

ENRICHMENT FACTOR AND GEOACCUMULATION INDEX APPLIED TO SEDIMENT SAMPLES FROM THE GUARAPIRANGA RESERVOIR, BRAZIL, FOR METAL AND TRACE ELEMENT ASSESSMENT

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ABSTRACT

This study aims to assess sediment contamination by metals and other trace elements in five sampling points of the Guarapiranga Reservoir. Two collection campaigns were undertaken and the samples were analyzed by Instrumental Neutron Activation Analysis (INAA) in order to determine the following elements: major (Fe, K and Na), trace (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Tb, Th, U and Zn) and rare earth elements (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu). Soil samples were collected in the Guarapiranga Park, located next to the reservoir. Composite top soil samples (0-20 cm) were collected in lines across the park at every 30m and were also analyzed by INAA. EF values was calculated using Sc as the conservative element for normalization purposes and soil from Guarapiranga region was used as background levels for the elements analyzed. EF > 1.5 were obtained for the elements As, Sb and Zn, with highest values for Zn (1.6<EF<4.0), mainly at sampling points near the water supply catchment point from the Water Treatment Agency of São Paulo State, indicating anthropogenic contribution. As for the other elements, a 0.5<EF<1.0 was obtained, indicating that they mostly originate from crustal contribution. The Igeo Index was calculated using soil values as background or pristine values as well. For Zn, Igeo values (1.0<EF<2.0) were obtained, and, according to this criteria, these sediments can be classified as moderately contaminated.

1. INTRODUCTION

The Metropolitan Region of São Paulo, Brazil, represents the largest and most populous urban area in South America, with an area of almost 8,000 km². The water supply in Metropolitan Region of São Paulo is done by a set of eight water production systems, which include the abstraction of water from water sources, treatment and distribution [1-3]. Water sources are surface sources or groundwater used for human supply and maintenance of economic activity [4], and Guarapiranga Reservoir is one of the main water sources of the Metropolitan Region of São Paulo (Figure 1a).

The Watershed Dam Guarapiranga is a sub-basin of the Upper Tietê Basin and is located fully in the State of São Paulo, extends over an area of approximately 63,911 hectares (639.11

km²) and is responsible for Guarapiranga Reservoir supply enough water to about 3.7 million people - 20% of the population of the Metropolitan Region of Sao Paulo [1,5,6].

The Guarapiranga Reservoir was constructed in 1906 to face the lack of water caused by dry seasons and since the 70s irregular buildings has been constructed in its neighborhood and as a consequence untreated sewage has been discharged directly into the waters.

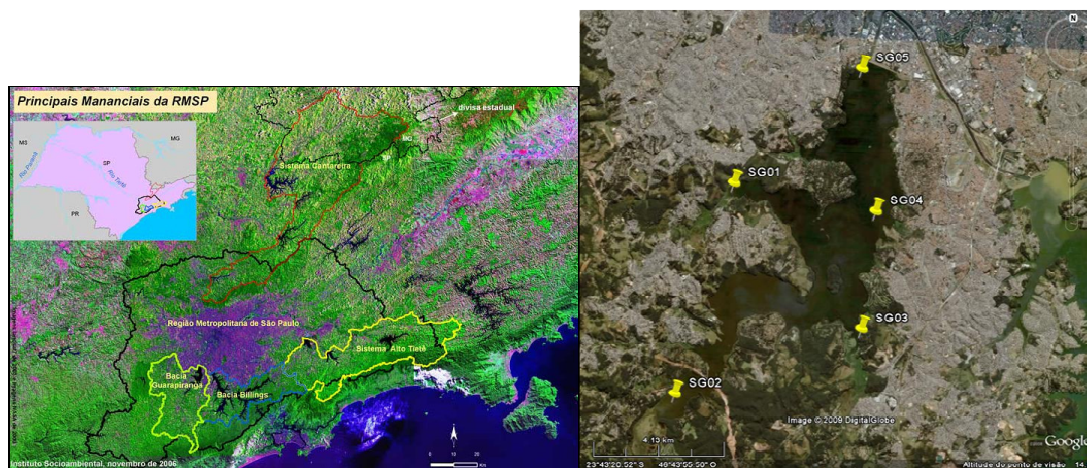


Figure 1: Metropolitanian region of São Paulo State (a) and sampling points (b)

The sediment is a complex array of aquatic ecosystems, because it is responsible for the transport, release and accumulation of toxic compounds and nutrients, and may represent a source of metal contamination of the aquatic environment. Therefore, the sediment is an important compartment for the study of the contamination since it acts as a sink for environmental contaminants [7] and may function as a source of exposure to aquatic organisms [8] and the knowledge of their chemical characterization is necessary for the understanding of natural processes and human influence on these proceedings [9]. In this sense the objective of this work is to characterize the sediments of the Guarapiranga Reservoir through the assessment of the concentrations of metals and trace elements present in samples collected throughout the reservoir and to understand their geochemical correlations by using multivariate analysis tools. For normalization and comparison purpose soil samples collected in the Guarapiranga Park (Figure 2) was used.

2. MATERIAL AND METHODS

2.1. Sample Collection and Preparation

For the sediment collection two sampling campaigns (April 2009 and June 2010) were carried out and five bottom sediment samples (SG01 to SG05) were collected in the Guarapiranga reservoir by a vanVeen sampler. Sampling points are shown in Figure 1b. The geographical positions and other details of the sampling points are presented in Table 1. Sediment samples were previously dried at 45°C in a ventilated oven until constant weight,

passed through a 2 mm sieve, ground in a mortar, once again passed through a 75 µm sieve and then homogenized before analysis. The total fraction (< 2 mm) was analyzed.

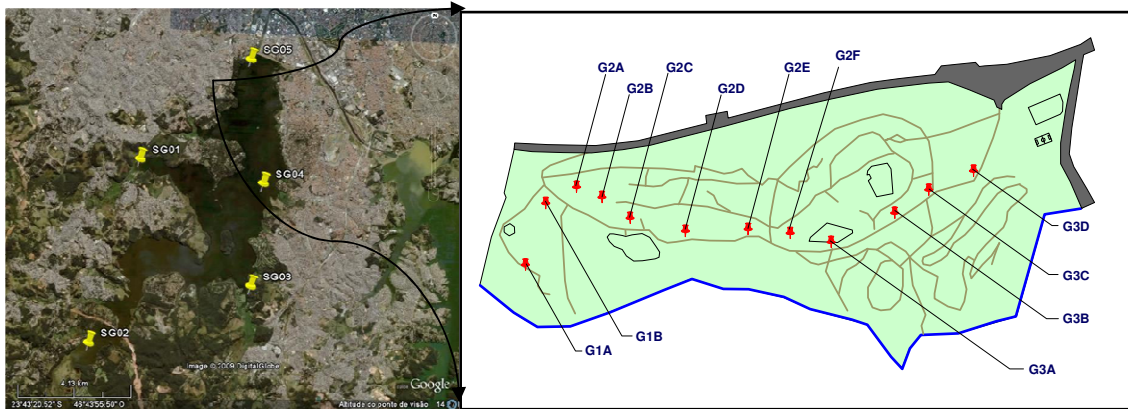


Figure 2: Location of Guarapiranga Park and sapling points inside the park.

The soil samples were collected in July 2007. Top soil samples (0–20 cm) were collected in lines across the park every 30 m. Sampling was performed in order to have representative samples of the entire park. A polyethylene tube with 4 cm diameter was used to take the samples, which were stored in inert plastic bags. In the laboratory, the samples were dried at 45 °C and were sieved through plastic-only sieves into <2 mm fractions. Before and after sieving, the samples were homogenized and quartered. Samples were then ground using an agate mortar in order to obtain a fine and homogeneous powder (<75 µm).

Table 1. Sampling points location in the Guarapiranga reservoir

Samplings Points	Location	Geographical Position (GPS)	Depth (m)
SG1	Tributary of the Embu-Mirim river, about 300 m downstream the Cumbica highway	S 23°42'37.50" W 046°46'026"	3.5
SG2	Tributary of Embu-Guaçu river, about 1 km upstream Rodoanel bridge	S 23°46'153" W 46°46'564"	6.0
SG3	Tributary of the Parelheiros river, about 1 km upstream Ilha dos Eucaliptos	S 23°45'107" W 46°43'318"	4.1
SG4	In the middle of the reservoir, in front of the Castelo country club	S 23°43'021" W 46°43'213"	8.5
SG5	In the middle of the reservoir, in front of Guarapiranga Park, about 500 m upstream from SABESP capitation point	S 23°40'351" W 46°43'434"	

2.1. Multielemental Determination by Instrumental Neutron Activation Analysis (INAA)

Soil, sediment samples and reference materials were sealed in pre-cleaned double polyethylene bags for irradiation. Single and multi-element synthetic standards were prepared by pipetting convenient aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman No.41 filter paper. In the IEA-R1 nuclear reactor at IPEN the sediment samples, reference materials and synthetic standards were irradiated for 8 h and counted after 7 to 20 days depending on the radionuclide half-life produced in the irradiation, under a thermal neutron flux of 1 to $5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co , respectively. The elements As, Ba, Br, Co, Cr, Cs, Cu, Fe, Hf, K, Na, Rb, Sb, Sc, Ta, Th, U, and Zn and the rare earth elements Ce, Eu, La, Lu, Nd, Sm, Tb and Yb were determined. The analysis of the data was done by using in-house gamma ray software, VISPECT program to identify the gamma-ray peaks and by an ESPECTRO program to calculate the concentrations. Detailed analytical methodology is described at Larizzatti et al. [10]. The precision and accuracy of short and long methodologies were verified by using the Z score according to Bode [11] for Buffalo River Sediment, Soil 7 and BEN-Basalt reference materials analyses.

3. RESULTS AND DISCUSSION

Results obtained for the elemental composition in soil samples are shown in Table 2 together with the mean values, standard deviation and the variation coefficient (V.C.). Although high V.C. has been observed for several elements, all the observed values were below the screening values established by CETESB for contaminated soils. Higher V.C. values were observed for Ba, Co, Eu, Rb, Ta and Zn.

Granulometric analysis, organic matter content and classification for the sediments samples (Table 3) indicates predominance of silt and clay in all the locations of sampling and only the point SG2 is composed by more than 10% of sand. The great content of organic matter was observed in the point SG1, although only in the first campaign this parameter was determined. Results of the elemental composition for sediment samples are shown in Tables 4 and 5 for each campaign of sampling. No significant differences were observed between the two campaigns except for Ba in the points SG2, 3, 4 and 5 and for Rb in the points SG1 and SG2.

Coefficient correlations calculated by using the results of soil concentration, shown in Table 6, indicates significant correlations between Ba, Co, Cs, Fe, Hf, Rb, Zn and LRRE (light rare earth elements); between As and Sb; Cr and U; Fe, Ba, Co and Sc. The elements Cr and U possess negative significant correlation with REE and with other metals. For sediment samples, the coefficient correlations, shown in Table 7, show positive significant correlations between Cr, Th and Zn and negative correlations between these elements and LREE. The elements Hf and Co show positive correlations their selves and with HREE (heavy rare earth elements) but negative correlations with LREE and U. In sediments it was also observed a positive correlation, even though at a not significant p level of 0.05, between U and LREE.

Elemental ratios performed for REE (Table 5) indicates that the sediment is enriched related to soil in LREE, fact that must occurs due to the different oxidations conditions of weathering as confirmed by the Ce/Ce* values, being the soil a more oxidized environment and sediment, a more reducing one.

Table 2. Results for the elements analyzed by INAA (mg kg⁻¹, except were indicated %) in soil samples: mean, standard deviation and variation coefficient.

	G1A	G1B	G2A	G2B	G2C	G2D	G2E	G2F	G3A	G3B	G3C	G3D	mean	S.D.	V.C.
As	3.9	6.6	5.1	5	5.6	4.3	6.2	2.4	2.8	4.6	6.7	5.2	4.9	1.4	28.1
Ba	241	112	94	224	213	251	470	342	368	570	158	431	289.5	148.1	51.1
Ce	98.4	78	181	134	101	117	164	168	158	134	105	126	130.4	32.1	24.7
Co	7.7	5	2.2	6.2	5.5	2.8	11.6	8.1	6.8	12.5	3	6.5	6.5	3.2	49.6
Cr	73	56	57	84	58	59	37	46	53	76	61	62	60.2	12.8	21.3
Cs	2.4	2.9	1.9	2.4	3.6	1.6	6.3	1.6	4.7	12.4	4.2	5.2	4.1	3.0	73.6
Eu	0.37	0.4	0.6	0.58	0.75	0.75	1.7	2	1.6	2.2	0.77	1.4	1.1	0.6	59.3
Fe (%)	3.7	3.35	3.08	4.5	3.2	3.73	4.6	4.57	3.45	3.96	3.18	3.86	3.8	0.6	14.6
Hf	8.5	11.3	11.3	10.1	10.5	11.6	13.3	13.9	13.3	13.4	11.5	13.8	11.9	1.7	14.3
La	23	22	58	35	38	37	73	69	70	77	45	58	50.4	19.6	38.9
Lu	0.8	0.39	0.39	0.64	0.52	0.6	0.38	0.3	0.35	0.67	0.58	0.8	0.5	0.2	32.5
Nd	22	18	55	42	43	27	66	42	68	75	48	58	47.0	18.4	39.0
Rb	34	21	21	48	38	35	97	19	77	138	20	59	50.6	36.8	72.8
Sb	0.64	0.83	0.62	0.19	0.61	0.3	0.63	0.19	0.41	0.64	0.56	0.84	0.5	0.2	40.9
Sc	13	11.1	9.4	15	10	14.1	13.6	12.3	11	14.2	10.9	11.3	12.2	1.8	14.9
Se	0.64	0.87	0.81	0.8	0.77	0.9	0.75	0.95	0.93	0.95	0.82	0.99	0.8	0.1	12.0
Sm	4.9	3.9	8.5	6.6	6.6	6.1	11.1	10.1	10.3	12.3	6.5	9.7	8.1	2.6	32.9
Ta	1.6	1.7	1.3	1.5	1.6	1.8	6.5	2.8	---	1.6	1.9	1.4	2.2	1.5	69.4
Tb	0.74	0.56	0.98	0.96	0.77	1.02	1.67	1.51	1.66	2.04	1.33	2	1.3	0.5	39.6
Th	20.3	16.9	23.5	24	19.8	18.4	23.3	18.3	17.6	17.6	21.9	18.9	20.0	2.5	12.6
U	8.6	6.3	6.4	8.5	5.1	6.7	4.4	5.5	4.3	6.9	6.6	6.1	6.3	1.4	21.7
Yb	4.8	4	2.4	3.9	3.7	4.8	1.7	2.6	2.9	6.9	5.4	7.8	4.2	1.8	43.0
Zn	27	25	23	24	39	17	64	32	59	83	35	61	40.8	20.8	51.1

Table 3. Results for granulometric analysis and organic matter (OM) content for the sediment samples

Sample	Organic matter content (g dm ⁻³)	Clay (%)	Silt (%)	Total Sand (%) (2.00 – 0.053 mm)	Textural classification
SG1-1	109.0	65.4	25.8	8.8	Very clayish
SG1- 2	n.d.	68.1	22.7	8.2	Very clayish
SG2-1	59.3	38.9	43.1	18.0	Mostly clay silt
SG2-2	42.0	28.1	24.9	47.0	Mostly clay sand
SG3-1	56.0	41.4	48.6	10.0	Clay silt
SG3- 2	51.0	54.7	47.4	6.9	Clay silt
SG4-1	59.0	48.7	50.2	1.1	Clay silt
SG4-2	56.0	51.0	46.8	2.2	Clay silt
SG5-1	68.0	56.5	41.9	1.6	Clay silt
SG5-2	60.0	53.6	44.0	2.4	Clay silt

SGX-1 – first campaign; SGX-2 – second campaign; n.d. – not determined

Despite these differences the similarity of the sediment with the local soil is clear when compared with others global reference values as NASC (North American Shale Composite) and UCC (Upper Continental Crust) as presented in Figure 3.

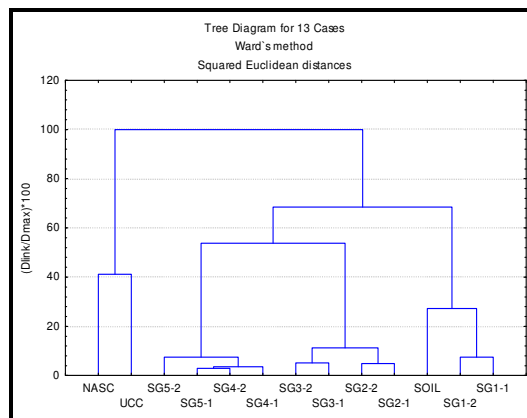


Figure 3: Dendrogram comparing the similarity of the sediment samples and global reference values: NASC and UCC.

It is well known that metals originating from the same source generally group together, mainly in silt and clay fractions and enrichment, if it occurs, can be observed by using a

normalization procedure that offsets the variability in mineralogy and grain size [12-14] by establishing the enrichment factor (EF) defined as ratio between the following ratios: the element concentration and the conservative element concentration in the sample and; the element concentration and the conservative element concentration in the background reference values, in this case, the surrounding soil of the dam. The elements of natural origin that are structurally combined with one or more mineral phases are considered conservative. The main assumption for the application of a geochemical normalization for conservative elements is the existence of a linear relationship between the normalizer and other metals [14] and its concentration should not be anthropogenically altered [15, 16]. In this study, Sc was used as a normalizer (Silva, 2011) according to the equation 1:

$$EF = [C_n/C_{Sc}]_{\text{sample}}/[C_n/C_{Sc}]_{\text{(shale)}} \quad (1)$$

According to Zhang and Liu [17], if $0.5 < EF < 1.5$, the elemental concentration is probably entirely due to crustal or natural weathering origin; values above 1.5 indicate anthropogenic contribution. The higher the EF value the more severe is the anthropogenic contribution.

Table 5 – Total concentration (mg kg^{-1}) of Σ REE. Σ LREE. Σ HREE. and ratios of La/Sm. La/Yb. Ce/La. Eu/Sm. Yb/Sm. and Ce/Ce* in sediments and soil from Guarapiranga reservoir and shale values

	SG1-1	SG1-2	SG2-1	SG2-2	SG3-1	SG3-2	SG4-1	SG4-2	SG5-1	SG5-2	Soil
La	62.70	61.75	40.90	39.91	43.70	46.10	48.60	47.92	44.50	43.73	50.4
Ce	134.2	125.5	85.90	80.01	96.90	91.03	98.50	96.41	100.8	81.79	130.4
Nd	48.90	51.70	33.00	30.50	33.70	35.40	39.10	34.90	42.70	47.50	47.0
Sm	9.60	9.20	7.30	7.06	7.40	7.43	6.80	6.65	7.20	6.89	8.05
Eu	2.16	1.95	1.28	1.09	1.26	1.27	1.25	1.11	1.41	1.39	1.09
Tb	0.80	0.79	1.00	0.87	0.90	n.d.	0.55	0.77	0.80	0.94	1.27
Yb	2.00	1.64	5.30	4.94	3.43	3.66	2.50	2.82	2.60	2.57	4.24
Lu	0.30	0.27	0.83	0.82	0.57	0.59	0.55	0.56	0.42	0.39	0.54
Σ REE	260.7	252.8	175.5	165.2	187.9	185.5	197.9	191.1	200.4	185.2	243.0
Σ LREE	257.6	250.1	168.4	158.6	183.0	181.2	194.3	187.0	196.6	181.3	236.9
Σ HREE	3.1	2.7	7.1	6.6	4.9	4.3	3.6	4.1	3.8	3.9	6.0
$\frac{\Sigma \text{LREE}}{\Sigma \text{HREE}}$	83.1	92.6	23.6	23.9	37.3	42.6	54.0	45.1	51.5	46.4	39.2
La/Yb	31.4	37.7	7.7	8.1	12.7	12.6	19.4	17.0	17.1	17.0	11.9
La/Sm	6.5	6.7	5.6	5.7	5.9	6.2	7.1	7.2	6.2	6.3	6.3
Ce/La	2.1	2.0	2.1	2.0	2.2	2.0	2.0	2.0	2.3	1.9	2.6
Eu/Sm	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1
Yb/Sm	0.2	0.2	0.7	0.7	0.5	0.5	0.4	0.4	0.4	0.4	0.5
Ce/Ce*	1.01	0.97	0.92	0.88	1.00	0.91	1.00	0.99	1.04	0.87	1.20

n.d. – not determined

Table 4. Results for the elements analyzed in sediment samples by INAA (mg kg⁻¹): mean and standard deviation

	SG1-1	SG1-2	SG2-1	SG2-2	SG3-1	SG3-2	SG4-1	SG4-2	SG5-1	SG5-2
As	5.3 ± 0.4	3.3 ± 0.2	10.5 ± 1.0	9.2 ± 0.4	8.3 ± 0.2	9.8 ± 0.4	14.7 ± 1.1	9.0 ± 0.3	12.7 ± 0.8	10.7 ± 0.4
Ba	467 ± 30	435 ± 34	680 ± 43	365 ± 22	321 ± 22	619 ± 42	209 ± 14	374 ± 24	344 ± 29	454 ± 60
Br	12.3 ± 0.2	14.3 ± 0.3	12.5 ± 0.1	10.9 ± 0.3	10.0 ± 0.1	14.6 ± 0.3	17.1 ± 0.2	21.4 ± 0.3	23.5 ± 0.3	28.3 ± 0.4
Ca(%)	1.34± 0.04	1.24± 0.04	1.51± 0.03	1.18± 0.06	1.61± 0.04	0.90± 0.06	2.45± 0.06	1.76± 0.05	1.73± 0.03	1.61± 0.07
Co	9.5 ± 0.2	7.4 ± 0.1	11.4 ± 0.2	10.8 ± 0.1	8.5 ± 0.1	9.0 ± 0.2	9.1 ± 0.2	8.3 ± 0.1	9.4 ± 0.2	9.7 ± 0.1
Cr	49 ± 2	47 ± 1	78 ± 4	74 ± 2	75 ± 3	77 ± 2	80 ± 3	84 ± 2	80 ± 4	78 ± 2
Cs	6.2 ± 0.2	5.5 ± 0.5	8.3 ± 0.3	8.1 ± 0.7	10.1 ± 0.4	10.0 ± 1.9	6.7 ± 0.3	6.6 ± 0.7	6.7 ± 0.3	6.5 ± 0.8
Fe(%)	4.82± 0.03	3.99± 0.03	4.56± 0.03	4.18± 0.02	3.51 ± 0.11	4.27± 0.03	6.13± 0.20	6.25± 0.04	6.04± 0.20	5.71± 0.04
Hf	2.4 ± 0.1	2.3 ± 0.1	13.9 ± 0.3	13.8 ± 0.6	10.4 ± 0.2	6.9 ± 0.3	7.4 ± 0.1	7.5 ± 0.3	6.7 ± 0.1	6.2 ± 0.2
K (%)	0.80± 0.13	0.71± 0.02	2.48± 1.14		1.42 ± 0.3	1.28± 0.08	0.81± 0.23	0.84± 0.24	0.73± 0.15	
Na(%)	0.085 ± 0.011	0.083 ± 0.006	0.100 ± 0.003	0.107 ± 0.001	0.094± 0.005	0.082± 0.004	0.116± 0.012	0.134± 0.005	0.063± 0.004	0.046± 0.011
Rb	139 ± 8	44 ± 3	92 ± 4	85 ± 5	93 ± 4	84 ± 11	42 ± 2	55 ± 3	68 ± 4	43 ± 3
Sb	1.34± 0.06	1.26± 0.18	0.80± 0.04	0.75 ± 0.11	1.22± 0.08	0.94± 0.08	1.58± 0.07	1.57± 0.12	1.46 ± 0.11	1.14± 0.06
Sc	15.1 ± 0.2	14.9 ± 0.2	17.2 ± 0.2	16.2 ± 0.3	14.5 ± 0.2	15.6 ± 0.3	17.1 ± 0.2	17.2 ± 0.3	15.7 ± 0.2	15.3 ± 0.3
Sm	9.6 ± 0.1	9.20± 0.09	7.3 ± 0.1	7.06± 0.07	7.40± 0.10	7.43± 0.07	6.8 ± 0.1	6.65± 0.06	7.20 ± 0.1	6.89± 0.07
Ta	2.3 ± 0.2	2.0 ± 0.3	2.6 ± 0.2	2.1 ± 0.2	2.1 ± 0.2	3.2 ± 0.2	1.8 ± 0.1	2.6 ± 0.1	2.5 ± 0.2	2.7 ± 0.1
Th	17.8 ± 0.5	17.4 ± 0.3	18.6 ± 0.5	16.9 ± 0.3	22.0 ± 0.6	22.5 ± 0.5	24.4 ± 0.7	27.7 ± 0.5	21.7 ± 0.6	20.2 ± 0.4
U	8.4 ± 0.4	8.7 ± 0.3	5.2 ± 0.2	5.1 ± 0.2	8.5 ± 0.4	9.9 ± 0.3	7.5 ± 0.4	7.3 ± 0.2	7.5 ± 0.3	7.1 ± 0.2
Zn	129 ± 4	81 ± 3	152 ± 5	152 ± 4	193 ± 6	200 ± 12	209 ± 7	231 ± 9	169 ± 5	140 ± 5

The calculations applied as stated above indicates EF values higher than 1.5 for the elements Rb, Sb and Zn in point SG1; As, Ba and Zn in point SG2; Ba, Cs, Rb, Sb, and Zn in point SG3 and As, Sb and Zn in points SG4 and SG5. Therefore anthropogenic contributions can be observed throughout the Guarapiranga Reservoir mainly due to the EF values obtained for Zn that varied from 1.6 to 4.4, including the points near the catchment of water supply from the Water Treatment Agency of State of São Paulo.

Another approach to assess the contamination level of sediments is the Igeo (Index of geoaccumulation) defined by Muller and Suess [18] according to the equation 2.

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

Where C_n = concentration of the examined element in the sediment sample; B_n = background of a given element in the geochemical reference. The geoaccumulation index distinguishes 6 classes of quality for sediments: $I_{geo} < 0$ unpolluted; $0 < I_{geo} < 1$ unpolluted to moderately polluted; $1 < I_{geo} < 2$ moderately polluted; $2 < I_{geo} < 3$ moderately to strongly polluted; $3 < I_{geo} < 4$ strongly polluted; $4 < I_{geo} < 5$ strongly to extremely polluted; $5 < I_{geo}$ extremely polluted. The class 6 is an open class and comprises all values of the geoaccumulation index higher than 5. Concentrations of geochemical background are multiplied each time by the constant 1.5 in order to allow content fluctuations of a given substance in the environment as well as very small anthropogenic influences. In this study the geochemical background reference used in the Igeo calculations was the soil of Guarapiranga park.

According to the classes established for Igeo the analyzed sediments can be considered unpolluted to moderately polluted by the elements Cs, Rb and Sb and moderated polluted by Zn, in accordance with the results obtained in the EF analysis.

Table 6: Coefficient correlations calculated for soil samples

Correlations Coefficient																										
Marked correlations are significant at $p < .05000$																										
N=12																										
Variable	As	Ba	Ce	Co	Cr	Cs	Eu	Fe (%)	Hf	La	Lu	Nd	Rb	Sb	Sc	Se	Sm	Ta	Tb	Th	U	Yb	Zn	Na	K	
As	1,00																									
Ba	-0,30	1,00																								
Ce	-0,45	0,33	1,00																							
Co	-0,19	0,85	0,22	1,00																						
Cr	-0,01	-0,07	-0,37	-0,04	1,00																					
Cs	0,13	0,76	0,06	0,71	0,16	1,00																				
Eu	-0,41	0,87	0,55	0,72	-0,31	0,65	1,00																			
Fe (%)	-0,29	0,58	0,38	0,65	-0,05	0,14	0,51	1,00																		
Hf	-0,21	0,67	0,53	0,39	-0,51	0,46	0,86	0,33	1,00																	
La	-0,32	0,73	0,78	0,54	-0,39	0,57	0,91	0,35	0,84	1,00																
Lu	0,12	0,17	-0,48	0,05	0,73	0,22	-0,22	-0,01	-0,36	-0,34	1,00															
Nd	-0,09	0,68	0,64	0,49	-0,14	0,71	0,74	0,17	0,66	0,89	-0,12	1,00														
Rb	-0,06	0,87	0,25	0,80	0,10	0,91	0,69	0,36	0,46	0,63	0,16	0,74	1,00													
Sb	0,58	0,03	-0,38	0,08	-0,08	0,36	-0,13	-0,45	-0,00	-0,10	0,25	0,06	0,15	1,00												
Sc	-0,18	0,47	0,00	0,51	0,38	0,26	0,23	0,75	-0,02	0,03	0,34	-0,02	0,45	-0,44	1,00											
Se	-0,29	0,40	0,23	0,05	-0,11	0,29	0,59	0,10	0,80	0,50	-0,14	0,36	0,23	-0,09	-0,03	1,00										
Sm	-0,33	0,82	0,74	0,64	-0,27	0,65	0,92	0,43	0,81	0,98	-0,19	0,91	0,73	-0,07	0,13	0,48	1,00									
Ta	-0,47	0,19	0,29	0,06	-0,21	0,07	0,27	-0,15	0,28	0,34	-0,36	0,38	0,24	-0,18	-0,19	0,24	0,29	1,00								
Tb	-0,23	0,86	0,49	0,57	-0,15	0,69	0,88	0,39	0,84	0,87	0,08	0,83	0,70	0,04	0,19	0,61	0,90	0,26	1,00							
Th	0,36	-0,27	0,34	-0,14	0,08	-0,21	-0,31	0,16	-0,35	-0,03	0,03	0,13	-0,13	-0,15	0,07	-0,59	-0,04	-0,29	-0,16	1,00						
U	0,04	-0,29	-0,38	-0,16	0,85	-0,15	-0,51	0,05	-0,67	-0,58	0,68	-0,47	-0,20	-0,10	0,43	-0,33	-0,49	-0,48	-0,38	0,23	1,00					
Yb	0,14	0,29	-0,48	0,05	0,57	0,44	0,06	-0,13	0,06	-0,10	0,82	0,05	0,24	0,38	0,16	0,37	-0,00	-0,26	0,34	-0,36	0,41	1,00				
Zn	-0,03	0,88	0,25	0,76	-0,09	0,91	0,79	0,23	0,65	0,74	0,10	0,83	0,89	0,34	0,12	0,37	0,81	0,29	0,84	-0,23	-0,42	0,31	1,00			
Na	0,29	-0,02	-0,71	0,05	0,49	0,23	-0,40	-0,36	-0,49	-0,51	0,74	-0,31	0,12	0,64	0,06	-0,33	-0,41	-0,21	-0,21	-0,21	0,50	0,62	0,07	1,00		
K	0,05	0,76	-0,10	0,65	0,44	0,82	0,41	0,28	0,19	0,29	0,63	0,48	0,86	0,27	0,54	0,14	0,44	-0,02	0,56	-0,14	0,17	0,62	0,74	0,48	1,00	

Table 7: Coefficient correlations calculated for sediment samples

Correlations Coefficient																											
Marked correlations are significant at p < ,05000																											
n = 10																											
Variable	As	Ba	Br	Ce	Co	Cr	Cs	Eu	Fe(%)	Hf	K (%)	La	Lu	Na(%)	Nd	Rb	Sb	Sc	Sm	Ta	Tb	Th	U	Yb	Zn		
As	1,00																										
Ba	-0,27	1,00																									
Br	0,41	-0,15	1,00																								
Ce	-0,64	-0,10	-0,23	1,00																							
Co	0,40	0,37	-0,11	-0,53	1,00																						
Cr	0,84	-0,11	0,40	-0,84	0,32	1,00																					
Cs	0,18	0,29	-0,47	-0,50	0,22	0,40	1,00																				
Eu	-0,67	0,13	-0,13	0,90	-0,30	-0,91	-0,52	1,00																			
Fe(%)	0,60	-0,35	0,79	-0,11	0,01	0,46	-0,55	-0,19	1,00																		
Hf	0,42	0,12	-0,31	-0,78	0,69	0,60	0,58	-0,76	-0,21	1,00																	
K (%)	0,14	0,67	-0,49	-0,58	0,73	0,30	0,58	-0,36	-0,40	0,84	1,00																
La	-0,68	-0,05	-0,14	0,95	-0,58	-0,86	-0,58	0,90	-0,07	-0,85	-0,59	1,00															
Lu	0,41	0,23	-0,38	-0,74	0,67	0,58	0,60	-0,76	-0,19	0,95	0,84	-0,78	1,00														
Na(%)	0,05	-0,24	-0,43	-0,05	-0,05	0,20	0,09	-0,38	0,06	0,36	0,09	-0,05	0,49	1,00													
Nd	-0,42	-0,05	0,37	0,70	-0,43	-0,67	-0,72	0,84	0,16	-0,88	-0,63	0,77	-0,92	-0,59	1,00												
Rb	-0,34	0,36	-0,61	0,31	0,37	-0,35	0,34	0,35	-0,44	0,10	0,30	0,17	0,13	0,02	-0,14	1,00											
Sb	0,14	-0,65	0,43	0,47	-0,63	0,00	-0,53	0,20	0,65	-0,59	-0,82	0,43	-0,61	0,16	0,40	-0,32	1,00										
Sc	0,56	0,02	0,14	-0,42	0,41	0,56	-0,12	-0,55	0,56	0,46	0,27	-0,38	0,58	0,64	-0,49	-0,25	0,05	1,00									
Sm	-0,81	0,22	-0,41	0,88	-0,29	-0,97	-0,32	0,95	-0,44	-0,63	-0,24	0,87	-0,60	-0,23	0,66	0,48	0,02	-0,57	1,00								
Ta	0,08	0,72	0,33	-0,32	0,15	0,33	0,34	-0,19	0,08	0,00	0,32	-0,26	0,11	-0,31	-0,13	0,11	-0,31	0,05	-0,19	1,00							
Tb	-0,26	0,75	-0,07	-0,36	0,46	0,03	0,44	-0,07	-0,47	0,42	0,73	-0,38	0,30	-0,39	-0,17	0,32	-0,74	-0,25	0,00	0,62	1,00						
Th	0,49	-0,35	0,40	-0,21	-0,39	0,65	0,09	-0,51	0,59	-0,03	-0,24	-0,21	0,03	0,43	-0,30	-0,39	0,62	0,42	-0,59	0,19	-0,46	1,00					
U	-0,31	-0,02	-0,01	0,52	-0,76	-0,33	0,12	0,41	-0,16	-0,72	-0,55	0,54	-0,64	-0,24	0,41	0,04	0,38	-0,58	0,41	0,21	-0,39	0,25	1,00				
Yb	0,28	0,42	-0,40	-0,71	0,76	0,47	0,64	-0,64	-0,33	0,94	0,95	-0,76	0,96	0,28	-0,84	0,27	-0,78	0,41	-0,46	0,23	0,54	-0,18	-0,64	1,00			
Zn	0,63	-0,27	0,12	-0,45	-0,03	0,79	0,45	-0,73	0,40	0,34	0,04	-0,49	0,41	0,53	-0,66	-0,10	0,30	0,49	-0,72	0,22	-0,33	0,87	0,06	0,22	1,00		

4. CONCLUSIONS

The application of normalization methods to analyze sediment contamination of Guarapiranga Reservoir was applied using soil samples of Guarapiranga Park as geochemical reference background values, both determined by instrumental neutron activation analysis. Coefficient correlation analysis indicated similarities between the soil and sediment samples mainly in the REE behavior. This result was confirmed by the cluster analysis that shows higher similarities between sediment samples and soil samples of Guarapiranga region than that obtained by comparison with global reference values. The application of enrichment factor as well as the geoaccumulation index indicated anthropogenic contribution mainly by the elements Zn. This man made contribution is certainly originated from the untreated sewage and human activities of the population inhabiting the region illegally and the uncontrolled occupation of the vicinity of the dam.

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