ni and Sb can be considered moderate in the first campaign. In the second campaign, only As and Ba can be considered as moderate pollutants in the reservoir.

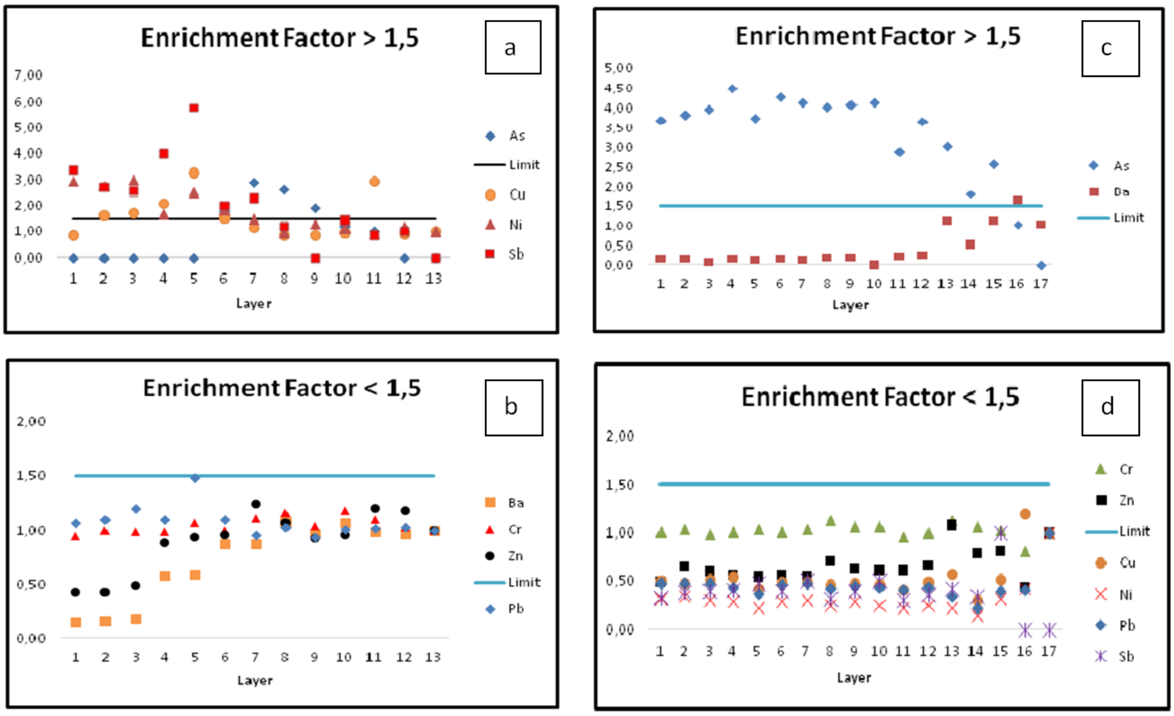

Figure 6: Enrichment Factor obtained for the elements analyzed by INAA and ICP-MS a) First campaign EF >1.5; b) First campaign EF < 1.5 c) Second campaign EF >1.5 d) Second campaign EF <1.5

4. CONCLUSIONS

The results showed that the studied reservoir did not present, in general, a significant contamination of the analysed elements. In comparison to previous literature data of this ecosystem, there was not an important change in the metal concentrations in the sediments. The elements Pb and Cr exceeded TEL values, but did not presented EF>1.5, which do not evidence contamination. Enrichment factors higher than 1.5 in both campaigns were obtained only for As, which may suggest anthropic origin.

ACKNOWLEDGMENTS

The authors wish to thank the Setor de Química Inorgânica and Setor de Amostragem from CETESB, the professionals and coworkers from CRPq/IPEN, for their help and support in this study, and to CNPq, for the financial support.

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