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METAL, TRACE AND RARE EARTH ELEMENTS ASSESSMENT IN A SEDIMENT PROFILE FROM TAIAÇUPEBA RESERVOIR, SÃO PAULO STATE, BY INAA

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ABSTRACT

The Taiaçupeba reservoir is located on the border of Mogi das Cruzes and Suzano counties and composes the Alto Tietê Producing System (SPAT). The region shows high population density and industrial production, which cause waste and contaminants generation, which can affect the water supply quality. The purpose of this study was to evaluate the concentration and distribution of As, Ba, Br, Co, Cr, Cs, Fe, Hf, K, Na, Rb, Sb, Sc, Ta, Th, U, Zn and the rare earth elements (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb), present in a sediment profile collected in the Taiaçupeba reservoir. Sampling was performed in 2016 by CETESB for monitoring purposes. Instrumental Neutron Activation Analysis technique was applied for multilemental determinations. A great variation of the concentration for the elements analyzed along the sediment profile was observed, with a concentration peak in the depth of 20cm for all elements and decreasing in the deepest slices. Enrichment factor (EF) and Geoacumulation Index (*IGeo*) tools used to evaluate the presence of anthropogenic pollution sources indicated As and Zn contamination, mainly in the more recent sediment samples (from 0 to 5 cm depth). When the concentration values for As, Cr and Zn were compared to TEL and PEL for quality sediment evaluation, none of the concentration values for As and Cr surpassed the PEL values but not Zn. The results showed that an important anthropogenic contribution for As, Cr and Zn in the upper layers of the sediment core is occurring.

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1. INTRODUCTION

Water is an essential natural resource to meet the demands of public and industrial supply, uses in agricultural irrigation and power generation. The demographic and industrial growth of the last decades has led to an increase in the use of this natural resource, and consequently, the deterioration of the water quality of rivers, lakes and reservoirs due to increased nutrient load and waste generation [1].

Water reservoirs are built to meet the demands of population growth. However, they cause environmental, social, economic and cultural impacts due to the alteration of the natural behavior of the water system and to the appearance of conflicts related to the use of water [2].

The damming of waters forms a lentic environment, where the flow and velocity of water currents favor the deposition of suspended particles, accumulating them in the bottom of the reservoirs and resulting in sedimentation [3,4].

The formation of the sediment comes from solid material carried by wind, ice and water from the earth's surface. It also comes from the deposition of organic material from animals and plants in the site. A large part of this material is deposited in rivers, lakes and reservoirs for many years [5,6].

In aquatic ecosystems, the bottom sediment represents the main compartment for accumulation, reprocessing and transfer of trace elements. These elements, potentially available for biota, can be released by microbial activity and changes in the various physicochemical factors affecting the environment, including pH, salinity, and oxide-reduction conditions [7].

Since 2002 CETESB (Environmental Company of the São Paulo State) evaluates the sediment quality of rivers and reservoirs of São Paulo State. In 2004 the Sediment Quality Criterion (CQS) was created and established quality classes for four lines of evidence: chemical substances, ecotoxicity, mutagenicity and benthic community. The CQS has been improved over the years and currently has nine lines of evidence distributed among the chemical, toxicological and biotic components [3].

Sediment has been an important study tool to evaluate the quality of aquatic ecosystems, since it portrays the historical conditions of the influence of anthropogenic activities on these environments, not always detectable by the use of water variables. Possible changes in the aquatic environment, such as increased flow and rainfall, or activities that interfere with the river bed such as dredging (whether of desanding or deepening of the channel), passage of ducts, construction of bridge support pillars, among others may stir the sediment. The sediment turnover can mobilize the contaminants from the solid phase to the dissolved phase, transferring the contaminants to the water column [3].

The sedimentary profiles allow the comparison of concentrations of elements in the surface sediments (that is, of the upper layers of the sediment, where the sedimentation is more recent) with the oldest sediments, going back to the formation of the reservoir. In addition to the visualization of concentrations in the profiles, the use of a geochemical tool associated to the basal values of the sedimentary profiles provides a better way of distinguishing between the geogenic and anthropogenic concentrations [8].

Since 2014, CETESB has been collecting sedimentary profiles in some rivers and reservoirs, in order to evaluate the depth distribution, to correlate the profile obtained with the history of land use and occupation and, consequently, with potential anthropogenic contributions [3].

In partnership with CETESB, a group of researchers from IPEN - CNEN / SP has studied various supply reservoirs in the state of São Paulo, complementing the data obtained for concentration metals obtained by CETESB using ICP-OES with concentration data for other elements of interest from the environmental point of view, including rare earth elements, using the Instrumental Neutron Activation technique (INAA). In some studies, in the Upper Tietê Region (UTR), superficial sediments were analyzed, while in others sedimentary profiles were studied [9,10,11].

FAVARO *et al* [9] analyzed surface sediments collected in 5 points of the Tietê River, from its headwaters to the municipality of Suzano, in 3 sampling campaigns. The results for Cd, Hg and Pb were compared to the values of TEL and PEL and at points P_3 and P_4, near industrial areas, P_3 located in Mogi das Cruzes and P_4 in Suzano after a sewage treatment plant, higher values were found for Pb and Hg in the sediments, exceeding the values of TEL in P_3 and between TEL and PEL in P_4.

ROCHA *et al* [10] analyzed the concentration and distribution of major and trace elements in bottom sediments in 12 points along the Tietê River, from Salesópolis to Pirapora do Bom Jesus, using INAA and FRX techniques. Using the criteria of TEL and PEL for the elements As, Cr and Zn, it was possible to classify the river as: less polluted (points 1A and 1B - river head); more polluted (2A to 3C, after crossing the city of São Paulo) and moderately polluted (points 4, 5, 6 and 7 - far from the city of São Paulo).

SILVA *et al* [11] evaluated the content of the toxic metals Cd, Cr, Cu, Hg, Ni, Pb and Zn in samples of surface sediments collected at strategic points of the Billings System, including the Rio Grande and Guarapiranga reservoirs. In general, the elements As, Cr, Cu, Ni, Pb and Zn presented values above PEL for most of the points sampled, being classified as of poor quality. Cd and Hg were between TEL and PEL for most points in both campaigns. The results indicated a greater compromise of the Billings reservoir in relation to toxic metals.

The aim of the present study was to determine the concentration and distribution of metals, trace elements and rare earth elements (REEs) in a sedimentary profile from the Taiaçupeba reservoir using the Instrumental Neutron Activation Analysis (INAA) technique. The enrichment factor (**EF**), Geoacumulation Index (***IGeo***) and also TEL and PEL guide values were used in the present study for sediment quality evaluation.

2. MATERIALS AND METHODS

2.1. Study Area

The Taiaçupeba reservoir is located in the municipalities of Mogi das Cruzes and Suzano, at 23°34‘S and 46°17‘W (CETESB, 2006) and at an altitude of 739.42m above sea level. It has a temperate climate, with temperatures ranging from 4 to 36 degrees centigrade and an average temperature of 20°C. Rainfall rates have averages ranging from 1,800 to 2,200 mm [12] The reservoir has a flooded area of 72.5 km^2, drainage area of 919 km^2 and flow of 9.7 m^3 / s.

The Taiaçupeba Reservoir is located in the Metropolitan Region of São Paulo (RMSP), one of the most densely populated areas of the country. The extensive urban occupation generates extremely high risks of pollution and contamination of the springs located in the region. The region's industrial growth promotes job creation and service sector growth. The development is based on the urbanization of the reservoir area [13].

The Taiaçupeba, together with the reservoirs of Ponte Nova, Biritiba-Mirim and Jundiaí, is used to feed the Alto Tietê Producer System [14] aiming at the multiple use of water resources, with emphasis on control of floods, public supply, irrigation, dilution of sewage and leisure.

The preservation of the water quality of the Taiaçupeba reservoir is of great importance, as it is in this reservoir that SABESP’s water capitation is located. In addition to the waters of its drainage basin, the reservoir also receives water from the other reservoirs of the producer system, through the transfer of water from the Jundiaí reservoir [15].

2.2. Sampling and sample preparation

The sediment profile was collected in 2016 by the specialized technicians of CETESB’s Sector of Sampling of Aquatic Environments – the geographic data are described in Table 1. The collected profile was sliced every 2.5 cm with the aid of an extruder, from top to bottom of the profile and the fractions were packed in properly identified plastic bags. The collected sediments were dried in an oven at 40°C until constant mass, macerated in agate mortar and stored in a Falcon bottle. The total fraction of the sediments (< 2mm) was analyzed.

Table 1. Data of the sediment profile sampling point, Taiaçupeba reservoir

Reservoir (Code CETESB)	Geographical coordinates of the sampling point	Date of sample collection	Number of fractions (profile depth, cm)
Taiaçupeba (PEBA 00900)	23^0 34”45’’ 46^0 17’18’’	6/30/2016	01 a 22 (55)

2.3.INAA Experimental Procedure

For multielemental determination about 150 mg of sediment (duplicate samples) and reference certified materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Sediment samples and reference materials were irradiated for a daily cycle (6-7 hs), under a thermal neutron flux of 5 x 10^{12} n cm^{-2} s^{-1} in the IEA-R1 nuclear reactor at IPEN. Two counting series were performed: the first after one-week decay and the second, after 15-20 days.

The measurements of the induced gamma-ray activity were carried out in a gamma-ray spectrometer with a GX20190 hyperpure Ge detector (Canberra) and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co, respectively. The elements analyzed 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 to identify the gamma-ray peaks and ESPECTRO to calculate the concentrations. The uncertainties of the results were calculated by error propagation. The methodology validation was verified by measuring the reference materials Lake Sediment (IAEA SL-1), Lake Sediment (IAEA SL-3) and BEN (Basalt –IWG-GIT), that presented certified concentration values for almost all elements analyzed [16].

2.4. Zeta–score Criteria

The Zeta-score criteria was used to check the INAA technique, in terms of accuracy and precision, analyzing the certified reference materials. For the approval of the results, the value of Zeta-score should be between -2 and +2 [17]. The Zeta score criteria are given by the relation:

$$Z = \frac{C_{cali} - C_{cert}}{\sqrt{(Scal)^2 - (Scert)^2}} \qquad (1)$$

where:
C_{cali} *= element i concentration in CRM analysis;*
C_{cert} *= certificate value of concentration / consensus for element i;*
S_{cal} *= expanded uncertainty of the concentration of element i in MR analysis;*
S_c *= expanded uncertainty of the certified consensus value for element i.*

2.5. Enrichment Factor (EF) and Geoaccumulation Index (*IGeo*)

EF and the Geoaccumulation index (*IGeo*) [18-20] are tools used for assessing pollution levels of metals in soils and sediments. 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 [18-20]:

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

In the present study, Sc was chosen as a reference element and NASC values and the basement (last layer) of the sediment profile as reference values. According to Zhang and Liu [20], 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. According to Sutherland [21], if EF<2.0 it means depletion or low enrichment; 2<EF<5, moderate enrichment; 5<EF<20, significant enrichment; 20<EF<40, very high enrichment and EF>40, extremely high enrichment.

The classification of pollution levels from the *IGeo* values are: <0, baseline; 0 to 1, unpolluted; 1 to 2, moderately polluted; 2 to 3, moderately to polluted; 3 to 4, polluted to strongly polluted; 4 to 5, strongly polluted and> 5, very strongly polluted. *IGeo* was calculated according to Equation 2.

$$Igeo = \mathbf{log}_2\left(\frac{C_{am}}{1.5C_{ref}}\right) \qquad (2)$$

where, C*am* = concentration of the element of interest in the sample; C*ref* = reference or background concentration of the element of interest.

3. RESULTS AND DISCUSSION

Figure 1 shows Zeta-score results obtained for the certified reference materials analyzed by INAA. All the results were in the range |Zeta| < 2, indicating the accuracy and precision of the analytical technique.

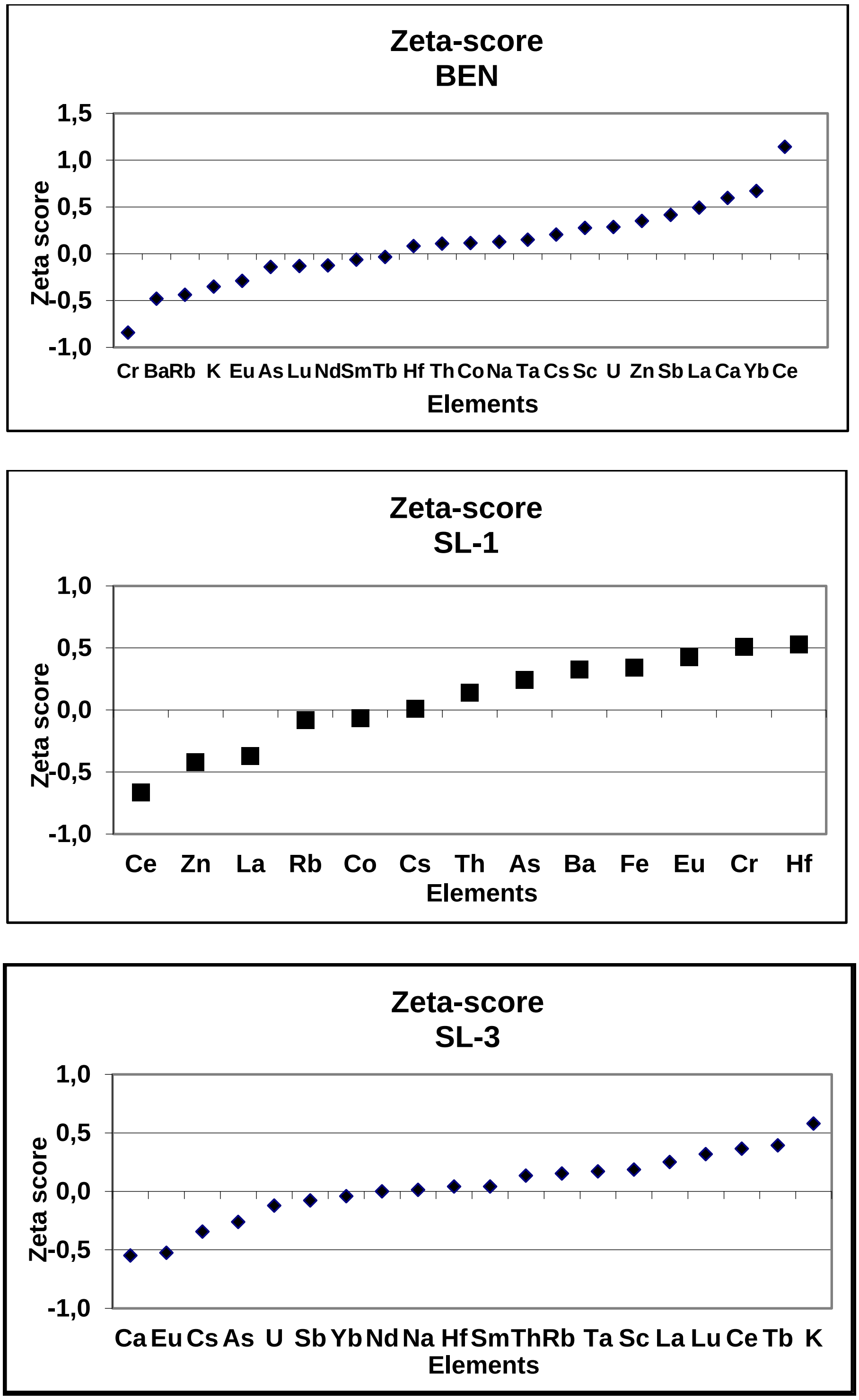

Figure 1. Zeta-score results for the certified reference materials analyzed by INAA

Table 2 presents the results obtained in the sediment core analysis by INAA, TEL and PEL guide values used by CETEB for sediment quality evaluation [18] and NASC (North American Shale Composite) [22]. For all the sediment profile a great concentration variation was observed with higher values in the superficial sediment mainly at 5 cm depth, showing the highest concentration for Zn (2112 mg kg^{-1}). Another concentration peak is clearly observed at

20 cm depth, with the highest concentration for all elements, except Hf, Sb, Ta and Zn. This tendency is better seen in Figure 2, where the concentration values versus depth is shown for all elements analyzed. It can be seen that, in general, lower concentrations for most elements are found in the deepest layers while higher concentrations are found in the top of the sediment profile, indicating an anthropogenic contribution along the core and consequently, along the time. There was an important anthropogenic contribution that corresponds to the 20.0 cm depth, but it was not possible to find a reasonable explanation for this finding.

The average values found for the Upper Tietê Region (UTR) in a Nascimento & Mozetto study [23], for bottom sediments for As, Co, Cr, Th, U and Zn (Table 2) were much higher than the values obtained in the present study, except for Cr and Zn. The UTR in this study included Salesópolis, Biritiba Mirim, Cotia, Sao Paulo and Pirapora do Bom Jesus Counties, the last two very polluted ones, which could explain such higher concentration values for some elements.

Souza [24] analyzed 4 sediment profiles, collected in 2015, in the Taiaçupeba reservoir, by INAA. The profiles were sliced every 3 cm. In one of the analyzed profiles, a slight increase in the concentration of the elements Sb, Co, Hf, Sc, Rb and Zn in the most superficial sediments (0 to 12 cm) was observed. The peak of Zn concentration (38157mg kg^{-1}) in this profile was observed at 12cm depth.

Table 2. Concentration results (mg kg^{-1}) for the sediment core analyzed by INAA, Taiaçupeba reservoir, TEL and PEL guide values and NASC values

Depth (cm)	As	Ba	Br	Co	Cr	Cs	Fe (%)	Hf	K (%)	Na	Rb	Sb	Sc	Ta	Th	U	Zn
2.5	6.7	322	17.9	15.5	66	7.0	5.9	9.1	0.83	861	61	0.6	13.4	1.8	16.5	3.7	783
5.0	**9.0**	**382**	**21.8**	**11.7**	**70**	**6.6**	**6.4**	**7.9**	**0.63**	**699**	**49**	**0.8**	**13.1**	**1.8**	**16.2**	**3.3**	**2112**
7.5	8.5	547	17.1	21.0	80	11.5	4.0	11.7	1.12	1103	85	0.6	16.9	2.2	19.4	4.3	490
10.0	7.7	817	12.4	25.5	84	9.9	4.4	14.0	1.12	1205	104	0.6	17.3	2.1	20.9	4.4	129
12.5	6.4	509	12.4	24.6	78	9.9	4.0	12.4	1.90	1093	100	0.5	16.2	2.2	21.9	4.9	120
15.0	6.2	249	10.9	20.4	66	8.6	3.6	12.8	1.70	995	84	0.4	13.7	1.9	19.3	4.7	109
17.5	7.7	288	13.3	22.1	75	10.0	4.2	12.9	2.25	1288	93	0.5	15.3	2.0	20.5	5.0	110
20.0	**10.9**	**886**	**17.1**	**27.4**	**162**	**13.3**	**8.2**	**10.2**	**5.18**	**2580**	**288**	**0.5**	**27.7**	**1.9**	**29.9**	**5.3**	**213**
22.5	7.1	683	13.9	22.8	76	9.0	5.1	11.7	1.43	1066	91	0.5	16.4	2.0	18.7	4.5	94
25.0	7.4	743	15.0	23.4	82	10.1	4.6	13.6	1.59	1153	105	0.5	17.9	2.0	20.6	4.5	111
27.5	6.5	539	19.7	19.8	71	8.4	3.5	10.8	1.42	982	83	0.5	15.1	1.7	14.8	4.1	116
30.0	4.6	480	11.1	12.7	60	7.2	2.7	10.8	1.52	914	99	0.4	12.5	1.5	15.7	3.9	102
32.5	2.8	380	7.8	10.2	27	8.0	1.9	11.2	1.24	870	66	0.3	10.4	1.2	12.1	3.7	69
35.0	4.5	517	11.2	15.4	62	9.7	2.6	11.9	1.54	1030	76	0.5	13.7	2.0	16.5	4.1	94
37.5	2.9	535	10.1	14.7	61	9.2	2.4	12.2	1.49	987	83	0.3	13.3	1.6	16.0	4.3	94
40.0	3.0	415	9.2	15.1	52	7.8	1.9	10.6	1.32	900	67	0.3	11.4	1.5	13.6	3.5	82
42.5	1.6	369	5.3	6.9	33	4.0	1.1	11.2	0.95	749	62	0.1	7.2	1.0	10.6	2.8	59
45.0	1.8	257	6.1	7.5	33	4.5	1.1	8.8	0.93	713	53	0.3	7.1	1.0	10.7	3.1	57
47.5	0.8	195	3.2	3.6	20	2.4	0.6	6.4	0.74	535	38	0.1	4.3	0.6	6.8	1.8	37
50.0	0.8	268	2.9	4.7	23	2.5	0.7	6.5	0.72	584	40	0.2	4.8	0.7	7.7	2.3	41
52.5	1.2	243	3.9	5.8	28	3.6	0.9	8.1	0.89	657	45	0.2	5.9	0.9	9.9	2.4	47
55.0	1.4	286	4.7	6.3	32	3.7	1.0	9.6	1.07	712	50	0.2	6.4	1.0	11.2	1.9	61
Mean	**5.0**	**450**	**11.2**	**15.3**	**61**	**7.6**	**3.2**	**10.7**	**1.44**	**985**	**83**	**0.4**	**12.7**	**1.6**	**15.9**	**3.7**	**233**
Sd	**3.0**	**196**	**5.5**	**7.5**	**31**	**3.0**	**2.1**	**2.1**	**0.93**	**411**	**51**	**0.2**	**5.4**	**0.5**	**5.4**	**1.0**	**453**
Min	**0.8**	**195**	**2.9**	**3.6**	**20**	**2.4**	**0.6**	**6.4**	**0.63**	**535**	**38**	**0.1**	**4.3**	**0.6**	**6.8**	**1.8**	**37**
Max	**10.9**	**886**	**21.8**	**27.4**	**162**	**13.3**	**8.2**	**14.0**	**5.18**	**2580**	**288**	**0.8**	**27.7**	**2.2**	**29.9**	**5.3**	**2112**
TEL	**5.9**				**37.3**												**123**
PEL	**17**				**90**												**315**
NASC [22]	**2.0**	**636**	**0.69**	**28**	**125**	**5.2**	**4.00**	**6.3**	**3.29**	**7500**	**125**	**2.1**	**15.0**	**1.1**	**12**	**2.7**	**85**
Nasc& Mozetto[23]	**23± 17**			**19± 3**	**36± 17**										**24± 8**	**12± 5**	**82± 14**

n.d. – not determined

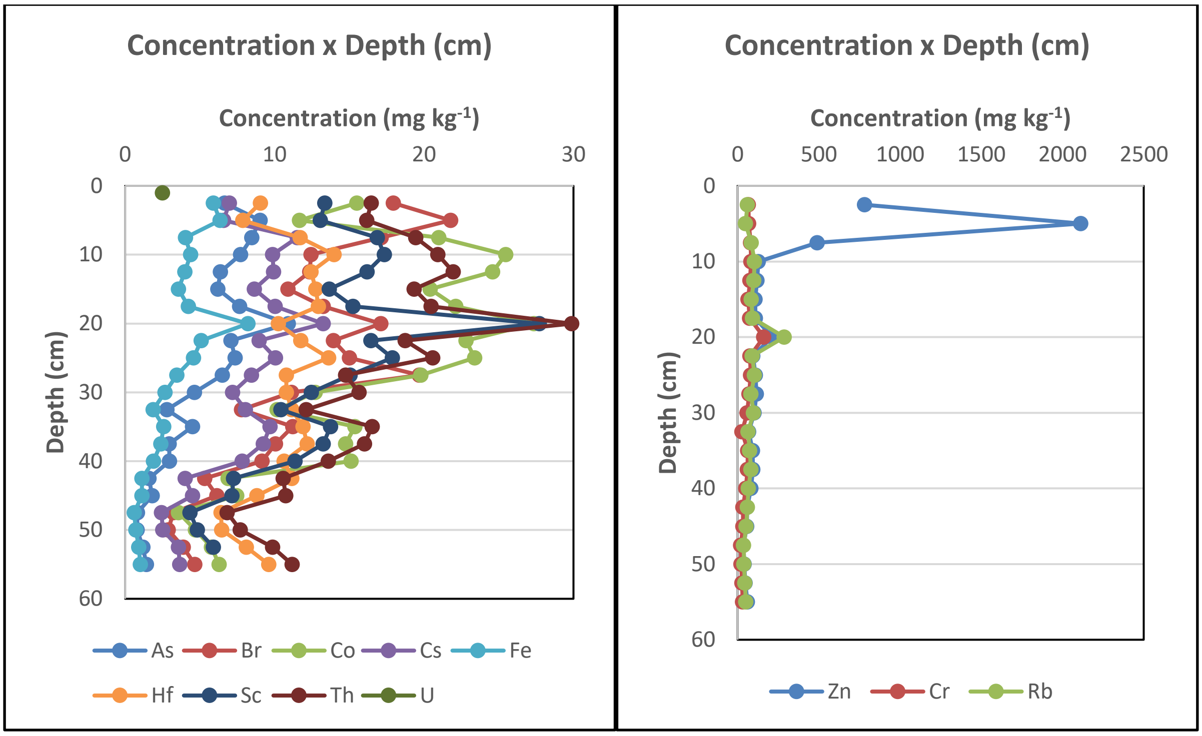

Figure 2. Concentrations (mg kg^{-1}) x depth (cm) in the sediment profile, Taiaçupeba reservoir

3.1. Sediment quality evaluation by TEL and PEL guide values

As a criterion for quality sediment evaluation for metals, CETESB adopted the TEL and PEL guide values, established by the Canadian Council of the Ministry of the Environment (CCME)[18] for the total concentration of As, 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 PEL (Probable Effect Level), the concentration above which there is frequent occurrence of these effects. In the present study, when As, Cr and Zn were compared to TEL and PEL values, sediment slices from 2.5 to 27.5 depths surpassed the TEL values for As (5.9 mg kg^{-1}). For Cr, slices situated from 2.5 to 40.0 cm depth surpassed the TEL value (35.3 mg kg^{-1}). For Zn, slices from 2.5, 5.0, 7.5, 10.0 and 20.0 cm depth surpassed the TEL value (123 mg kg^{-1}). None of the concentration values for As and Cr surpassed the PEL values. Zn surpassed PEL values in slices taken at 2.5, 5.0, 7.5 and 20.0 cm. These results show that an important anthropogenic contribution for As, Cr and Zn in the upper layers of the sediment core is occurring.

Concentration values of Cu and Zn above PEL, As, Cd, Cr, Ni, Hg and Pb above TEL were found by CETESB [3], in the analysis of this same sediment profile, using ICP OES analytical technique. According to CETESB, As, Cr and Pb occur naturally in the region where the Taiaçupeba reservoir is located. Domestic sewage and agricultural inputs in the reservoir can be responsible for the enrichment of both natural and anthropogenic elements in this reservoir. However, sources of contaminants of anthropogenic origin still need to be better investigated. CETESB [3]. They also concluded that the contaminants are bio-available and may be causing damage to the benthic community and, consequently, to the rest of their aquatic fauna [3].

3.2. Contamination assessment applying the EF and *IGeo* indexes

For the other elements determined by INAA without a guide value for comparison, the **EF** and ***IGeo*** indexes were calculated. Sc was used due to its low occurrence variability, as it is a conservative element, and has been applied in other studies [9,10,25]. Table 3 displays the points with EF>2.0 or *IGeo*>1.5 calculated by using NASC values and concentration values of the bottom sediment profile (last layer) as reference or background values. Arsenic (**As)** presented 2<EF<5, considered moderate enrichment, and Zn 5<EF<20, significant enrichment according to the Sutherland criteria [20]. Other elements such as Ba, Br, Co, Cr, Cs, Fe and U presented 2.0<EF<5.0, moderate enrichment, in general, along the sediment profile (from the top 2.5 cm to 40.0 cm depth), when the concentration values of the last layer of the sediment profile were used as background values. The higher EF values for these elements were also found in the layer correspondent to 20.0 cm depth. The *IGeo* analysis confirmed the results presented for EF values only for As, Fe and Zn but with lower values (1.5< *IGeo<4.5*): from 1 to 2, moderately polluted; 2 to 3, moderately to polluted; 3 to 4, polluted to heavily polluted, according the *IGeo* classification criteria (Table 3).

The data published by CETESB on its report about this sediment profile analysis by ICP OES also found high EF values for Zn in the more recent layers of the sediment profile confirming our findings for this element [3].

Table 3. EF results (EF>2.0) and *IGeo* results (>1.5) calculated by using NASC values and concentration values of the sediment profile basement

	EF (NASC)		**EF (basement of the sediment profile)**									***IGeo* (NASC)**		***IGeo* (basement)**		
Depth (cm)	**As**	**Zn**	**As**	**Ba**	**Br**	**Co**	**Cr**	**Cs**	**Fe (%)**	**U**	**Zn**	**As**	**Zn**	**As**	**Fe (%)**	**Zn**
2.5	2.9	8.2	4.4		3.6	2.3	2.0		5.5	1.9	12.2		2.6	1.6	2.0	3.1
5.0	3.9	**21.4**	5.8		4.3		2.0		5.7		**32.0**	1.6	**4.1**	2.1	2.1	**4.5**
7.5	3.6	4.9	5.4		3.3	3.0	2.3	2.9	3.6	2.1	7.4	1.5	1.9	2.0		2.4
10.0	3.1		4.7	2.5	2.3	3.5	2.3	2.3	3.7	2.0				1.8	1.5	
12.5	2.7		4.0		2.4	3.6	2.2	2.5	3.6	2.4				1.6		
15.0	2.6		3.9		2.1	2.9	1.9	2.1	3.2	2.3				1.5		
17.5	3.3		4.9		2.6	3.2	2.2	2.5	3.8	2.4				1.8	1.5	
20.0	**4.9**	**2.2**	**7.2**	**2.9**	**3.5**	**4.1**	**4.9**	**3.4**	**7.7**	**2.7**	**3.3**	**1.9**		**2.3**	**2.4**	
22.5	3.0		4.5	2.2	2.7	3.3	2.2	2.2	4.5	2.2				1.7		
25.0	3.0		4.4	2.2	2.8	3.2	2.2	2.4	3.9	2.0				1.8		
27.5	2.7		4.1		3.8	2.8	2.0	2.1	3.1	1.9				1.6		
30.0	1.9		2.9		2.1				2.3	1.8						
32.5			1.9					2.1	1.8	1.9						
35.0	2.0		3.0		2.3	2.3		2.5	2.4	2.0						
37.5					2.0	2.2		2.4	2.2	2.1						
40.0						2.2										

3.3.Distribution pattern of the Rare Earth Elements (REEs)

Table 4 presents the REEs concentration results for the sediment core analyzed in the present study, ΣREE (La to Lu), ΣLREE (Light Rare Earth Elements - La to Eu), ΣHREE (Heavy Rare Earth Elements - Tb to Lu), some relations between concentrations of La, Sm and Yb and anomalies of Eu and Ce.

The measured concentrations of REEs are commonly normalized to different data sets. The "shales" NASC [21] and Post-Archean Australian Shale values (PAAS) [26] are commonly utilized in environmental studies [19]. This normalization is calculated dividing the concentration values obtained in the present study by PAAS or NASC values, for each element. In the present study, PAAS values were used for this normalization. Eu and Ce anomalies are not present according to the (Eu/Eu*) and (Ce/Ce*) ratios, which values were lower than 1.0. The ΣLREE/ ΣHREE ratios found along the core presented very similar results to the same relation in NASC and PAAS values (Table 4). In general, the ratios were higher in the upper layers and lower at the deeper layers of the sediment profile, showing a light REEs (LREE) enrichment. At 20.0 cm depth, in general, higher concentrations were observed for all REEs analyzed in the present study.

Table 4. Total REE, light REE (LREE) (La to Eu), heavy REE (HREE) (Tb to Lu) concentrations (mg kg^{-1}), LREE/HREE, Ce/Ce*, Eu/Eu* ratios in the sediment core from Taiaçupeba reservoir

Depth (cm)	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	ΣREE	ΣLREE	ΣHREE	ΣLREE/ ΣHREE	Eu/Eu*	Ce/Ce*
2.5	36.9	69	23	4.9	0.87	0.66	2.89	0.51	**138.4**	134.3	4.1	33.1	0.98	0.78
5.0	33.3	66	36	4.2	0.81	0.56	2.69	0.45	**143.5**	139.8	3.7	37.8	1.02	0.61
7.5	43.8	83	22	6.2	1.09	0.79	4.11	0.62	**161.4**	155.9	5.5	28.2	0.99	0.87
10.0	49.7	92	20	6.8	1.17	1.25	4.29	0.79	**176.2**	169.9	6.3	26.8	0.82	0.97
12.5	48.5	101	23	10.2	1.23	1.06	4.37	0.76	**190.7**	184.5	6.2	29.8	0.91	0.95
15.0	44.7	93	32	6.3	0.96	0.97	4.66	0.70	**183.2**	176.9	6.3	27.9	0.84	0.77
17.5	54.1	94	28	7.5	1.03	1.09	4.20	0.67	**190.7**	184.8	6.0	31.0	0.82	0.82
20.0	**65.3**	**158**	**26**	**9.4**	**2.31**	**0.99**	**4.89**	**0.70**	**267.4**	**260.9**	**6.6**	**39.6**	**1.29**	**1.12**
22.5	42.1	88	40	6.3	1.02	0.93	3.68	0.58	**182.2**	177.1	5.2	34.1	0.89	0.68
25.0	42.8	92	45	6.0	1.15	0.85	4.09	0.64	**192.3**	186.7	5.6	33.5	0.99	0.65
27.5	39.0	78	24	5.3	0.92	1.03	3.44	0.52	**151.2**	146.8	5.0	29.4	1.19	0.81
30.0	39.0	74	36	6.4	0.94	0.82	3.69	0.56	**160.9**	155.8	5.1	30.7	0.91	0.65
32.5	33.9	64	34	6.4	0.86	0.95	4.00	0.78	**144.3**	138.6	5.7	24.2	0.80	0.62
35.0	43.4	77	41	8.2	1.03	1.00	3.91	0.69	**175.7**	170.1	5.6	30.4	0.86	0.62
37.5	41.8	79	35	7.8	1.10	1.02	4.51	0.72	**171.2**	165.0	6.2	26.4	0.88	0.67
40.0	37.0	68	23	5.3	0.97	0.98	3.97	0.70	**139.7**	134.0	5.6	23.7	0.84	0.77
42.5	30.3	57	30	5.8	0.64	0.86	3.68	0.56	**128.8**	123.7	5.1	24.3	0.73	0.62
45.0	31.7	61	31	6.0	0.68	0.89	3.63	0.57	**136.1**	131.1	5.1	25.7	0.74	0.63
47.5	19.3	38	19	2.8	0.50	0.68	1.84	0.28	**81.4**	79.2	2.8	28.3	0.81	0.63
50.0	22.5	40	22	3.9	0.51	0.91	2.58	0.39	**92.8**	88.9	3.9	22.9	0.63	0.62
52.5	27.8	53	27	4.3	0.63	0.84	2.90	0.48	**117.7**	113.5	4.2	26.9	0.73	0.63
55.0	32.7	61	27	6.4	0.73	1.39	3.89	0.67	**133.8**	127.9	6.0	21.5	0.62	0.68
Mean	**39.1**	**77**	**29**	**6.2**	**1.0**	**0.9**	**3.7**	**0.61**						
Sd	**10.4**	**25**	**7**	**1.8**	**0.4**	**0.2**	**0.7**	**0.13**						
Min	**19.3**	**38**	**19**	**2.5**	**0.4**	**0.5**	**1.8**	**0.28**						
Max	**65.3**	**158**	**45**	**10.2**	**2.3**	**1.4**	**4.9**	**0.79**						
PAAS	**38.2**	**79.6**	**33.9**	**5.55**	**1.08**	**0.774**	**2.82**	**0.433**	162.4	**158.3**	**4.0**	**39.3**		
NASC	**31.00**	**67.0**	**27.40**	**5.6**	**1.20**	**0.85**	**3.1**	**0.46**	136.6	**132.2**	**4.4**	**30.0**		

CONCLUSIONS

Instrumental Neutron Activation Analysis (INAA) proved to be highly appropriate to determine some metals, trace and rare earth elements in sediment samples and thus can be an important tool for sediment monitoring as its sensitivity, precision and accuracy are extremely reliable.

In general, lower concentrations for most elements analyzed in the last layers and higher concentrations in the top of the sediment profile were found, indicating an anthropogenic contribution along the core and consequently, along the time. There was an important anthropogenic contribution that corresponds to the 20.0 cm depth, but it was not possible to find a reasonable explanation for this finding.

When the As, Cr and Zn were compared to TEL and PEL guide values, sediment slices from 2.5 to 27.5 depths surpassed the TEL values for As (5.9 mg kg^{-1}) and for Cr, slices situated from 2.5 to 40.0 cm depth surpassed the TEL value (35.3 mg kg^{-1}). For Zn, slices from 2.5, 5.0, 7.5, 10.0 and 20.0 cm depth surpassed the TEL value (123 mg kg^{-1}). None of the concentration values for As and Cr surpassed the PEL values. Zn surpassed PEL values in the slices 2.5, 5.0, 7.5 and 20.0 cm depths. These results show that an important anthropogenic contribution for As, Cr and Zn in the upper layers of the sediment core is occurring.

According to CETESB, As and Cr occur naturally in the region where the Taiaçupeba reservoir is located. Domestic sewage and agricultural inputs in the reservoir can be responsible for the enrichment of both natural and anthropogenic elements in the Taiaçupeba reservoir. However, sources of contaminants of anthropogenic origin still need to be better investigated. They also concluded that the contaminants are bio-available and may be causing damage to the benthic community and, consequently, to the rest of their aquatic fauna.

For the other elements determined by INAA without a guide value for comparison, the **EF** and ***IGeo*** indexes were used, and at many points EF>2.0 and *IGeo*>1.5 were found. A**s** presented moderate enrichment, and Zn significant enrichment. Other elements such as Ba, Br, Co, Cr, Cs, Fe and U presented moderate enrichment, in general along the sediment core (from the top to the 40.0 cm depth). The higher EF values for these elements were found in the layer correspondent to 20.0 cm depth. The *IGeo* values confirmed the results presented for EF values only for As, Fe and Zn but with lower values.

The present study contributed to a data bank results for REEs concentration in sediment profiles for the Taiaçupeba reservoir. When REEs concentrations were used for distribution pattern according to PAAS normalization, an enrichment in LREE (La to Sm) was observed in the upper layers of the sediment profile. At 20.0 cm depth, higher concentrations were observed for all REEs analyzed in the present study.

Based on the results for the elements analyzed, by using different criteria of pollution assessment, the Taiaçupeba Reservoir can be considered a non-polluted aquatic body, except for Zn.

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