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DISTRIBUTION AND CONCENTRATION EVALUATION OF TRACE AND RARE EARTH ELEMENTS IN SEDIMENT SAMPLES OF THE BILLINGS AND GUARAPIRANGA RESERVOIR SYSTEMS

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ABSTRACT

Concentration and distribution of trace and rare earth elements in bottom sediment samples collected in the Billings System (including Rio Grande and Guarapiranga Reservoirs) were assessed by using Instrumental Neutron Activation (INAA). To evaluate the sources of anthropogenic contamination the enrichment factor (FE) and the geoacumulation index (*IGeo*) were calculated using NASC and Guarapiranga Park Soil as Reference Values. Results were compared to the concentration guideline values established by CCME (Canadian Council of Ministers of the Environment) environmental agency for As, Cr and Zn, and values in other published studies. Most points exceeded TEL values and, in some points, PEL values for these elements, indicating poor sediment quality in these reservoirs. In general terms, the elements As, Cr, Sb and Zn through EF and *IGeo* calculations present enrichment at all points analyzed, in both collection campaigns, except for the Rio Grande Reservoir points. The region where the reservoirs are located receive untreated sewage as well as pollution from urban occupation, industrial and mining activities, making it difficult to accurately identify the pollution sources. This study found higher concentrations of the elements analyzed in the Billings Reservoir, indicating a greater contamination level in relation to the other reservoirs.

1. INTRODUCTION

The reservoirs are aquatic systems constructed as a consequence of the industrial and socioeconomic growth of Brazil, with the purpose of generating electricity and for water supply purposes. Environmental impacts occurred during and after the construction of the reservoirs, changing the soil of the surrounding area. With reservoirs construction, artificial lake ecosystems arose in great quantity, resulting in hydrological, atmospheric and biological alterations [1,2].

The damming of the waters is responsible for the change in these regimes, changing from lotic (common to rivers) to lentic, reducing the flow and speed of the water, which favors the deposition of suspended particles, accumulating them in the bottom of the reservoirs, resulting in sedimentation [1,2].

Sediments are a major and important source of study, since their formation comes from solid material carried by wind, ice and water from the earth's surface. They also originate from the deposition of organic material from animals and plants that live in this environment. Most of these materials have been deposited in rivers, lakes and reservoirs for many years [3,4].

In relation to bottom sediments, these play an important role in polluting rivers via toxic metals. These sediments represent the quality of the aquatic system and can be used to verify the presence of contaminants that do not remain soluble after being released into surface water. They can also be used in the study of pollution as indicators of the presence of toxic metals, trace and rare earth elements [5].

The biogeochemical processes are responsible for the concentration of the chemical species, together with the particle size of the sediment as smaller the particle, the higher the concentration of the contaminants, which influences the adsorption of these contaminants [5].

Several studies have been and are being developed with regard to the determination of REEs in sediments [6-12]. In Brazil, several authors carried out studies where concentrations of major, trace and REEs were determined in sediment samples collected in the Alto Tietê Basin, using the INAA technique [5, 13-18].

The present study verified the environmental quality of bottom sediments collected in the Billings System (including Rio Grande and Guarapiranga Reservoirs), by evaluating the concentrations of some toxic metals, trace and rare earth elements. These reservoirs are of great importance, since they guarantee the water supply for a large part of the Metropolitan Region of São Paulo (RMSP) population.

2. MATERIAL AND METHODS

2.1 Study Area

The study area comprises points from the Billings and Guarapiranga Reservoir Complex, located at UGRHI-6 (Water Resources Management Unit - Alto Tietê Basin), and cataloged in the studies of CETESB (Companhia Ambiental do Estado de São Paulo). The collections were carried out at nine points chosen by CETESB (BITQ 00100, BILL 02100, RGDE 02200, BILL 02030, BILL 02500, BILL 02900, RGDE 02900, GUAR 00900, GUAR 00100), all with a considerable history of environmental information, but requiring updated information. Two collection campaigns were carried out in the reservoirs: May and November 2015 (periods of drought and rainfall). Table 1 presents location, collection dates and geographical position of the sampling points, and Figure 1 shows the map of the studied region.

Table 1: Description and location of the sampling sites and their geographical coordinates

| UGRHI	Description	Sample Code	Location	Collections	Geographical coordinates
6	Ribeirão tributary Taquacetuba	BITQ 00100	In the bay located at the end of Tomekichi Inouye Street - SABESP capture	05 - 21 -15[1] 11 - 12 - 15[2]	23° 50' 41" (S) 46° 39' 20" (W)
	Billings Reservoir	BILL 02100	In the middle of the central body in the direction of the Bororé tributary	05 - 21 - 15[1] 11 - 12 - 15[2]	23° 44' 57" (S) 46° 38' 52" (W)
		BILL 02030	In the middle of the central body, about 1.5 km from the Pedreira Dam	05 - 21 - 15[1] 11 - 12 - 15[2]	23° 43' 04" (S) 46° 39' 51" (W)
		BILL 02500	In the middle of the central body, under the bridge of the Immigrants Highway	05 - 21 - 15[1] 11 - 12 - 15[2]	23° 47' 27" (S) 46° 35' 54" (W)
		BILL 02900	Near the Billings-Pedreira Regulatory Dam (Summit Control)	05 - 21 - 15[1] 11 - 12 - 15[2]	23° 49' 04" (S) 46° 24' 16" (W)
	Rio Grande Reservoir	RGDE 02200	At the Prainha Clube Nautica Tahiti Camping, at km 42 of highway SP-31	-[1] 11 - 12 - 15[2]	23° 44' 23" (S) 46° 26' 44" (W)
		RGDE 02900	Next to Anchieta highway, next to the SABESP capture	-[1] 11 - 12 - 15[2]	23° 46' 07" (S) 46° 32' 00" (W)
	Guarapiranga Reservoir	GUAR 00900	At the SABESP capture, near the pump house	05 - 21 - 15[1] 11 - 26 - 15[2]	23° 40' 27" (S) 46° 43' 40" (W)
		GUAR 00100	In the middle of the Parelheiros River, in the São José Balneário District	-[1] 11 - 26 - 15[2]	23° 45' 15" (S) 46° 43' 37" (W)

[1]1st campaign; [2]2nd campaign
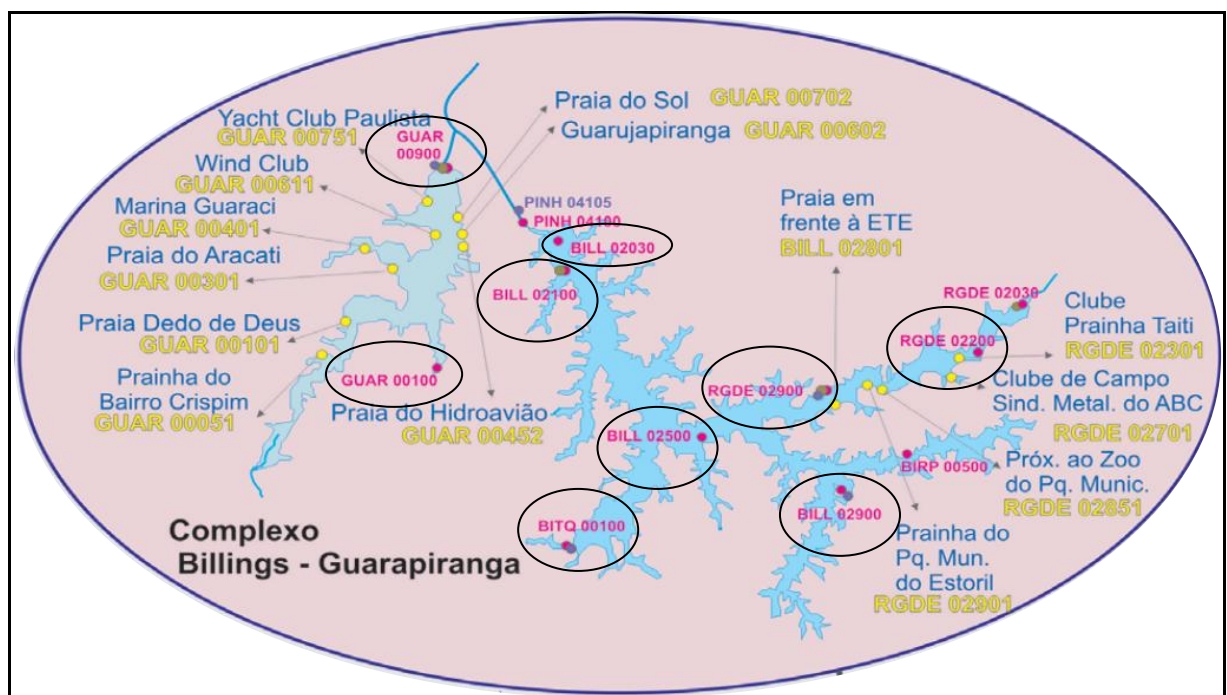
Figure 1: Location of the sampling points [1]

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2.2 Sampling and sample preparation

Sediment samples were collected using CETESB's entire structure and techniques, with technical specialties from the Aquatic Environment Sampling Sector of CETESB. Bottom sediment samples were taken according to the "National Guide for Collection and Preservation of Samples: Water, Sediment, Aquatic Communities and Liquid Effluents", according to the Agência Nacional de Águas (ANA) and CETESB [19, 20].

After collection, the sediment was stored in pre-washed plastic bags with HCl solution and rinsed with distilled and deionized water. The material was kept refrigerated until analysis. The material was oven dried at a temperature of 40 ° C to constant mass, sieved (< 2 mm), macerated in agate mortar and sieved again in the 120 mesh fraction, stored in a pre-washed flask with acid solution and rinsed with distilled and deionized water. Under these conditions, the sediment samples were ready for chemical analyzes for the determination of metals, trace and rare earth elements.

2.3 Granulometric analysis

The granulometric analysis was performed according to the CETESB standard L 6.160 [21], by the laboratory of the Environmental Agency of Limeira, CETESB. The granulometric analysis was performed only for the sediment samples from the first collection campaign. For the second campaign there were no results due to operational problems.

2.4   Instrumental Neutron Activation Analysis (INAA)

The irradiation and counting occurred as follows: approximately 150 mg of sediment samples (duplicate) and reference materials were weighed and packed in polyethylene bags, previously decontaminated with dilute HNO_3 and water Ultrapure (MilliQ). Samples, reference materials and synthetic standards were irradiated for a daily cycle (6-7 hs) under a thermal neutron flux of 1 to 5x 10^{12} n cm^{-2} s^{-1} in the Nuclear Research Reactor IEA-R1, IPEN-CNEN/SP. The first count was performed after a decay time of 5 to 7 days, for approximately one and a half hours, for samples and reference materials, and 15 to 30 minutes for the synthetic standards. The second count was performed after a decay time of fifteen to twenty days, and a counting time identical to that used in the first count. The samples were counted in a gamma ray spectrometer consisting of a hyperpure germanium semiconductor crystal detector (HPGe) associated with a CANBERRA electronic data acquisition system, whose resolution to the 121.97 KeV peak of the ^{57}Co was of 1.1 KeV and the peak of 1332.49 KeV of ^{60}Co, 2.0 KeV. From the activities obtained and their deviations, the concentration calculations were done using Excel® worksheets. The uncertainty of the results was calculated taking into account the error propagation and considering, mainly, the errors associated to the statistical counting (largest source of error in the NAA technique), the weighing of samples and reference materials, in the preparation of synthetic standards, and the concentrations and uncertainties of certified reference materials.

In the present study, the trace elements (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Th, U, Zn), the major (Ca, Fe, Na and K) and the rare earth elements (Ce, Eu, La, Lu, Nd, Sm, Tb, Yb) were determined. In order to verify the accuracy and precision of the analytical method, the

certified reference materials *Soil-5* (IAEA-Soil-5), *Lake Sediment* (IAEA-SL-1), *Lake Sediment* (IAEA-SL-3) and *BEN* (Basalt-IWG-GIT) were analyzed. These materials shows certified concentration values for all elements analyzed.

2.5 Z-score criterion

The Z score criterion was used to check the INAA method, in terms of accuracy and precision, analyzing the certified reference materials. The Z score values have to be in the interval $|Z| \leq 2$ [22]. The Z score criterion was calculated using the relation:

$$Z_i = \frac{C_i - C_{ref}}{\sqrt{\sigma_i^2 + \sigma_{ref}^2}} \qquad (1)$$

Where:

C_i = *element i concentration in CRM analyses;*
C_{ref} = *certificate value of concentration / consensus for element i;*
σ_i = *uncertainty of the element i concentration in CRM analyses;*
σ_{ref} = *uncertainty of the certified/ consensus value for element i.*

2.6 Enrichment Factor (EF)

The Enrichment factor (**EF**), can be defined as a double ratio normalized against a reference element (**RE**) and is an useful index used as a tool to evaluate overall metal pollution [24-26]:

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

Fe, Al and Sc are generally used as reference elements for normalization purposes [26]. In the present study Sc was chosen as a reference element and NASC as reference values for sediments [23]. According to Zhang and Liu [25], if $0.5<EF<1.5$, the elemental concentration is probably due entirely to crustal or natural weathering origins. Values $EF>1.5$ tend to indicate anthropogenic contributions. Higher the EF value, the more severe the anthropogenic contribution. [25]

2.7 Geoacumulation Index (*IGeo*)

The geoaccumulation index [26] is another tool for assessing pollution levels in soils and sediments. The classification of pollution levels from the Igeo values are: <0, baseline; 0 to 1, not polluted; 1 to 2, moderately polluted; 2 to 3, moderately to polluted; 3 to 4, polluted to heavily polluted; 4 to 5, highly polluted and> 5, very highly polluted. *IGeo* was calculated according to Equation 3 below:

$$Igeo = \log_2\left(\frac{C_{am}}{1{,}5 C_{ref}}\right) \qquad (3)$$

Where:

C_{am} = *concentration of the element of interest in the sample;*
C_{ref} = *reference concentration of the element of interest.*

3. RESULTS AND DISCUSSION

3.1 Results of particle size analysis

The results of the granulometric analysis, performed in the CETESB laboratory in Limeira, SP are presented in Table 2.

By means of the granulometric analysis we can observe that most of the analyzed sampling points (BITQ 00100, BILL 02100, BILL 02030 and GUAR 00900) were classified as clay-silt, since they present a greater amount of clay, suggesting the possibility of a higher concentration of some metals in these points. Points BILL 02500 and BILL 02900 presented higher sand quantity, being classified as sand-silt and sand-clay, respectively.

Table 2. Result of granulometric analysis in sediment samples collected in May/21/2015, 1st campaign

Samples	Sand (%)	Clay (%)	Silt (%)	Textural classification
BITQ 00100	18.61	43.54	37.85	clay-silt
BILL 02100	6.46	70.78	22.76	clay-silt
BILL 02030	12.51	46.33	41.16	clay-silt
BILL 02500	87.14	2.09	10.77	sand-silt
BILL 02900	70.25	17.75	12.00	sand-clay
GUAR 00900	15.27	52.97	31.76	clay-silt

3.2 Results obtained for samples of sediment by INAA

Z score values are presented in Figure 2 for the reference materials Soil-5, SL-1, SL-3 and BEN-Basalt. The reference materials used presented satisfactory results, with values of $|Z| \leq 2$ for the determined elements, attesting to precision and accuracy of the INAA method.

Tables 3 and 4 present the results obtained by INAA, for the sediments collected in the 1st and 2nd campaigns, respectively. They also present TEL and PEL values for the elements As, Cr and Zn, NASC (North American Shale Composite) values [23] and Guarapiranga Park soil [17].
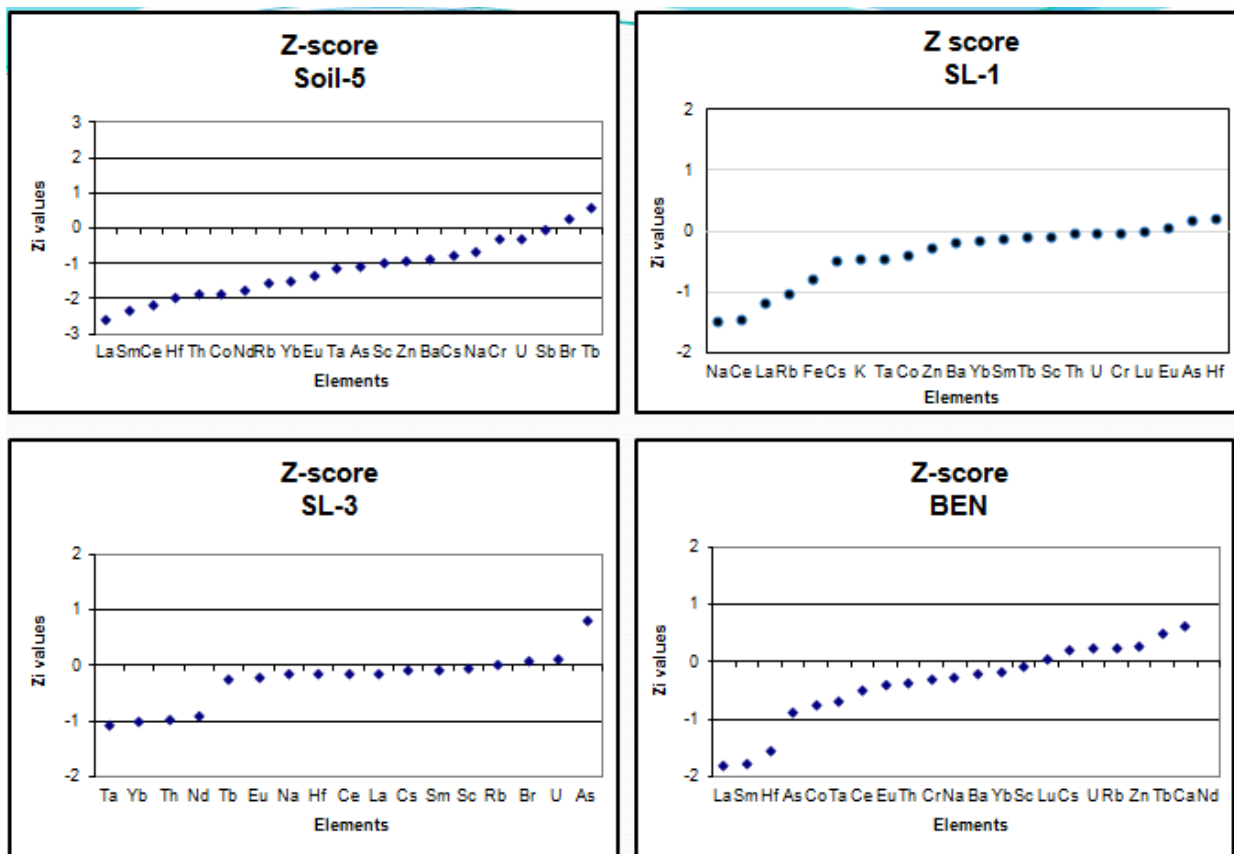

Figure 2: Z score results for the certified reference materials analyzed

In Tables 3 and 4 the values in blue for As, Cr and Zn surpassed the TEL oriented value and in red, the PEL oriented value. In general, the values for As, Cr and Zn exceeded TEL limits in all points analyzed, in both campaigns. Some points, mainly BILL 02100 (03/12/15, 05/21/15 and 11/12/15), presented values that surpassed PEL limits, for the three elements. BILL 02030 point also exceeded PEL limits for Cr and Zn, in both campaigns. These two points were stood out in regards to TEL and PEL oriented values for As, Cr and Zn, because they were classified as the worst situation according to the sediment quality criteria.

These two points are located at the entrance of the reservoir that suffered with the enormous urban occupation in its surroundings and with untreated sewage and industrial activities discharges. These two points also receive all the contribution of the Pinheiros River waters [1] and consequently, and are the more polluted ones. Due to all these pollution problems, the Billings   Reservoir   showed   to   be   the   most   polluted   one.

Table 3: Concentrations and uncertainties (mg kg^{-1}) obtained by the INAA technique for sediment samples (1st campaign) (n=2), and TEL and PEL values [25], NASC values [23] and Soil values [17]

Elements	BITQ 00100 05/21/2015	BILL 02100 05/21/2015	BILL 02100 03/12/2015	BILL 02030 05/21/2015	BILL 02500 05/21/2015	BILL 02900 05/21/2015	GUAR 00900 03/19/2015	GUAR 00900 05/21/2015	TEL	PEL	NASC	SOIL
As	14.4 ± 0.2	17.3 ± 0.4	20.5 ± 1.1	6.7 ± 0.1	23.4 ± 0.5	13.6 ± 0.3	7.7 ± 0.2	11.2 ± 0.2	5.9	17.0	2	4.9
Ba	279 ± 12	419 ± 19	546 ± 22	575 ± 61	424 ± 19	266 ± 10	481 ± 38	435 ± 18			636	289.5
Br	52 ± 2	63 ± 2	56 ± 2	31 ± 1	2.6 ± 0.1	11.1 ± 0.3	40 ± 2	24.1 ± 0.8			-	-
Ca (%)	1.71 ± 0.04	1.52 ± 0.05	1.60 ± 0.05	2.4 ± 0.1	1.10 ± 0.04	1.05 ± 0.03	2.0 ± 0.1	1.93 ± 0.05			2.59	-
Ce	77 ± 1	123 ± 2	142 ± 2	132 ± 2	130 ± 2	47.5 ± 0.6	105 ± 2	115 ± 2			73	130.4
Co	8.36 ± 0.08	13.9 ± 0.1	14.7 ± 0.1	11.7 ± 0.1	18.9 ± 0.2	6.40 ± 0.06	11.4 ± 0.1	10.0 ± 0.1			28	6.5
Cr	94 ± 2	193 ± 4	206 ± 4	143 ± 4	87 ± 2	78 ± 1	61 ± 2	84 ± 2	37.3	90.0	125	60.5
Cs	6.5 ± 0.3	5.0 ± 0.2	5.2 ± 0.1	5.6 ± 0.3	4.2 ± 0.1	2.1 ± 0.1	7.6 ± 0.4	8.2 ± 0.2			5.2	4.1
Eu	0.80 ± 0.01	1.11 ± 0.02	1.23 ± 0.02	1.60 ± 0.03	1.65 ± 0.03	0.51 ± 0.01	1.44 ± 0.03	1.63 ± 0.03			1.2	1.09
Fe (%)	4.74 ± 0.03	7.81 ± 0.05	7.36 ± 0.05	5.60 ± 0.05	3.00 ± 0.02	3.40 ± 0.02	4.75 ± 0.05	5.70 ± 0.04			4	3.77
Hf	12.1 ± 0.1	3.90 ± 0.04	3.80 ± 0.04	5.5 ± 0.1	4.95 ± 0.05	5.7 ± 0.1	9.2 ± 0.1	7.1 ± 0.1			6.3	11.9
K(%)	0.93 ± 0.04	1.01 ± 0.03	0.94 ± 0.05	1.1 ± 0.1	2.4 ± 0.1	1.21 ± 0.05	0.94 ± 0.05	1.16 ± 0.04			3.3	0.9
La	34.5 ± 0.3	55.0 ± 0.5	58.0 ± 0.5	56.5 ± 0.5	65.5 ± 0.6	21.0 ± 0.2	49.5 ± 0.5	53.5 ± 0.4			32	50.4
Lu	0.47 ± 0.02	0.36 ± 0.01	0.36 ± 0.01	0.50 ± 0.04	0.42 ± 0.02	0.47 ± 0.02	0.57 ± 0.04	0.54 ± 0.02			0.5	0.5
Na	514 ± 6	816 ± 12	799 ± 9	1682 ± 19	2529 ± 29	1026 ± 12	758 ± 8	792 ± 12			7500	800
Nd	22 ± 1	51 ± 6	23 ± 1	39 ± 2	42 ± 3	17 ± 1	43 ± 4	51 ± 3			27.4	47
Rb	58 ± 2	50 ± 2	54 ± 2	73 ± 4	100 ± 3	49 ± 1	91 ± 4	76 ± 3			125	50.6
Sb	1.6 ± 0.1	4.3 ± 0.3	5.6 ± 0.7	3.9 ± 0.2	0.51 ± 0.04	1.1 ± 0.1	1.3 ± 0.1	1.5 ± 0.1			2.1	0.5
Sc	15.6 ± 0.2	17.4 ± 0.2	18.3 ± 0.3	17.1 ± 0.2	12.4 ± 0.2	9.7 ± 0.1	13.1 ± 0.2	16.1 ± 0.2			15	12
Sm	4.63 ± 0.07	7.0 ± 0.1	6.30 ± 0.09	7.4 ± 0.1	11.7 ± 0.2	3.40 ± 0.05	8.0 ± 0.1	9.1 ± 0.2			5.7	8.05
Ta	2.5 ± 0.1	2.1 ± 0.1	2.3 ± 0.1	2.0 ± 0.1	1.31 ± 0.04	1.01 ± 0.03	2.0 ± 0.1	2.6 ± 0.1			1.1	2.2
Tb	0.66 ± 0.04	0.54 ± 0.04	0.71 ± 0.05	1.2 ± 0.2	1.00 ± 0.05	0.50 ± 0.03	0.8 ± 0.1	1.0 ± 0.1			0.9	1.3
Th	23.0 ± 0.4	21.9 ± 0.4	23.2 ± 0.4	20.2 ± 0.5	12.7 ± 0.2	10.7 ± 0.2	20.6 ± 0.5	22.7 ± 0.4			12	20
U	6.9 ± 0.2	6.0 ± 0.2	5.6 ± 0.2	7.1 ± 0.3	3.3 ± 0.1	2.4 ± 0.1	8.1 ± 0.4	8.9 ± 0.3			2.7	6.3
Yb	2.7 ± 0.1	2.4 ± 0.1	2.1 ± 0.05	2.9 ± 0.1	2.6 ± 0.1	2.8 ± 0.1	3.5 ± 0.1	3.5 ± 0.1			3.1	4.2
Zn	127 ± 3	478 ± 6	492 ± 7	712 ± 20	90 ± 1	123 ± 2	169 ± 5	151 ± 3	123.0	315.0	85	41

Values in red > PEL; values in blue > TEL

Table 4: Concentrations and uncertainties (mg kg^{-1}) obtained by the INAA technique for sediment samples (2nd campaign) (n=2), and TEL and PEL values [25]

Elements	BITQ 00100 11/12/15	BILL 02100 11/12/15	BILL 02030 11/12/15	BILL 02500 11/12/15	BILL 02900 11/12/15	RGDE 02200 11/12/15	RGDE 02900 11/12/15	GUAR 00900 11/26/15	GUAR 00100 11/26//15	TEL	PEL
As	14.2 ± 0.3	18.7 ± 0.4	7.9 ± 0.4	21.5 ± 1.2	10.9 ± 0.7	0.43 ± 0.04	23.3 ± 1.9	8.9 ± 0.3	7.1 ± 0.5	5.9	17.0
Ba	305 ± 18	372 ± 22	512 ± 29	358 ± 16	239 ± 11	79 ± 4	639 ± 29	494 ± 45	359 ± 31		
Br	36.9 ± 0.6	55.5 ± 0.7	31.1 ± 0.4	0.6 ± 0.1	31.5 ± 0.5	1.0 ± 0.1	21.6 ± 0.4	24.3 ± 0.5	9.4 ± 0.2		
Ca (%)	2.0 ± 0.1	0.7 ± 0.1	2.2 ± 0.1	0.89 ± 0.05	1.4 ± 0.1	0.51 ± 0.03	2.0 ± 0.1	2.3 ± 0.1	1.0 ± 0.1		
Ce	65 ± 6	130 ± 10	126 ± 7	91 ± 5	32 ± 2	69 ± 6	80 ± 6	121 ± 7	66 ± 5		
Co	7.5 ± 0.2	13.7 ± 0.4	10.9 ± 0.3	6.8 ± 0.2	5.3 ± 0.2	0.97 ± 0.03	11.5 ± 0.3	13.6 ± 0.4	6.7 ± 0.2		
Cr	77 ± 4	232 ± 11	139 ± 6	78 ± 4	47 ± 2	7.9 ± 0.4	79 ± 4	75 ± 4	57 ± 3	37.3	90.0
Cs	7.3 ± 0.3	5.0 ± 0.2	5.0 ± 0.2	3.5 ± 0.1	1.9 ± 0.1	0.31 ± 0.02	4.0 ± 0.2	11.4 ± 0.8	6.9 ± 0.4		
Eu	0.76 ± 0.02	1.32 ± 0.03	1.58 ± 0.04	0.95 ± 0.02	0.38 ± 0.01	0.36 ± 0.01	0.79 ± 0.02	2.2 ± 0.1	0.94 ± 0.03		
Fe (%)	4.91 ± 0.06	7.25 ± 0.09	5.61 ± 0.07	2.81 ± 0.03	3.28 ± 0.04	0.488 ± 0.005	11.05 ± 0.16	6.00 ± 0.09	2.48 ± 0.04		
Hf	13.5 ± 0.2	4.1 ± 0.1	5.8 ± 0.1	6.3 ± 0.1	5.1 ± 0.1	5.2 ± 0.1	7.0 ± 0.1	11.6 ± 0.2	9.4 ± 0.1		
K(%)	0.97 ± 0.04	0.7 ± 0.1	1.4 ± 0.1	1.9 ± 0.1	0.49 ± 0.04	0.21 ± 0.02	1.8 ± 0.2	1.2 ± 0.1	0.9 ± 0.1		
La	33.5 ± 0.5	60.9 ± 0.8	56.8 ± 0.7	52.1 ± 0.9	13.8 ± 0.2	41.0 ± 0.7	32.5 ± 0.5	67.9 ± 0.9	32.5 ± 0.5		
Lu	0.49 ± 0.03	0.37 ± 0.02	0.45 ± 0.02	0.84 ± 0.05	0.29 ± 0.01	0.46 ± 0.02	0.50 ± 0.03	0.9 ± 0.1	0.55 ± 0.03		
Na	542 ± 4	764 ± 5	1659 ± 9	1013 ± 6	502 ± 4	611 ± 4	2771 ± 15	759 ± 7	1004 ± 7		
Nd	21 ± 2	31 ± 2	37 ± 2	34 ± 2	12 ± 1	30 ± 1	22 ± 1	94 ± 11	60 ± 21		
Rb	45 ± 2	46 ± 2	71 ± 2	80 ± 2	21 ± 1	7.9 ± 0.4	77 ± 3	120 ± 5	68 ± 3		
Sb	1.7 ± 0.1	4.3 ± 0.3	5.2 ± 0.4	0.44 ± 0.02	0.8 ± 0.1	0.22 ± 0.07	2.0 ± 0.2	1.0 ± 0.1	0.78 ± 0.05		
Sc	15.4 ± 0.3	19.2 ± 0.3	17.2 ± 0.3	10.7 ± 0.2	5.8 ± 0.1	1.62 ± 0.03	15.0 ± 0.3	16.2 ± 0.3	11.1 ± 0.2		
Sm	4.6 ± 0.1	7.3 ± 0.1	8.1 ± 0.1	7.9 ± 0.1	2.13 ± 0.03	6.6 ± 0.1	4.2 ± 0.1	11.8 ± 0.1	5.7 ± 0.1		
Ta	3.4 ± 0.2	2.4 ± 0.1	2.6 ± 0.1	0.98 ± 0.04	0.54 ± 0.03	0.24 ± 0.01	1.4 ± 0.1	2.5 ± 0.1	2.2 ± 0.1		
Tb	0.53 ± 0.04	0.9 ± 0.1	0.9 ± 0.1	1.4 ± 0.1	0.26 ± 0.03	0.92 ± 0.04	0.7 ± 0.1	1.3 ± 0.1	0.9 ± 0.1		
Th	22.1 ± 0.7	24.0 ± 0.7	19.0 ± 0.6	15.0 ± 0.4	6.8 ± 0.2	15.3 ± 0.6	15.9 ± 0.5	21.3 ± 0.7	16.7 ± 0.6		
U	6.9 ± 0.3	6.3 ± 0.2	6.7 ± 0.2	3.7 ± 0.2	1.8 ± 0.1	2.6 ± 0.1	4.8 ± 0.2	9.4 ± 0.5	6.2 ± 0.3		
Yb	2.9 ± 0.1	2.7 ± 0.2	3.4 ± 0.2	3.0 ± 0.2	1.8 ± 0.1	2.9 ± 0.1	3.3 ± 0.2	4.7 ± 0.2	3.5 ± 0.2		
Zn	99 ± 6	543 ± 25	622 ± 29	68 ± 5	115 ± 8	11.6 ± 1.0	241 ± 19	180 ± 19	83 ± 8	123.0	315.0

values in red > PEL; values in blue > TEL

INAC 2017, Belo Horizonte, MG, Brazil.

From the results obtained by INAA technique the enrichment factor (EF) and the geoacumulation index (*IGeo*) were calculated, using Sc as a normalizer element for EF and NASC [23] and soil concentration values collected at the Guarapiranga park [17], as reference values.

Figures 3 and 4 present the results obtained for the EF values for NASC and Soil values, respectively, only for the elements that resulted in EF> 1.5, indicating probable contamination of anthropogenic origin. The other elements analyzed did not present enrichment, so their presence in the sediment was considered of crustal origin or weathering.

When NASC values was used for EF calculation (Figure 3), an enrichment for the elements As, Fe, Hf, Sb, Ta, Th, U, Zn and REE (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) was observed, with high values for As at some collection points. For soil values (Figure 4), enrichment was observed mainly for the elements As, Cr, Sb and Zn, except for point RGDE 02200 that presented enrichment for several elements, showing a different behavior from the other points analyzed.

Figures 5 and 6 present the *IGeo* results by using NASC and Soil reference values, respectively.
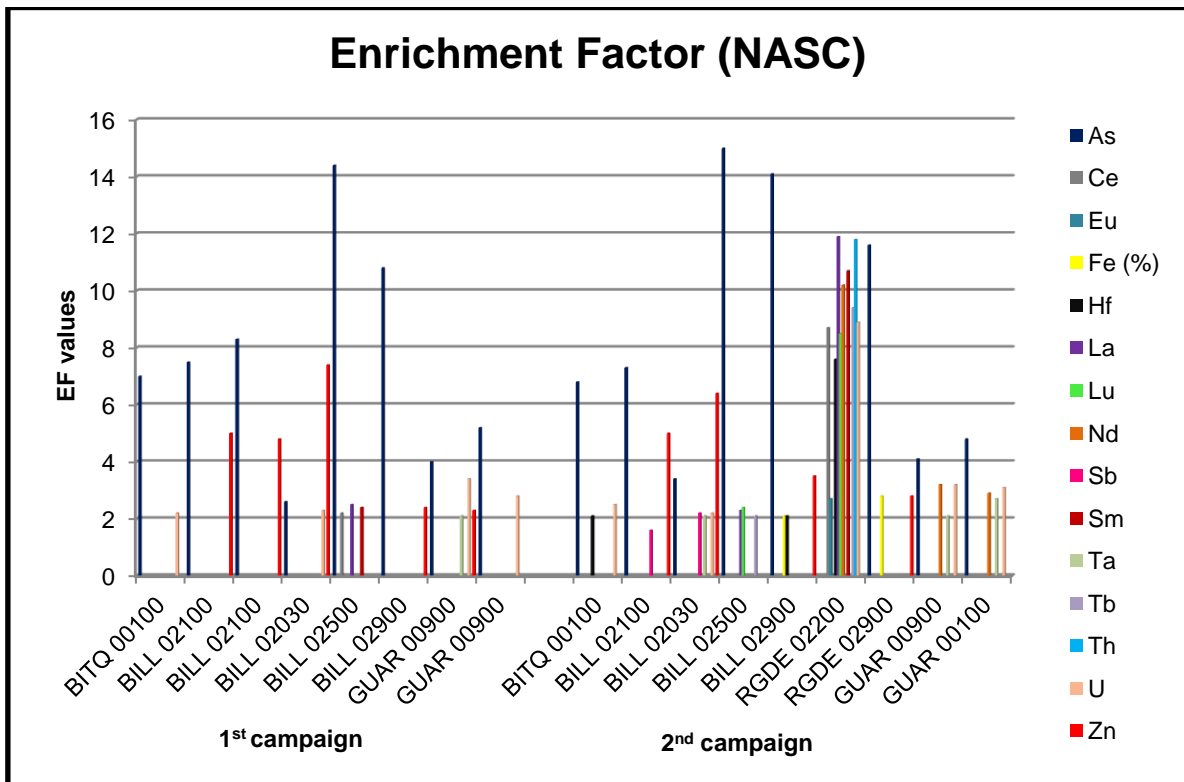
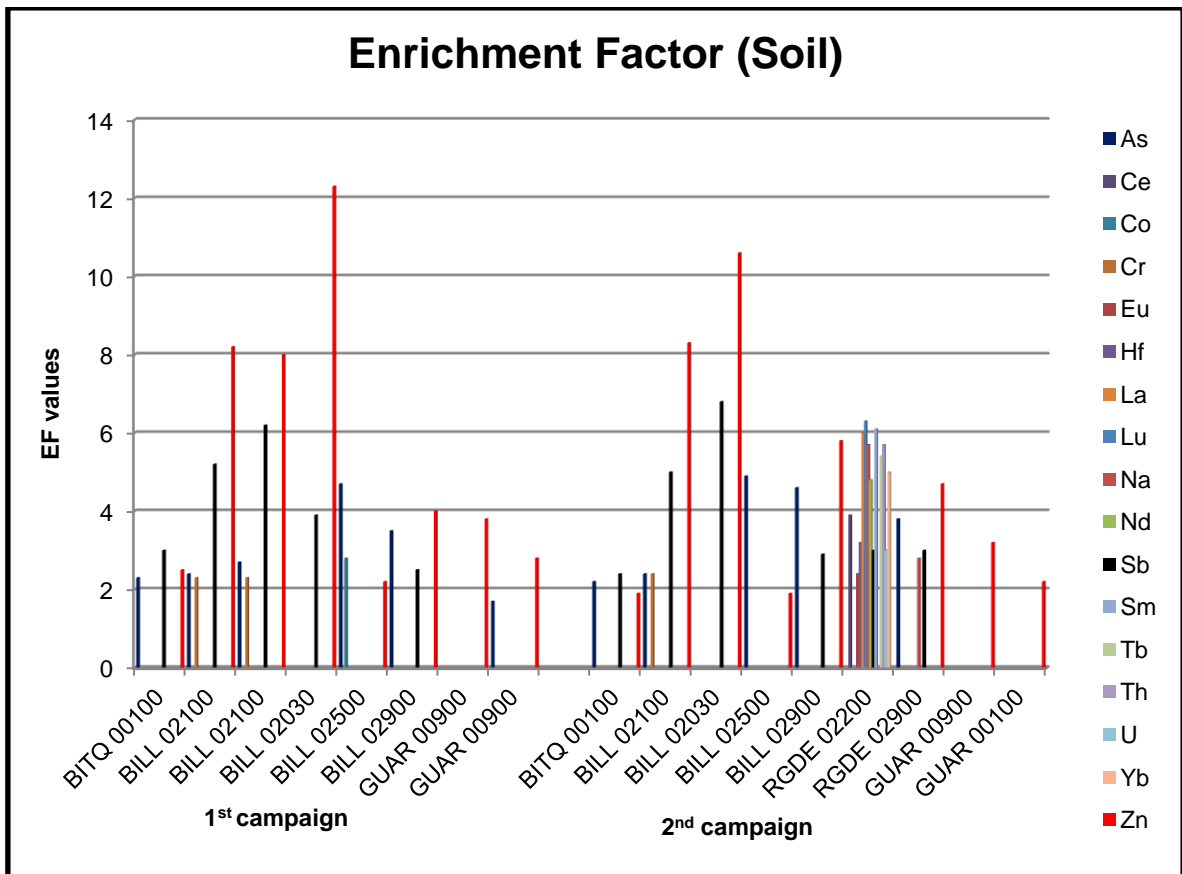**Figure 3:** EF values calculated for NASC reference values

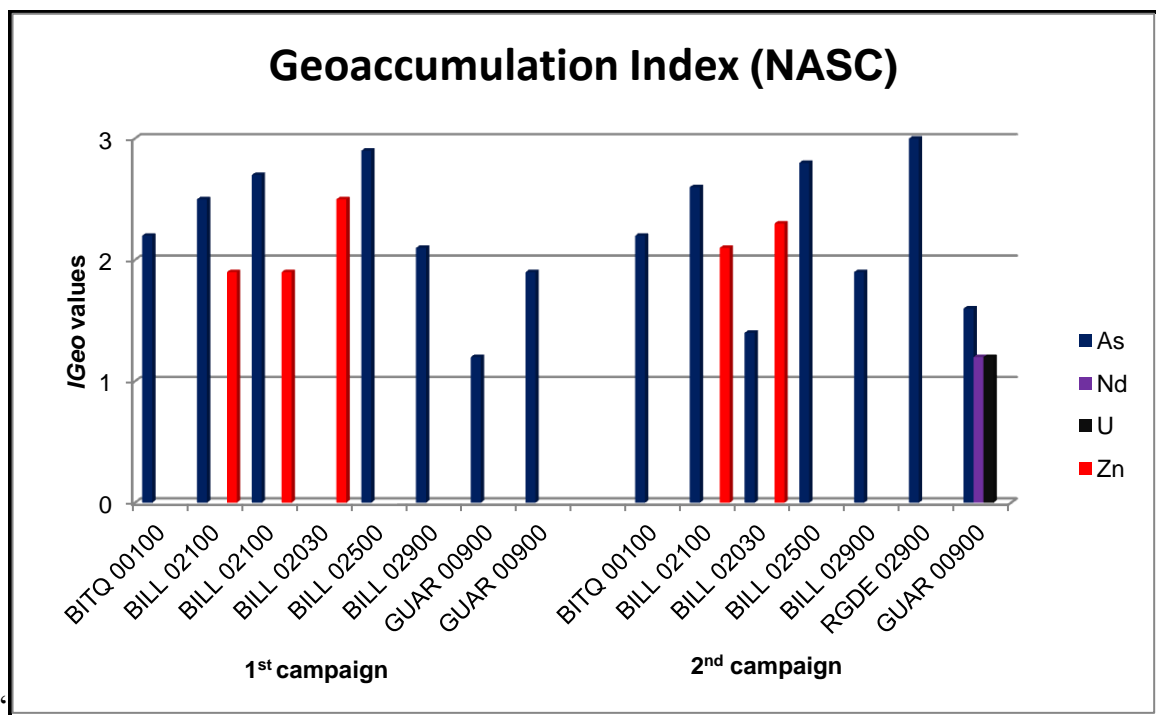**Figure 4:** FE values calculated with soil reference values

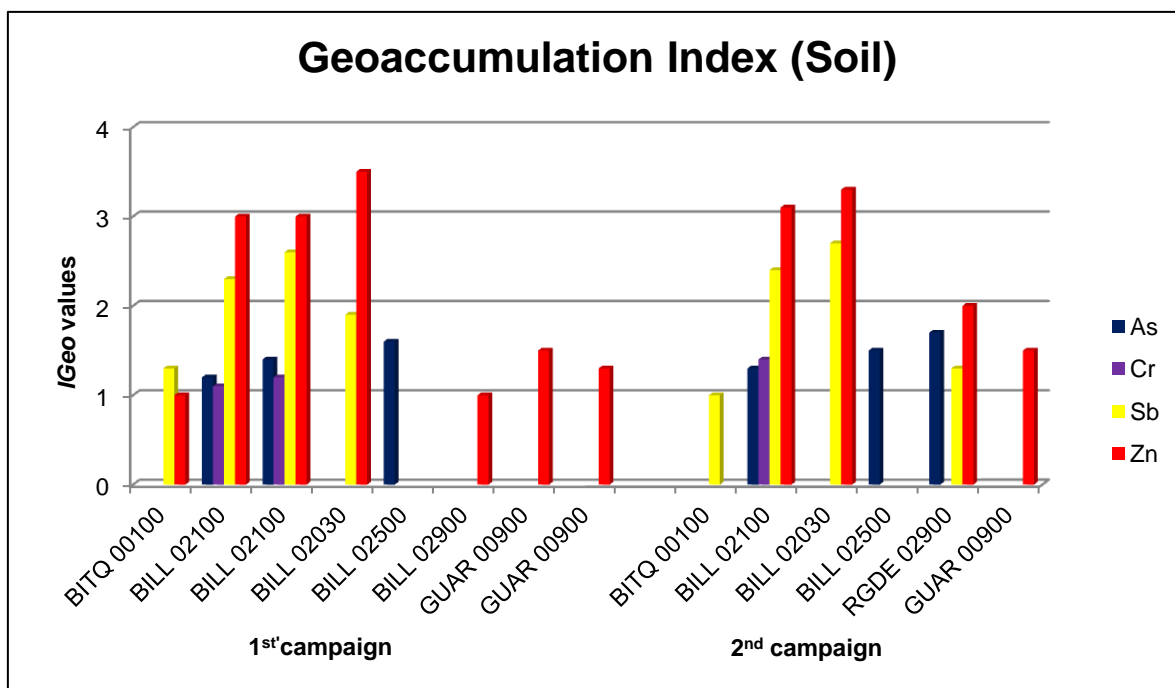**Figure 5:** *IGeo* for NASC reference values

Figure 6: *IGeo* values for soil reference values

Figure 5 shows **1<*IGeo*<3** mainly for As and Zn the sediment being classified as moderated polluted (1<*IGeo*<2) to moderated to polluted (2<*IGeo*<3). The elements Nd and U presented *IGeo* >1.0 only for point GUAR 00900.

From Figure 6, **1<*IGeo*<3.5** was observed for As, Cr, Sb and Zn, with lower values for As and Cr and higher for Sb and Zn. This result indicated that the values obtained for EF and *IGeo* tools for contamination evaluation of sediment samples by using soil values as reference values are more realist or reliable.

Guimarães et. al. [18], in a study in the Guarapiranga reservoir, analyzed sediment samples by INAA technique. EF and *IGeo* indexes were calculated and the results showed an enrichment for As, Ba, Cs, Rb, Sb and Zn and for *IGeo* results, Cs, Rb, Sb and Zn presented *IGeo* > 1.0, both using values of regional soil as reference values.

In general, the Billings, Rio Grande and Guarapiranga reservoirs showed similar trace element concentrations in their sediment samples. The reservoirs undergo anthropogenic interventions by high occupation in their surroundings, untreated sewage and industrial and mining activities discharges. The elements that contributed the most to a possible contamination were mainly As, Cr, Sb and Zn. However, it was not possible to identify which or which were the main sources of these elements, since the region receives discharges of several industries besides untreated sewers of municipalities located in the surroundings.

However, the Billings Reservoir presented the higher concentration values mainly for As, Cr, Sb and Zn and showed to be more affected probably due to the high occupation in its surroundings and suffering with untreated sewage and industrial activities discharges. Besides all these serious pollution problems, this reservoir also receives the Pinheiros River waters. According to CETESB [1], the main anthropogenic contributions to the Billings Reservoir are

located at beginning of the reservoir (Point BILL 02030) (Pedreira's dam) and BILL 02100 (Bororé tributary), due to the Pinheiros River discharges and anthropogenic contribution of drainage basins of the Cocaia and Bororé tributaries. Consequently, points BILL 02100 and BILL 02030, situated at the entrance of the reservoir, are the more polluted points. Points BILL 02500 and BILL 02900 presenting the lower urban occupation in their surroundings but suffered with the high occupation around the reservoir, in general.

4   CONCLUSIONS

The Instrumental Neutron Activation Analysis Technique proved to be an adequate and important tool in the determination of metals and trace elements in sediment samples. The technique also presents high sensitivity, precision and accuracy and the possibility of obtaining data of total concentration up to 26 elements. This technique allows an evaluation of total elemental concentration for an aquatic system pollution diagnosis.

When the values of total concentration of As, Cr and Zn were compared to TEL and PEL oriented values, points BILL02030 and BILL02100 and RGDE02900 presented values above PEL for the 3 elements. These two points at Billings Reservoir are located at the entrance of the reservoir that suffer with high urban occupation in its surroundings and with untreated sewage and industrial activities discharges. These two points also receive all the contribution from the Pinheiros River waters and consequently, and are more polluted.

Regarding the EF and *IGeo* calculations for the INAA technique, the elements As, Cr, Sb and Zn by means of FE calculation present enrichment in all the points analyzed, in both collection campaigns. On the other hand, the Rio Grande Reservoir was different from the others and presented enrichment for the elements As, Ce, Eu, Fe, Hf, La, Lu, Nd, Sb, Se, Sm, Tb, Th, U, Yb and Zn. The *IGeo* calculation was similar to the EF calculation, indicating the contamination of the reservoirs by As, Cr, Sb and Zn. The values obtained for EF and *IGeo* tools for contamination evaluation of sediment samples by using soil as reference values are more realist or reliable. However, it was not possible to identify which or which were the main sources of these elements, since the region receives discharges of several industries as well as untreated sewers of surrounding municipalities.

The Rio Grande Reservoir, by means of the EF calculation, again differed from the others, presenting enrichment by some elements mentioned above, along with the elements Ba, K and Na.

In general, the results obtained in this study identified some of the problems of the reservoirs. The high concentrations found in this study indicated the contamination of the reservoirs by some metal and trace elements present in the sediment and, therefore, seem to confirm that the monitoring carried out by CETESB is of great relevance. The present study also contributes with REEs concentration in the sediment analyzed, which can be used in the future for a database and to help establish legal limits for these elements, whose use has increased considerably in the last decades.

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