TRACE ELEMENT ASSESSMENT IN SEDIMENT CORES FROM GRAMINHA RESERVOIR, SÃO PAULO STATE, BY INAA

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Abstract

In the present study, sediment cores were collected in the Graminha (Caconde) water supply reservoir in Feb/2015 (points 1 and 3) and Aug/2015 (points 1 and 4) sampling campaigns. The four sediment cores with different depths were cut every 2.5 cm, yielding 36, 21, 33 and 37 slices of sediments, respectively, that were individually analyzed by INAA (Instrumental Neutron Activation Analysis). This analytical technique was used to quantify the elements: As, Ba, Br, Co, Cr, Cs, Fe, Hf, Rb, Sb, Sc, Ta, Zn, U and Th. The validation of precision of the methodolody was made by analyzing certified reference material. The concentration values obtained for As, Cr and Zn were compared with TEL and PEL oriented values established by the CCME (Canada) and adopted by CETESB for sediment quality evaluation. None of the sediment cores analyzed surpassed the PEL value for these elements. Sediment samples from points 2 and 3 presented the worst sediment quality but were still classified as good quality for sediments. The enrichment factor (EF) and Geoacumulation Index (*IGeo*) tools used for contamination level assessment were used for all sediment cores and mostly presented enrichment on As and U. The results from concentrations, EF and *IGeo* showed a significant increase mostly below 30 cm of depth in every core. Statistical analyses were applied to the elemental concentration values for better interpretation of the results.

1. INTRODUCTION

Dams have been built by mankind for thousands of years, serving various functions such as flood control, navigation and recreation. Today, dams are mostly used to create reservoirs used for industrial activities such as power generation [1].

The sediment-carrying water flow changes as it enters the reservoir area and sediment begins to be deposited immediately. The dynamics of sediment deposition alone can cause numerous effects on the dam and on the lifespan of the reservoir. When one considers what may be present in the sediment, the situation only gets worse. [1]

Although the concentration of elements in the sediment cannot be directly correlated with its toxicity due to bioavailability dynamics [2], the increase of these concentrations has a reason, and each element has its main sources. For example, the main source of As, a toxic semi-metal, is industry [3]. Thus, increasing As concentrations in the sediment of a region may serve as an indication that regional industrial activity, or material dumping around the reservoir, has increased.

In addition, chronostratigraphy techniques can determine the date when the sediment was deposited on the bottom of the reservoir [4], allowing correlations to be established between varying element concentrations and periods in which there occurred atypical natural phenomena, the exploitation of natural resources or the installation of new industries.

The objective of this paper is to determine the concentrations of metals and trace elements in sediment from the Graminha reservoir. This study is part of a bigger project entitled: **Determination of toxic metals, rare earth and trace elements in sediments: assessment of rivers and water supply reservoirs in the Sao Paulo State.**

2. MATERIALS AND METHODS

2.1. Study area

The Graminha reservoir is located in Caconde, São Paulo State, close to the border with Minas Gerais. The water from the reservoir is utilized only for energy generation. The reservoir is equipped with two turbines capable of generating around 80 MW and the power plant, which covers an area of 31 km^2, has been operating since 1966. The reservoir's main source of water comes from Pardo River. Point 3 is located next to point 4 and point 2 is located in the center of the reservoir. Figure 1 shows the Graminha Reservoir and the positions of the sampling points.

Figure 1. The Graminha reservoir and the positions of the sampling points

2.2. Sampling and sediment sample preparation

Six sediment cores were collected from the Graminha reservoir (Table 1). Three sampling campaigns were made, altering the season of the collection (August/2014, January/2015 and August/2015). During every campaign, sediment cores were collected from 2 points: point 1 (close to the dam) was always in the same location, while the other points (2, 3 and 4) varied for each campaign. This paper presents only the results from points 1, 2 and 3 of January/2014 and August/2015.

Sedimentary profiles were sampled using a core sampler made of acrylic tubes 6 cm in diameter and 100 cm-long. In the field, the profiles were sectioned every 2.5 cm and the respective fractions were packed in pre-cleaned plastic bags and sent to the laboratory. Details of sediment sample preparation and data for the multi-elemental analyses of the sediment cores collected at points 1 and 4 (Aug/2014), were already described in Junqueira et. al. [6]

Table 1: Geographical positions of the sampling points and sediment cores collected

Reservoir	Campaign	Point	Coordinates		Water column	Number of	Core
			latitude	longitude	depth	core fractions	depth
Graminha	Aug/14	1	21°35'47.0"	46°36'49.52"	25 m	36	90 cm
		4	21°38'18.13"	46°34'2.20"	4.6 m	29	72.5 cm
	Feb/15	1	21°35'47.0"	46°36'49.52"	36 m	36	90 cm
		3	21°38'14.9"	46°36'49.52"	7 m	21	52.5 cm
	Aug/15	1	21°35'47.0"	46°36'49.52"	36 m	33	82.5 cm
		2	21°36'30.6"	46°34'46.4"	29 m	37	92.5 cm

2.3. Instrumental Neutron Activation Analysis (INAA)

2.3.1. Preparation of samples for irradiation and counting

About 150 mg of each sample (duplicate) and reference materials were packaged in small double-polyethylene bags that had been previously decontaminated with diluted HNO_3 in ultra-pure water (Milli-Q). Samples and reference materials were irradiated in the IPEN-CNEN / SP IEA-R1 nuclear research reactor under a thermal neutron flux of 1 to 5 10^{12} n cm^{-2} s^{-1} for a daily cycle (6–7 hours). After irradiation, two counting series were performed. The first counting was performed after 5 to 7 days of decay time and the second counting after 20 days. The elements determined were: As, Ba, Br, Co, Cr, Cs, Fe, Hf, Rb, Sb, Sc, Ta, Th, U and Zn.

The measurements of induced gamma-ray activity were carried out in a gamma-ray spectrometer with a GX20190 hyper-pure Ge detector (Canberra) and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co, respectively

Validation of the INAA methodology in terms of precision and accuracy was performed by analyzing certified reference materials (CRM): Lake Sediment (IAEA-SL-3), Lake Sediment (IAEA-SL-1) and GS-N (Granite-CNRS), which have certified concentration values for almost all elements analyzed.

2.3.2. Methodology validation of INAA – Z-score criteria

The validation of the INAA methodology to verify the precision and accuracy of the method was performed by analyzing the certified reference materials cited above. The calculation of the standardized difference or “Z” value of an analytical result is given by equation 1:

$$\mathbf{Z_i = C_i - C_{ref,i} /(\sigma_i^2 + \sigma_{ref,i}^2)^{1/2}} \qquad (1)$$

where:
C_i: Element i concentration measured on the standard;
$C_{ref,i}$: certified value of concentration of the standard;
σ_i: uncertainty on the concentration of element i in the measured standard;
$\sigma_{ref,i}$: uncertainty on the concentration of element i in the standard.

In the case of the INAA technique, the use of the “Z” value for approval of the results considers that $| Z | < 3$ is the individual result of the control sample (in this case, the reference material being analyzed), which must be within 99% of the confidence interval of the expected value [7].

2.4. Anthropogenic influence evaluation – Enrichment Factor (EF) and Geoaccumulation Index (*IGeo*)

To assess the occurrence of anthropogenic influence at a given location, in soil and sediment samples, certain assessment tools are used, such as the enrichment factor (EF) and the geoaccumulation index (*IGeo*). [8,9]

In the present study, Sc was used as a normalizing element and EF was calculated through equation 2:

$$\mathbf{FE = (C_x/C_{ref})\ amostra/(C_x/C_{ref})_{\textit{"Background"}}} \qquad (2)$$

where:
$(C_x/C_{ref})_{Amostra}$: ratio between the element in the sediment sample and the normalizing element in the sample;
$(C_x/C_{ref})_{\textit{"Background"}}$: ratio between the element in the global reference value and the normalizing element in that material or regional basal value (background value)

There are divergences in the literature as to which EF value would be considered as an indication of anthropogenic influences on sediments [7] and regarding which values should be used as baseline values. According to Sutherland [10], EF values between 2 and 5 are indicative of moderate enrichment, while values below 2 represent element depletion or low enrichment. These values were adopted in the present study. In the present study, basal concentration values were used as reference values/background values for the analyzed elements. These basal values were obtained in the previous study [6], since the sediment core analyzed presented very low concentration levels, considered background values for this reservoir. Only for Rb, the North American Shale Composite (NASC) value was used as the background value [11].
The geoaccumulation index (*IGeo*) was determined using Müller equation 3 (1979) [12]:

$$IGeo=\log_2 (C_n/1.5.B_n) \quad (3)$$

Where:
C_n is the concentration of the metal (mg kg^{-1}) in the regional sediment, B_n is the background concentration (mg kg^{-1}) of the metal, and the 1.5 factor is utilized to compensate possible background variations due to lithogenic effects.

The geoaccumulation index (*IGeo*) has seven degrees of contamination intensity: (*IGeo*) <0 means uncontaminated and / or metal deficient sediment (background) (class 0); 0 < *IGeo* <1, unpolluted (class 1); 1 < *IGeo* <2, moderately polluted (class 2); 2 < *IGeo* <3, moderately polluted to polluted (class 3); 3 < *IGeo* <4, polluted to highly polluted (class 4); 4 < *IGeo* <5, very polluted (class 5); *IGeo* > 5, highly polluted (class 6). [8]

3. RESULTS AND DISCUSSION

3.1. INAA methodology validation: Z-score criteria

As can be seen in figure 2, all Z-score values were within the -2 <Z <2 range, indicating that the INAA method was precise and accurate for the determination of these elements for the reference materials analyzed.

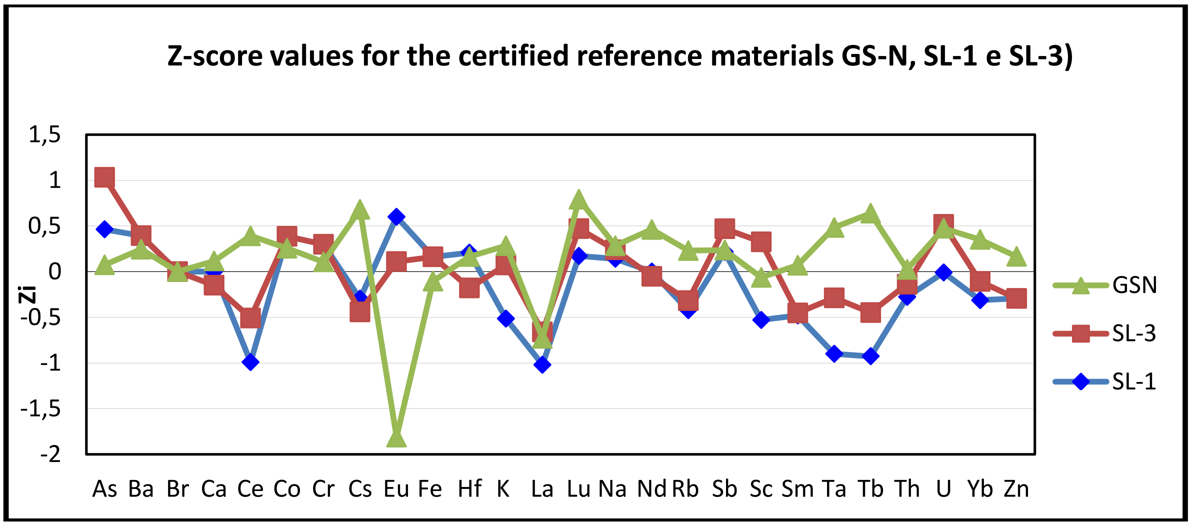

Figure 2: Z-Score values obtained on the reference materials analyses SL-1, SL-3 and GSN

3.2. Sediment core results by INAA

Tables 2, 3, 4 and 5 present the results obtained in the sediment profile analysis by INAA for points 1 and 2 (Aug / 2015) and 1 and 3 (Feb / 2015), respectively. Most of the values in the table have uncertainties of less than 20% and significant figures are in accordance with the GUM standard. [13]

The results for point 1 show that, in both campaigns (Tables 2 and 3), the elements Br, Cr and Sc showed an enrichment in the superficial layers of the sediment core. In general, the element concentrations of As, Ba, Co, Cs, Hf, Rb, Ta, Th, U and Zn increased in the middle of the profile, perhaps indicating some anthropogenic influence during this time period. For the elements Cs, Fe and Sb there were no considerable changes in concentration along the entire profile. The results from the basal layer (90 cm) of the sediment profile from point 1 (Feb/2015) (Table 3), presented a concentration decrease for most of the elements analyzed, indicating that this core perhaps reached the background level for these elements in the reservoir. The same pattern was not observed in the other sediment core analyzed at point 1 (Table 2).

At point 2 (Aug/2015) (Table 4), an enrichment in Br was observed in the sediment samples from more recent (upper) layers, and Zn was enriched in the basal sediments. As, Co, Cr, Cs and Rb varied in concentration along the sediment profile but without a tendency. Hf, Th and U presented concentration increases from the middle to the basal portion of the sediment core. Ba, Hf and Sb increased in concentration in the middle of the sediment core. The same patterns were observed for these elements in the sediment core samples from point 1. Despite the sediment core being 92.5 cm deep (point 2), we did not observe a significant decrease in the concentrations of the analyzed elements in the basal layer of the profile, indicating that the background level was not reached for these elements at this point in the reservoir.

Table 5 shows the results for the sediment core samples from point 3 (Feb/2015). Ba, U and Zn showed higher concentrations in the upper layers of the sediment core, perhaps an indication of recent anthropogenic influence. However, Cr, Hf and Rb showed increased concentrations in the middle of the sediment profile. For the other elements (As, Br, Co, Cs, Fe, Sb, Ta and Th), a small concentration variation was observed along the sediment profile. It should be noted that this sediment profile was the shortest, with a depth of 57.5 cm.

Figure 3 shows the concentration distribution for all elements analyzed along the sediment profile (point 1/Aug 2015). We can see a strong enrichment for U in the interval of 30-50 cm deep.

Table 2: Concentration results (mg kg^{-1}) for sediment core samples from Point 1, AUG 2015

Depth (cm)	Fractions	As	Ba	Br	Co	Cr	Cs	Fe (%)	Hf	Rb	Sb	Sc	Ta	Th	U	Zn
5	**2**	5.5	508	8.8	19.1	50.8	2.47	8.92	6.58	49.8	0.42	17.0	3.45	35.6	4.1	103
7.5	**3**	5.5	493	6.9	18.2	44.0	2.52	8.05	8.0	59.5	0.47	15.7	4.07	36.2	4.8	111
12.5	**5**	5.5	418	6.2	19.8	43.3	2.41	7.67	7.2	54.7	0.43	14.8	3.64	33.1	4.6	102
15	**6**	5.9	452	5.6	17.7	43.9	2.33	7.22	8.8	57.4	0.40	14.3	4.36	34.5	5.4	104
17.5	**7**	6.6	597	5.5	15.0	46.8	3.1	7.40	14.4	69	0.67	14.1	8.0	40.8	8.4	140
22.5	**9**	6.7	531	7.8	16.1	45.3	2.7	8.15	8.00	50	0.45	15.2	4.7	36.5	6.9	125
25	**10**	6.3	443	8.1	17.5	44.4	2.47	8.25	8.67	58	0.50	14.4	4.2	36.5	7.0	123
27.5	**11**	7.8	453	7.9	17.7	40.4	2.6	8.92	9.6	55	0.68	12.8	5.3	37.3	8.6	129
30	**12**	**n.d**	469	6.7	21.0	40.9	2.25	8.0	7.27	54	0.39	13.5	3.87	30.3	7.7	107
32.5	**13**	10.2	528	7.4	21.6	39.6	2.17	9.9	9.2	57	0.43	12.8	5.0	34.1	10.9	121
35	**14**	8.7	698	7.0	18.4	44.2	2.90	8.9	13.2	71	0.39	13.4	7.0	41.6	15.0	142
37.5	**15**	8.8	716	6.8	19.4	45.1	3.36	8.2	13.5	74	0.56	14.5	7.0	43.9	19.9	150
40	**16**	6.6	742	7.6	21.4	47	2.70	8.5	12.1	73	0.53	14.6	5.8	39.7	16.4	139
42.5	**17**	7.4	636	5.6	15.8	42	3.08	7.4	16.7	66	0.66	13.2	7.6	44.7	14.6	147
45	**18**	8.0	663	6.8	23.6	42	2.95	7.5	14.6	63	0.54	13.7	7.1	43.6	13.6	141
47.5	**19**	9.2	610	6.0	16.7	39	3.17	6.8	17.7	63	0.63	12.5	7.6	45.6	12.4	167
50	**20**	6.6	686	7.2	16.2	40.9	2.46	7.56	14.1	46.1	**n.d**	12.8	6.7	43.0	12.6	130
52.5	**21**	6.6	762	6.6	15.4	36.3	3.03	6.83	17.6	51.7	**n.d**	12.5	6.8	49.4	14	125
55	**22**	7.5	818	6.8	17.6	43.5	2.75	7.28	15.9	58.8	0.68	14.0	8.0	47.4	12.1	115
57.5	**23**	9.5	719	8.1	19.7	42.8	3.11	7.76	17.5	54.3	0.94	13.1	9.7	52.0	11.6	117
62.5	**25**	9.2	619	5.4	17.1	42.1	2.86	7.9	17.3	76	0.71	12.9	10.4	44	9.4	139
65	**26**	8.1	511	8.0	19.2	40.7	2.55	9.5	16.4	64	0.87	12.2	9.4	45	10.7	115
67.5	**27**	7.1	476	6.7	18.4	43.9	2.8	7.84	13.6	70	0.68	13.4	8.3	42	5.1	128
70	**28**	7.6	508	6.9	21.6	41.0	3.1	8.8	13.3	62	0.52	13.7	7.9	39	5.9	120
72.5	**29**	6.5	535	3.9	21.5	39.7	2.96	9.25	13.1	52.8	0.52	13.0	7.12	39.2	6.0	**n.d**
75	**30**	10.2	500	4.12	25.5	42.0	2.71	9.14	12.9	49.4	0.71	13.5	7.72	39.2	4.1	**n.d**
77.5	**31**	8.0	446	4.3	26.0	36.3	2.61	9.54	14.5	45.8	0.61	11.8	8.3	39.4	6.4	**n.d**
80	**32**	**n.d**	448	3.8	23.1	34.1	2.61	7.77	13.1	40.2	0.58	10.8	6.7	34.0	5.5	**n.d**
82.5	**33**	5.9	611	3.17	19.5	39.1	3.16	7.76	16.9	59.8	0.58	11.7	7.13	38.0	5.7	102
Mean		**7.5**	**572**	**6.41**	**19.3**	**42.1**	**2.75**	**8.16**	**12.82**	**58.8**	**0.58**	**13.5**	**6.65**	**40.2**	**9.3**	**126**
St dev		**1.4**	**114**	**1.45**	**2.9**	**3.5**	**0.31**	**0.83**	**3.58**	**9.1**	**0.14**	**1.28**	**1.89**	**5.1**	**4.2**	**17**
Mín		**5.5**	**418**	**3.17**	**15.0**	**34.1**	**2.17**	**6.75**	**6.58**	**40.2**	**0.39**	**10.8**	**3.5**	**30.3**	**4.1**	**102**
Máx		**10.2**	**818**	**8.83**	**26.0**	**50.8**	**3.36**	**9.91**	**17.70**	**75.5**	**0.94**	**17.0**	**10.45**	**52.0**	**19.9**	**167**
BG [6]		**0.3**	**273**	**0.81**	**4.2**	**6.7**	**0.44**	**0.86**	**2.95**	125	**0.07**	**3.19**	**1.10**	**5.3**	**0.5**	**20**

n.d. – not determined; NASC [11]

Table 3: Concentration results (mg kg^{-1}) for sediment core samples from Point 1, FEB 2015

Depth (cm)	Cortes	As	Ba	Br	Co	Cr	Cs	Fe (%)	Hf	Rb	Sb	Sc	Ta	Th	U	Zn
2.5	**1**	6.0	**n.d.**	11.2	19.1	47.0	2.51	8.77	6.4	41	0.51	16.4	2.9	34.8	4.40	206
5	**2**	5.5	943	8.7	17.7	43.0	2.49	8.31	6.04	42	0.31	16.9	3.5	37.2	4.3	126
10	**4**	6.5	515	7.5	19.3	44.2	2.95	7.97	6.9	49	0.22	15.1	3.70	35.4	5.3	122
15	**6**	5.2	307	9.2	**n.d.**	46.3	2.51	8.49	6.4	74	0.79	15.9	3.8	36.3	4.1	119
20	**8**	5.8	531	7.4	19.7	44.9	2.44	8.5	7.1	63	0.39	16.0	3.75	34.0	5.6	109
25	**10**	6.2	683	5.2	16.3	45.5	3.12	7.4	16.0	73	0.48	14.1	8.7	41.9	10.0	138
30	**12**	6.0	429	6.8	15.1	41.7	1.33	7.5	8.3	60	0.34	15.0	4.07	35.0	7.2	110
35	**14**	7.0	407	8.3	20.2	40.4	2.48	8.2	7.1	51	0.41	14.3	3.53	32.4	7.4	106
40	**16**	5.7	662	9.3	15.8	39.4	3.48	8.07	14.6	75	0.64	13.7	6.7	45.8	13.1	132
45	**18**	6.3	803	8.2	18.2	39.6	2.64	7.82	13.3	69	0.48	13.5	6.0	41.2	18.3	125
50	**20**	5.7	507	7.7	19.6	36.9	2.85	6.86	13.7	60	0.59	13.1	6.0	41.3	14.0	121
55	**22**	5.7	599	6.1	14.3	34.1	2.93	6.27	15.9	60	0.54	11.6	7.3	41.3	10.9	125
60	**24**	9.7	714	5.8	14.6	40.7	3.18	6.73	19.3	75	0.90	12.4	11.1	57	15.1	122
65	**26**	8.4	630	4.8	13.7	42.5	2.93	6.41	18.0	70	**n.d.**	13.7	10.9	50	10.8	118
70	**28**	9.2	504	8.6	18.8	39.4	2.51	8.32	16.1	60	0.57	12.6	9.4	50	9.8	101
75	**30**	7.9	534	6.9	18.5	37.2	2.75	7.37	15.3	52	0.50	12.4	9.7	45	6.3	105
80	**32**	6.5	553	7.8	21.0	43.2	3.02	8.60	13.1	76	0.48	14.3	8.0	39.3	4.0	125
85	**34**	6.0	600	6.2	18.3	35.8	2.45	6.66	14.4	68	0.80	11.2	8.2	36.2	5.2	110
90	**36**	2.7	750	4.0	12.0	18.1	1.40	3.21	5.91	66	0.20	5.4	2.56	15.5	2.0	54
Mean		**6.4**	**593**	**7.3**	**17.3**	**40.0**	**2.63**	**7.45**	**11.77**	**62**	**0.51**	**13.6**	**6.30**	**39.5**	**8.3**	**120**
St dev		**1.6**	**152**	**1.7**	**2.6**	**6.4**	**0.53**	**1.29**	**4.64**	**11**	**0.19**	**2.53**	**2.83**	**8.7**	**4.5**	**27**
Mín		**2.7**	**307**	**4.0**	**12.0**	**18.1**	**1.33**	**3.21**	**5.91**	**41**	**0.20**	**5.44**	**2.56**	**15.5**	**2.0**	**54**
Máx		**9.7**	**943**	**11.2**	**21.0**	**47.0**	**3.48**	**8.77**	**19.31**	**76**	**0.90**	**16.9**	**11.05**	**57.5**	**18.3**	**206**

n.d. – not determined

Table 4: Concentration results (mg kg^{-1}) for sediment core samples from Point 2, AUG 2015

Depth (cm)	Corte	As	Ba	Br	Co	Cr	Cs	Fe (%)	Hf	Rb	Sb	Sc	Ta	Th	U	Zn
2.5	**1**	4.3	767	8.5	18.1	47.1	3.1	7.63	9.4	63	0.37	16.5	5.1	38	6.2	139
5	**2**	4.4	579	9.6	20.0	47.6	2.4	7.86	8.7	55	0.45	17.2	4.7	38	5.5	131
7.5	**3**	3.9	776	9.3	20.8	48.0	2.42	8.45	8.3	56	0.45	16.3	4.6	37	5.5	148
10	**4**	4.3	749	9.6	17.9	40.4	2.33	7.91	9.2	40	0.35	15.5	4.4	36	6.3	133
12.5	**5**	5.7	**n.d.**	10.0	18.7	43.6	2.93	7.18	8.88	39	0.53	16.5	5.4	34.9	7.3	126
15	**6**	4.8	443	7.6	15.8	40.0	2.88	7.61	9.3	42	0.63	15.9	5.4	35.3	5.9	124
17.5	**7**	5.3	802	9.0	18.1	40.9	2.51	7.47	8.5	37	0.52	15.5	5.1	34.4	5.7	127
20	**8**	5.6	723	7.1	19.9	42.3	2.32	6.98	8.3	40	0.55	14.8	5.0	33.2	6.7	115
25	**10**	5.3	951	8.4	18.2	49.1	3.1	8.03	8.48	47	0.53	17.2	5.0	37	5.5	132
27.5	**11**	4.9	590	8.6	19.3	43.6	2.7	7.02	8.45	40	0.53	16.3	4.9	37	5.8	126
30	**12**	4.3	800	8.4	17.9	47.1	2.43	8.10	6.9	47	0.38	16.2	4.5	34	4.9	119
32.5	**13**	6.5	632	7.6	24.3	39.2	2.3	7.10	10.6	54	0.59	13.4	6.1	32.5	6.4	134
35	**14**	4.6	661	7.3	19.0	44.5	3.2	7.48	12.4	50	0.63	14.2	6.3	37.8	6.5	136
37.5	**15**	6.2	849	6.3	19.4	48.9	2.93	7.99	13.0	53	0.72	14.8	7.3	38.3	4.7	134
42.5	**17**	6.4	1191	5.3	15.7	43.1	3.01	6.38	16.8	70	0.61	13.4	**n.d.**	41.5	10.5	152
45	**18**	5.8	694	2.7	14.3	39.8	2.43	6.45	18.9	51	**n.d.**	11.3	10	40.6	9.5	171
47.5	**19**	5.3	436	5.5	17.9	46.4	2.37	8.41	8.6	46	0.48	15.9	5.0	34.9	7.4	138
50	**20**	5.5	702	5.0	19.3	47.3	2.65	8.33	9.9	48	0.46	15.9	5.9	36.6	8.5	134
55	**22**	**n.d.**	**n.d.**	7.5	14.5	45.0	2.7	7.25	11.3	38	0.74	14.6	5.7	41.9	9.7	138
60	**24**	**n.d.**	1204	6.6	14.4	35.4	2.7	7.62	11.1	59	0.53	12.6	6.0	42.6	10.3	139
65	**26**	6.8	681	7.0	20.9	41.2	2.93	8.15	11.4	47	0.65	14.2	5.8	37.7	8.8	113
70	**28**	6.2	**n.d.**	5.8	16.3	39.2	2.67	7.46	16.7	48	0.63	13.1	8.2	47	12.1	142
75	**30**	6.3	**n.d.**	5.1	13.5	36.3	3.3	6.70	17.1	39	0.66	11.9	8.5	47	14.3	162
77.5	**31**	7.1	**n.d.**	6.1	15.2	31.6	3.12	7.46	16.0	56	0.66	12.1	7.4	51	7.9	170
80	**32**	8.3	**n.d.**	6.1	27.2	41.4	3.24	7.56	16.4	46	0.57	14.0	7.5	49	18.4	163
85	**34**	7.4	**n.d.**	6.1	20.2	41.2	2.5	7.96	15.8	44	0.55	13.9	7.7	44	16.8	159
90	**36**	7.3	**n.d.**	6.1	18.2	36.9	2.4	7.23	19.2	37	0.45	13.1	6.4	49	6.7	168
92.5	**37**	5.4	**n.d.**	5.2	17.1	38.0	2.3	6.97	19.1	62	0.50	12.9	6.5	51	26	167
Mean		**5.7**	**749**	**7.0**	**18.3**	**42.3**	**2.70**	**7.5**	**12.1**	**48.4**	**0.55**	**14.6**	**6.1**	**39.9**	**8.9**	**141**
St dev		**1.1**	**202**	**1.7**	**3.0**	**4.5**	**0.32**	**0.6**	**4.0**	**8.7**	**0.10**	**1.67**	**1.4**	**5.6**	**4.8**	**17**
Min		**3.9**	**436**	**2.7**	**13.5**	**31.6**	**2.32**	**6.4**	**6.9**	**36.5**	**0.35**	**11.3**	**4.4**	**32.5**	**4.7**	**113**
Max		**8.3**	**1204**	**10.0**	**27.2**	**49.1**	**3.33**	**8.5**	**19.2**	**69.8**	**0.74**	**17.2**	**10.0**	**51.4**	**25.8**	**171**

n.d. – not determined

Table 5: Concentration results (mg kg^{-1}) for sediment core samples from Point 3, FEB 2015

Depth (cm)	fractions	As	Ba	Br	Co	Cr	Cs	Fe (%)	Hf	Rb	Sb	Sc	Ta	Th	U	Zn
2.5	**1**	6.3	1367	6.5	19.9	44.0	3.03	6.70	16.5	62	0.70	15.1	8.1	38.4	10.1	229
5	**2**	3.4	**n.d.**	5.2	17.6	44.6	3.23	6.03	20.2	99	0.56	14.1	9.3	36.5	10.5	195
7.5	**3**	4.2	990	4.5	18.3	45.0	3.09	6.14	21.8	71	0.62	14.4	7.9	38.1	9.5	183
10	**4**	4.0	1111	4.3	18.1	46.1	2.71	5.95	21.2	109	0.48	14.4	8.0	37.3	10.3	176
12.5	**5**	4.8	1006	5.1	18.9	49.6	3.02	6.26	18.2	102	0.44	15.3	8.2	39.4	10.6	163
15	**6**	5.1	1164	5.5	18.4	47.7	3.05	6.11	19.7	87	0.42	15.0	8.1	38.9	8.6	154
17.5	**7**	4.2	1053	4.9	17.0	45.0	3.01	5.73	20.1	90	0.48	13.8	7.8	36.9	9.1	147
20	**8**	4.0	1278	4.9	17.1	42.7	2.86	5.59	17	83	0.44	13.5	7.9	36.2	9.0	140
22.5	**9**	4.3	856	3.9	17.9	45.5	2.93	5.68	21.1	142	0.43	13.8	5.7	35.9	7.7	137
25	**10**	3.9	553	3.8	18.6	45.3	3.4	5.92	20.7	119	0.31	14.5	6.1	35.9	7.5	151
27.5	**11**	4.7	1096	4.6	19.5	49.8	3.22	6.27	24	190	0.44	15.0	5.9	36.9	9.0	164
30	**12**	4.5	1032	4.4	21.0	52.9	3.5	6.60	25.6	152	0.52	16.0	6.3	39.3	8.3	160
32.5	**13**	4.4	1607	4.8	18.5	52.9	3.42	6.46	23.5	115	0.50	15.1	6.6	42.2	5.6	152
35	**14**	5.5	1199	4.7	18.5	49.0	3.22	6.20	21.1	101	0.62	14.7	7.2	38.0	6.5	165
37.5	**15**	5.1	953	4.5	18.5	52.4	3.28	6.47	16.9	87	0.6	15.3	7.0	40.2	9.8	168
40	**16**	5.4	758	6.0	19.3	47.6	2.53	6.43	15.4	81	0.62	15.7	7.0	40.6	9.5	150
52.5	**21**	4.6	939	5.4	19.9	51.0	2.8	6.50	15.4	79	0.69	16.1	8.0	40.0	8.3	166
55	**22**	5.9	817	6.1	18.8	49.0	2.7	6.49	14.1	77	0.68	15.5	8.3	39.0	7.3	165
57.5	**23**	6.4	867	6.1	18.2	49.4	2.6	6.55	14.4	95	0.85	15.6	7.7	38.9	6.7	179
Mean		**4.8**	**1036**	**5.0**	**18.6**	**47.9**	**3.03**	**6.22**	**19.3**	**102**	**0.55**	**14.9**	**7.43**	**38.4**	**8.6**	**166**
St dev		**0.8**	**241**	**0.8**	**1.0**	**3.1**	**0.28**	**0.33**	**3.3**	**31**	**0.13**	**0.74**	**0.97**	**1.8**	**1.4**	**21**
Mín		**3.4**	**553**	**3.8**	**17.0**	**42.7**	**2.53**	**5.59**	**14.1**	**62**	**0.31**	**13.5**	**5.69**	**35.9**	**5.6**	**137**
Max		**6.4**	**1607**	**6.5**	**21.0**	**52.9**	**3.49**	**6.70**	**25.6**	**190**	**0.85**	**16.1**	**9.34**	**42.2**	**10.6**	**229**

n.d. – not determined

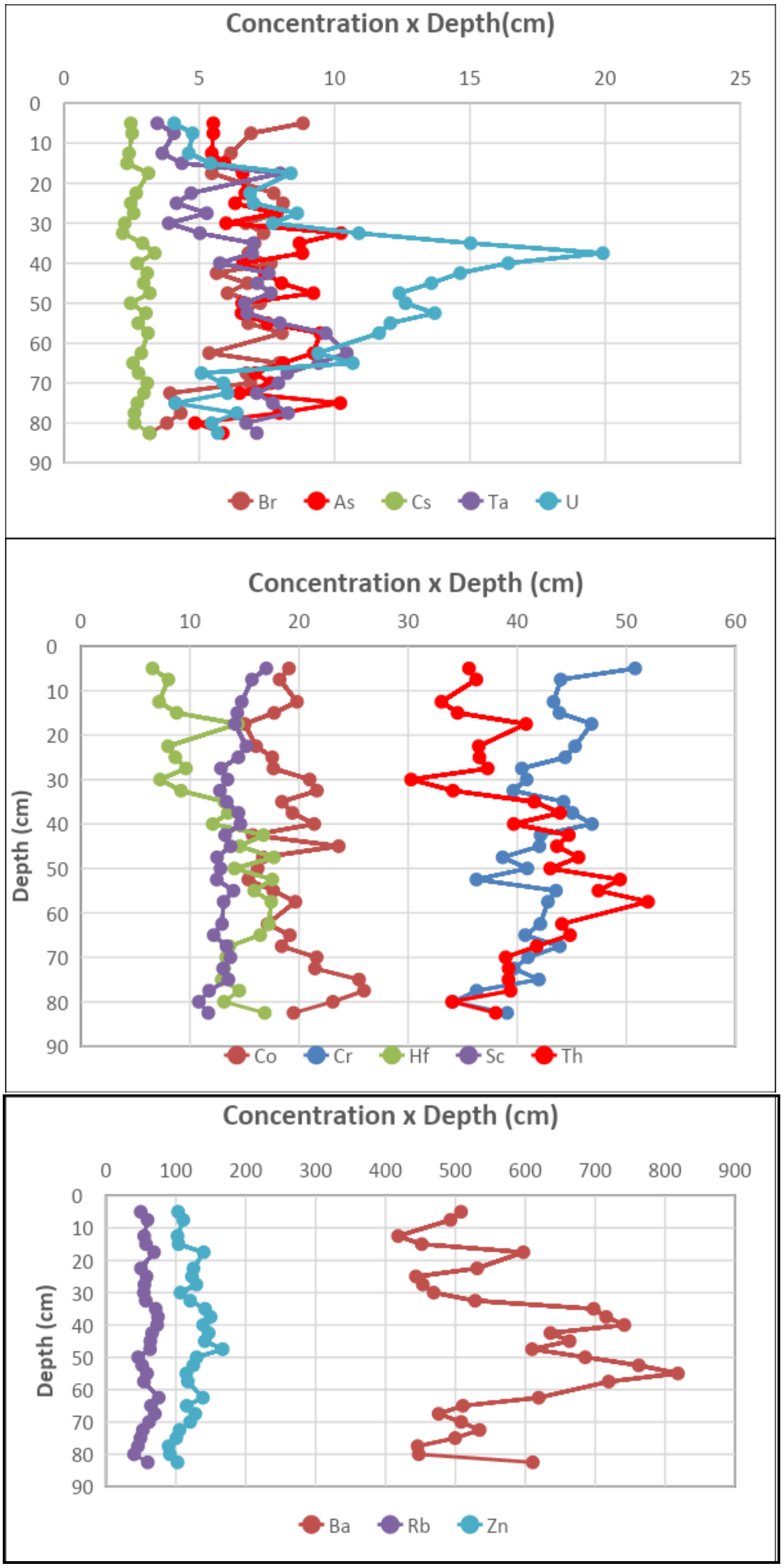

Figure 3. Concentration distribution profile for all elements analyzed along the sediment core (point 1/Aug 2015)

3.3. Sediment Quality Evaluation according to TEL and PEL oriented values

Table 1 shows the oriented values TEL (Threshold Effect Level) and PEL (Probable Effect Level) adopted by CETESB [14] from CCME [15] for the elements As, Cr and Zn, for aquatic life protection. TEL indicates the concentration below which there is a rare occurrence of adverse effects to biota. PEL is the concentration above which there is frequent occurrence of these effects.

The concentration values for As, Cr and Zn are presented in Tables 2 to 5. It was observed that some fractions of the analyzed sediment profiles maintained concentrations for As, Cr, and Zn that were close to or below the TEL values, only some values were above TEL. The concentrations of these elements, therefore, should not cause adverse effects on the reservoir biota and the sediment can be classified as good quality, according to the TEL and PEL criteria for these elements.

Table 6: Oriented values for sediment quality evaluation for aquatic life protection (mg kg^{-1}) (freshwater)

	VERY GOOD (TEL)	GOOD	REGULAR	FAIR (PEL)	VERY POOR
As	< 5.9	≥ 5.9-11.5	>11.5-<17.0	17.0-25.5	> 25.5
Cr	< 37.3	≥ 37.3-63.7	>63.7-<90.0	90.0-135.0	> 135.0
Zn	< 123	≥ 123-219	>219-<315	315-473	> 473

3.4 Enrichment Factor (EF) and Geoaccumulation Index (*IGeo*) – sediment contamination evaluation

3.4.1 Enrichment Factor

Table 7 shows only the EF values obtained for the elements As, Sb, Th and U in the four sediment profiles that reached values higher than 2. Most of the EF values found were 2.0 < EF < 5.0, indicating a moderate enrichment according to Sutherland [10]. EF>5.0 (in bold) was found for As (points 1 and 2) and U (point 1), mainly for the fractions below 30 cm depth, indicating a more significant enrichment of these two elements in the sediment profiles from point 1. The other elements analyzed showed an EF < 2.0 indicating a low enrichment or depletion according to Sutherland criteria [10].

3.4.2 Geoacumulation Index (*IGeo*)

Cr, Cs, Fe, Sb, Th and Zn were classified as class 3, moderately polluted, for all sampling points and most of the fractions in the sediment cores. As, Br and U were classified as class 3, moderately polluted to polluted, for all points and fractions of the cores, but also reached class 4, polluted to highly polluted, in some fractions of the cores. In general, the *IGeo* values found in the present study confirmed the results obtained by EF index.

Table 7: EF values obtained for As, Sb, Th and U in all sediment cores analyzed

	POINT 1 (FEB/ 2015)				POINT 1 (AUG/ 2015)				POINT 3 (FEB/ 2015)			POINT 2 (AUG/2015)			
Depth (cm)	**As**	**Sb**	**Th**	**U**	**As**	**Sb**	**Th**	**U**	**As**	**Sb**	**U**	**As**	**Sb**	**Th**	**U**
2.5	3.6								4.1	2.2	4.2	2.6			2.3
5	3.2				3.2				2.4		4.6	2.5			
7.5					3.4				2.9	2.0	4.1	2.4			2.1
10	4.2			2.2					2.7		4.4	2.7			2.5
12.5					3.6				3.1		4.3	3.4			2.8
15	3.2	2.3			4.1			2.3	3.3		3.6	2.9			2.3
17.5					4.6	2.2		3.7	3.0		4.1	3.3			2.3
20	3.5			2.2					2.9		4.1	3.7			2.8
22.5					4.3			2.8	3.1		3.4				
25	4.3			4.4	4.3			3.0	2.6		3.2	3.0			
27.5					**5.9**	2.5		4.2	3.1		3.7	2.9			2.2
30	3.9			3.0	4.4			3.6	2.7		3.2	2.6			
32.5					**7.9**			**5.3**	2.9		2.3	**4.8**	2.1		3.0
35	4.8			3.2	**6.4**			**7.0**	3.7	2.0	2.7	**3.2**	2.1		2.8
37.5					**6.0**			**8.5**	3.3		4.0	**4.1**	2.3		
40	4.1	2.2	2.0	**5.9**	4.4			**7.0**	3.4		3.7				
42.5					**5.5**	2.4	2.0	**6.9**				**4.7**	2.2		4.9
45	4.6			**8.4**	**5.7**			**6.1**				**5.0**	3.1	2.2	**5.2**
47.5					**7.2**	2.4	2.2	**6.1**				**3.3**			2.9
50	4.3	2.1		**6.6**	5.0		2.0	**6.1**				**3.4**			3.3
52.5					**5.2**	2.8	2.4	**6.8**	2.8	2.0	3.2				
55	4.8	2.2	2.1	**5.8**	**5.3**	2.3	2.0	**5.3**	3.7	2.1	2.9	**6.3**	2.4		4.1
57.5					**7.1**	3.4	2.4	**5.5**	4.0	2.6	2.7				
60	**7.7**	3.4	2.8	**7.6**								**6.4**		2.0	5.1
62.5					**7.0**	2.6	2.0	4.5							
65	**6.0**	2.3	2.2	4.9	**6.5**	3.4	2.2	5.4				4.7	2.2		3.9
67.5					**5.2**	2.4		2.4							
70	**7.2**	2.1	2.4	4.8	**5.5**			2.7				4.6	2.3	2.1	5.7
72.5					4.9			2.9							
75	**6.3**		2.2	3.1	**7.4**	2.5						**5.2**	2.6	2.3	7.5
77.5					**6.6**	2.5	2.0	3.4				**5.8**	2.6	2.5	4.0
80	4.4				4.4	2.5		3.1				**5.8**		2.1	**8.1**
82.5					4.9	2.4		3.0							
85	**5.2**	3.4		2.9								**5.2**			**7.5**
87.5															
90	4.8			2.2								**5.5**		2.3	3.2
92.5												4.1		2.4	2.4

3.5 Multivariate Statistical Analysis

Principal Component Analysis (PCA) and Factor Analysis (FA) (Table 8) were applied only to the chemical data from point 1 (Feb/2015) sediment cores (Table 3). The purpose of this analysis was to verify possible similarities between core samples and elements (Figure 3). In Figure 4, when Factor 1 x Factor 2 is graphed, 2 groups of elements are separated: Br, Co, Cr, Fe, Sc and Zn, and As, Cs, Rb, Sb, Ta, Th and U. Factor Analysis applied to the same data resulted in 3 factors that were responsible for the 67% of total variance. Factor 1 showed a strong correlation (>0.70) between As, Cs, Hf, Sb, Ta, Th and U, and Factor 2 for the elements Br, Cr, Fe, Sc and Zn. In Factor 3, only the element Ba presented a high correlation. These results also confirmed those obtained from the PCA analysis.

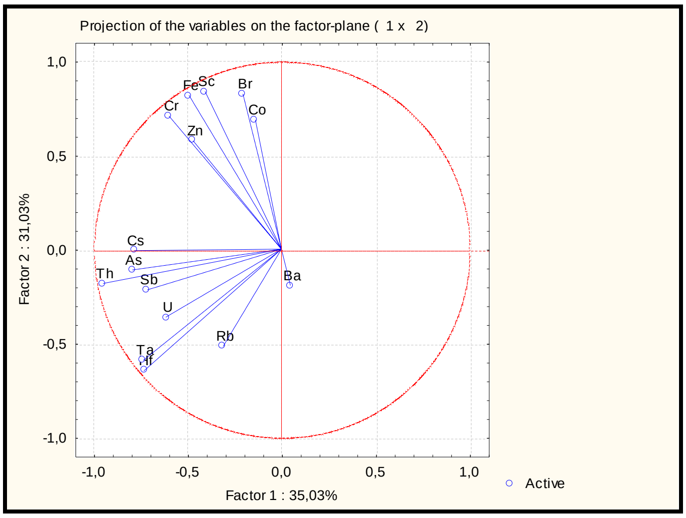

Figure 4: PCA of the chemical data for the sediment core samples from point 1 (Feb/2015)

Table 8: Factor Analysis for the sediment core results from point 1 (Feb/2015)

	Factor 1	Factor 2	Factor 3
As	**0.76**	0.24	-0.04
Ba	0.02	-0.04	**0.88**
Br	-0.17	**0.83**	-0.07
Co	-0.16	0.56	-0.71
Cr	0.24	**0.88**	-0.17
Cs	**0.71**	0.35	0.09
Fe	0.09	**0.93**	-0.22
Hf	**0.94**	-0.26	0.10
Rb	0.51	-0.41	-0.38
Sb	**0.75**	0.06	-0.31
Sc	0.00	**0.93**	-0.09
Ta	**0.92**	-0.22	0.00

Th	**0.93**	0.26	0.04
U	**0.71**	-0.02	0.24
Zn	0.16	**0.79**	0.32
Expl.Var	5.14	4.67	1.78
Prp.Totl	0.34	0.31	0.12

The PCA and FA analyses confirmed that sediment core samples at point 1 were grouped according to metal and trace element concentrations present in the core. In addition, these results confirmed those obtained from the EF and *IGeo* contamination indexes for As, Sb, Th and U.

4 CONCLUSIONS

The results obtained by Z-score criteria for methodological validation proved that the INAA technique presented good accuracy and precision for the determination of the elements analyzed in the present study.

In general, the results obtained for the sediment cores collected at point 1 showed a significant increase in element concentrations in the middle of the sediment profile for most elements: As, Ba, Co, Cs, Hf, Rb, Ta, Th U and Zn. This pattern can be interpreted as an indication of anthropogenic influence during the time period that corresponds to the middle of the reservoir (30 to 60 cm deep). Results from the sediment core samples from point 2 showed the same pattern in the deeper layers for the elements Hf, U, Th and Zn. Results from sediment core samples from point 3 showed an enrichment for the elements Ba, Zn, U and Zn in the upper layers of the sediment profile.

When the Enrichment Factor was used to assess the contamination in this reservoir, only the elements As, Sb, Th and U presented a $2.0 < EF < 5.0$, indicating moderate enrichment according to the Sutherland criteria. $EF>5.0$ was found for As (Points 1 and 2) and U (Point 1), mainly for the fractions below 30 cm deep, which could be an indication of more significant enrichment of these two elements in the sediment profiles collected at Point 1. The other elements analyzed had an $EF < 2.0$, indicating low enrichment or depletion.

As some elements showed an increase in concentration and higher values for EF and *IGeo* below the 30 cm level, this may be evidence of some past activity that raised the enrichment of the sediment for most of the elements analyzed.

When the concentration values of As, Cr and Zn were compared to the oriented values TEL and PEL, none of the results surpassed the PEL value for these elements. Overall, the concentration results in the four sediment cores analyzed in this study were lower than, or similar to, the TEL value, inferring little likelihood of adverse biological effects in this water body.

In addition to As enrichment, U enrichment was also evident in the sediment of the Graminha reservoir. Such enrichment may come from the Poços de Caldas region, Minas Gerais State, where a depleted uranium mine exists, but operated only from 1982 to 1995. The mine region is commonly drained by the Pardo River, the same river that drains its waters into the reservoir. However, there are as yet no studies that confirm the possibility of such transportation and, subsequently, reservoir contamination during the period of mine operation.

No data were found in the literature regarding the concentration of metals and trace elements of environmental interest in sediments of the Graminha reservoir. The present study contributes concentration data for some elements of interest in the sediment profiles from this reservoir. From the results, it is clear that the reservoir received anthropogenic contribution in the recent past, during the period of time that corresponds to the middle of the reservoir, mainly for the elements As and U.

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