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Metal and trace element assessment of sediments from Guarapiranga reservoir, São Paulo State, by neutron activation analysis

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ABSTRACT

Guarapiranga Reservoir is extremely important due to the fact that it is one of the main water reservoirs for South America’s largest city, São Paulo, Brazil. Guarapiranga Basin is located within the Metropolitan Region of São Paulo – RMSP, and occupies an area of approximately 630 km^2, and the reservoir itself is located in the northern part of the basin occupying approximately 26 km^2. This reservoir is characterized by environmental impacts from urban invasion, industrial and sewage wastes, all of which seriously affect its water quality. Due to its vulnerability CETESB (Environmental Control Agency of the São Paulo State) regularly monitors the contamination levels of waters and once a year sediment samples. In order to better understand geochemical and environmental processes and their possible changes due to anthropogenic activities trace metals analyses and their distribution in sediments are commonly undertaken. The present study reports results concerning the distribution of some major (Fe, K and Na), trace (As, Ba, Br, Co, Cr, Cs, Hf, Hg, Rb, Sb, Sc, Ta, Tb, Th, U and Zn) and rare earth (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) elements in sediments from the Guarapiranga Reservoir. Multielementar analysis was carried out by instrumental neutron activation analysis (INAA). Multielemental concentrations in the sediment samples were compared to NASC (North American Shale Composite) values. The concentration values for metals As, Cr and Zn in the sediment samples were compared to the Canadian Council of Minister of the Environment (CCME) oriented values (TEL and PEL values) and adopted by CETESB.

1. INTRODUCTION

Reservoirs located in highly populated and industrialized regions receive discharges of organic compounds, heavy metals and nutrients which greatly impair water quality and threaten aquatic life. The Guarapiranga reservoir is located in the Metropolitan area of São Paulo city, São Paulo State, Brazil (23º 41’ S and 46º 43’ W) and is an important drinking water reservoir for the city, providing 25% of its water needs [1]. The reservoir has been reported as eutrophic since 1960 based on the discharge of untreated urban sewage [2]. Total heavy metal and nutrient concentrations show strong anthropogenic contamination [3,4].

One of the most important worries refers to environmental impacts caused by anthropogenic liberation of heavy metals in various natural environments [5,6]. Sediments are considered a compartment of pollutant species accumulation, due to its high capacity of absorption and accumulation [7,8]. The element concentrations are higher than the corresponding water column, making possible the use of heavy metal and trace elements concentration as a good environmental pollution indicator. It is even possible to identify the main sources of pollution within aquatic systems. However, many biotic and abiotic processes can remobilize these species, becoming itself a secondary pollution source, affecting the water quality, originating bioaccumulation and changes in the trophic chain. [9] Therefore, the evaluation of sediment quality is substantial to understand the processes that contribute to the availability and destination of pollutants disposed in aquatic systems.[10]

Instrumental neutron activation analysis (INAA) has been widely applied for soil and sediment analysis at LAN [11-14], allowing the determination of several elements such as Zn, As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, Sb, Se, Ta, Th, U, W, Zr and rare earth elements (REE). For total Hg determination, the cold vapor atomic absorption technique (CV AAS) is largely used for biological, geological and environmental samples [15].

The objective of this study was to assess the concentration of some heavy metals and trace elements in sediment samples from the Guarapiranga reservoir by instrumental neutron activation analysis, and thus, evaluate the pollution conditions of its aquatic system. The results obtained for multielemental concentrations in the sediment samples were compared to NASC (North American Shale Composite) values. For As, Cr and Zn the results were also compared to the Canadian Council of Minister of the Environment (CCME) oriented values (TEL and PEL values) and adopted by CETESB for sediment quality monitoring.

2. MATERIAL AND METHODS

2.1. Sampling and sample preparation

Five bottom sediment samples (SG01 to SG05) were collected in the Guarapiranga reservoir by a vanVeen sampler. The geographical positions of the sampling points are presented in Table 1. Sediment samples were previously dried at 45°C in a ventilated oven until constant weight. After this step, sediment samples were passed through a 2 mm sieve, ground in a mortar, once again passed through a 200 mesh sieve and then homogenized before analysis. The total fraction (< 2 mm) was analyzed. Sampling stations are presented in Figure 1.

Table 1 – Sampling points location in the Guarapiranga reservoir

Samplings Points	Location	Geographical Position (GPS)	Deep (m)
SG01	Tributary of the Embu-Mirim river, about 300 m downstream the Cumbica highway	S 23º42’37.50’’ W 046º46’026’’	3.5
SG02	Tributary of Embu-Guaçú river, about 1 km upstream Rodoanel bridge	S 23º46’153’’ W 46º46’564’’	6.0
SG03	Tributary of the Parelheiros river, about 1 km upstream Ilha dos Eucaliptos	S 23º45’107’’ W 46º43’318’’	4.1
SG04	In the middle of the reservoir, in front of the Castelo country club	S 23º43’021’’ W 46º43’213’’	8.5
SG05	In the middle of the reservoir, in front of Guarapiranga Park, about 500 m upstream from SABESP capitation point	S 23º40’351’’ W 46º43’434’’	

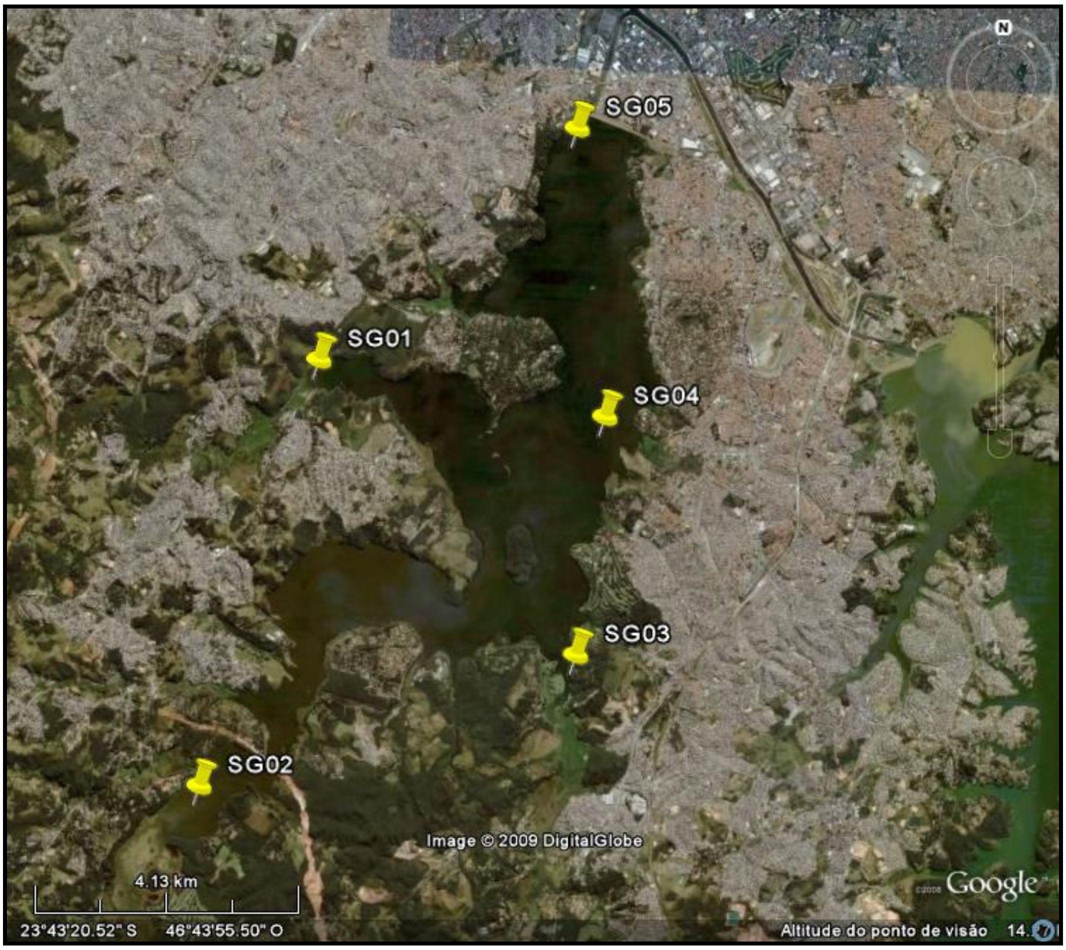

Figure 1 - Sampling points locations in the Guarapiranga reservoir

2.2 Granulometric analysis and organic matter content of the sediment samples

These chemical analyses were carried out at Instituto Agronômico de Campinas (IAC). The granulometric analysis was done according to Camargo et al [16]. The organic matter content was performed by using pipetting methodology.

2.3 Multielemental determination by Instrumental Neutron Activation Analysis

For the multielemental analysis, approximately 200 mg of sediment (duplicate samples) and about 150 mg of reference materials were accurately weighed and 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. Sediment samples, reference materials and synthetic standards were irradiated for 16 hours, under a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} in the IEA-R1 nuclear reactor at IPEN. Two series of counting were made: the first, after one week decay and the second, after 15-20 days. 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 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 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. The uncertainties of the results were calculated by errors propagation. The methodology validation was verified by measuring the reference materials Buffalo River Sediment (NIST SRM 2704), Soil 7 (IAEA) and BEN (Basalt –IWG-GIT). Details of the analytical methodology is described at Larizzatti et al [11].

3. RESULTS AND DISCUSSION

Table 2 presents the results for the granulometric analysis and organic matter (OM) content for the sediment samples.

Points SG01 and SG05 presented the highest OM content followed closely by points SG02, SG03 and SG04.

Regarding granulometric distribution SG01 presented the highest clay composition and lowest silt percentage. Points SG03, 04 and 05 presented a very similar granulometric composition, with very similar clay and silt proportions. Point 2, presented a higher silt percentage than clay in its composition. This point presented the highest sandy fraction (18%) as well. Points SG01 and SG03 and, SG04 and 05 presented very similar proportions of sandy fractions: 8.8 and 10%, and 1.1 and 1.6 %, respectively.

Table 2 – 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
SG01	109	65.4	25.8	8.8	Very clayish
SG02	59 3	38.9	43.1	18	Mostly clay silt
SG03	56	41.4	48.6	10	Clay silt
SG04	59	48.7	50.2	1.1	Clay silt
SG05	68	56.5	41.9	1.6	Clay silt

The results obtained by INAA for Buffalo River Sediment, Soil 7 and BEN-Basalt reference materials analyses are presented in Figure 2. The Z value calculation was according to Bode [17]. If $|Z| < 3$ the individual result of the control sample (reference material) lies on the 99% confidence interval of the target value. All Z-score values were in this interval range ($|Z| < 3$), indicating good precision and accuracy of the INAA technique. The data are presented in Figure 2.

Table 3 presents the mean (duplicate) and standard deviation (mg kg^{-1}) for the elements analyzed by INAA for the sediment samples collected in the summer of 2009. Table 3 also shows the NASC (North American Shale Composite) values [18] and Canadian Council of Minister of the Environment (CCME) oriented values (TEL and PEL) [19]. These are the limits established by Canadian legislation and adopted by the Environmental Control Agency of Sao Paulo State (CETESB). TEL is the limit below which no adverse effects on the biological community is observed and PEL, the probable level of occurrence of adverse effects on the biological community.

When the results obtained for multielemental concentrations (Table 3) were compared with NASC values [18] it could be observed that there was an enrichment for Cs, Rb, Sc, Ta, Th, U and light REE (La, Ce, Eu, Nd, Sm) at point **SG01**. The elements Co, Cr, Hf, Lu and Yb were depleted and Sc and Tb are of the same order of magnitude of NASC values. This point is located at the entrance of the Embu-Mirim River, where the domestic sewage from Itapecerica da Serra county are thrown without any treatment. According to CETESB [20] this site shows no register of any metal contamination in its water body or the presence of nearby industries.

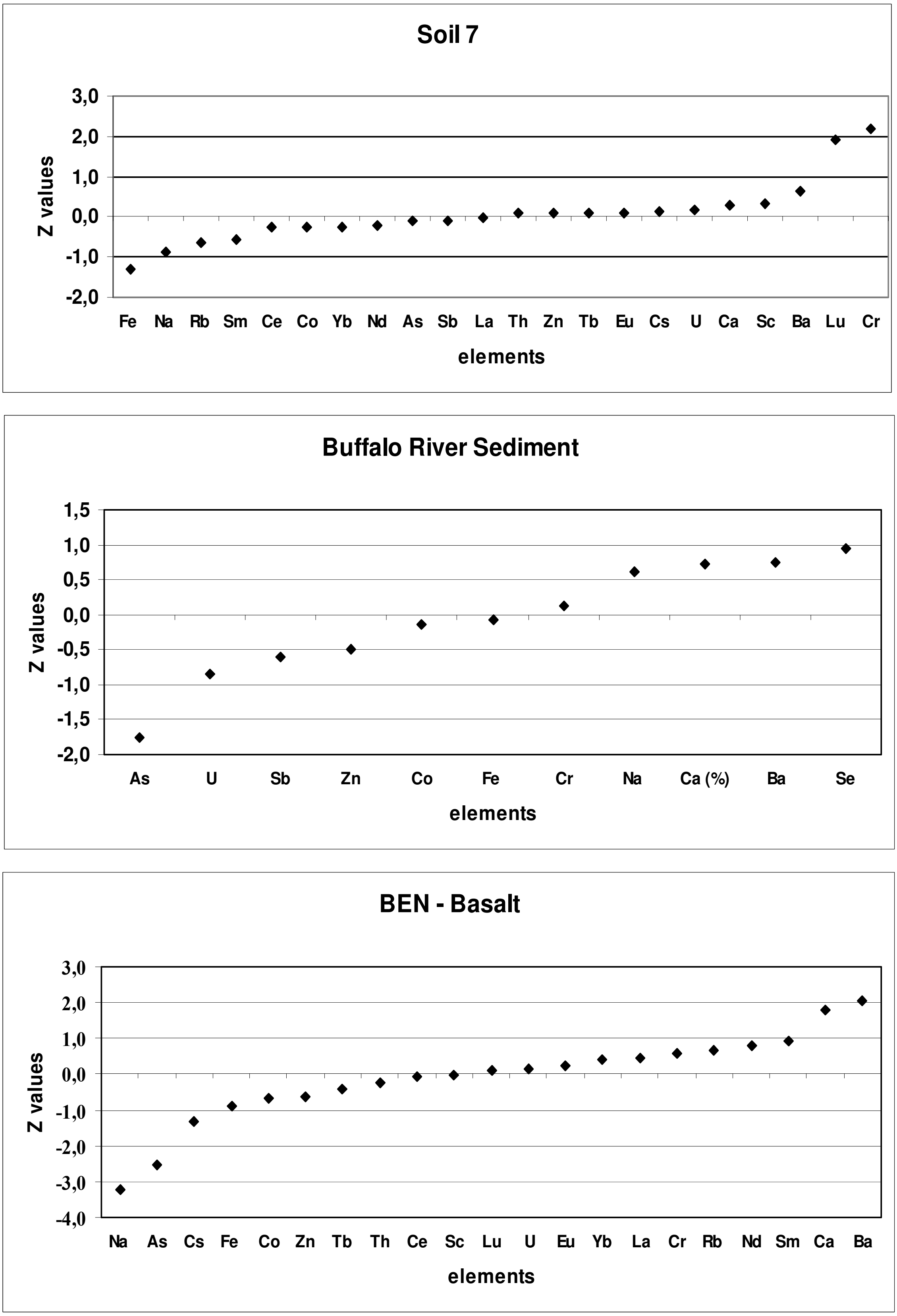

Figure 2. Control chart (Z-values) for inspection of the normalized concentrations of certified elements in the SOIL-7, Buffalo River Sediment and Basalt-BEN reference material samples.

Table 3. Results for the elements analyzed by INAA (mg kg^{-1}): mean, standard deviation, NASC, TEL and PEL values

elements	Sampling Points					NASC [18]	TEL [19]	PEL [19]
	SG01	**SG02**	**SG03**	**SG04**	**SG05**			
As	5.3 ± 0.4	10.5 ± 1.0	8.3 ± 0.2	14.7 ± 1.1	12.7 ± 0.8		**5.9**	**17**
Ba	467 ± 30	680 ± 43	321 ± 22	209 ± 14	344 ± 29	**636**		
Br	12.3 ± 0.2	12.5 ± 0.1	10.0 ± 01	17.1 ± 0.2	23.5 ± 0.3			
Ca(%)	1.34 ± 0.04	1.51 ± 0.03	1.61 ± 0.04	2.45 ± 0.06	1.73 ± 0.03			
Ce	134.2 ± 4.1	85.9 ± 2.7	96.9 ± 2.7	98.5 ± 2.8	100.8 ± 2.3	**73.0**		
Co	9.5 ± 0.2	11.4 ± 0.2	8.5 ± 0.1	9.1 ± 0.2	9.4 ± 0.2	**26.0**		
Cr	49.0 ± 2.4	78.2 ± 3.8	75.0 ± 3.1	80.3 ± 3.4	80.3 ± 3.9	**125.0**	**37.3**	**90.0**
Cs	6.2 ± 0.2	8.3 ± 0.3	10.1 ± 0.4	6.7 ± 0.3	6.7 ± 0.3	**5.2**		
Eu	2.16 ± 0.08	1.28 ± 0.04	1.26 ± 0.04	1.25 ± 0.04	1.41 ± 0.04	**1.20**		
Fe(%)	4.82 ± 0.03	4.56 ± 0.03	3.51 ± 0.11	6.13 ± 0.20	6.04 ± 0.20			
Hf	2.44 ± 0.04	13.9 ± 0.3	10.4 ± 0.2	7.4 ± 0.1	6.7 ± 0.1	**6.3**		
K(%)	0.38 ± 0.05	1.10 ± 0.09	1.44 ± 0.09	1.08 ± 0.09	0.53 ± 0.07			
La	62.7 ± 0.4	40.9 ± 0.2	43.7 ± 0.3	48.6 ± 0.3	44.5 ± 0.3	**32.0**		
Lu	0.30 ± 0.02	0.83 ± 0.03	0.57 ± 0.02	0.23 ± 0.01	0.42 ± 0.02	**0.5**		
Na(%)	0.072 ± 0.001	0.103 ± 0.001	0.090 ± 0.001	0.105 ± 0.001	0.067 ± 0.001			
Nd	49 ± 4	17 ± 2	36 ± 5	41 ± 5	43 ± 3	**33**		
Rb	139 ± 8	92 ± 4	93 ± 4	42 ± 2	68 ± 4	**125**		
Sb	1.34 ± 0.06	0.80 ± 0.04	1.22 ± 0.08	1.58 ± 0.07	1.46 ± 0.11			
Sc	15.1 ± 0.2	17.2 ± 0.2	14.5 ± 0.2	17.1 ± 0.2	15.7 ± 0.2	**15.0**		
Sm	9.6 ± 0.1	7.3 ± 0.1	7.4 ± 0.1	6.8 ± 0.1	7.2 ± 0.1	**5.7**		
Ta	2.3 ± 0.2	2.6 ± 0.2	2.1 ± 0.2	1.8 ± 0.1	2.5 ± 0.2	**1.1**		
Tb	0.8 ± 0.1	1.0 ± 0.1	0.9 ± 0.1	0.5 ± 0.1	0.8 ± 0.1	**0.9**		
Th	17.8 ± 0.5	18.6 ± 0.5	22.0 ± 0.6	24.4 ± 0.7	21.7 ± 0.6	**12.0**		
U	8.4 ± 0.4	5.2 ± 0.2	8.5 ± 0.4	7.5 ± 0.4	7.5 ± 0.3	**2.7**		
Yb	2.0 ± 0.1	5.3 ± 0.2	3.4 ± 0.1	2.5 ± 0.1	2.6 ± 0.1	**3.1**		
Zn	129 ± 4	152 ± 5	193 ± 6	209 ± 7	169 ± 5		**123**	**315**

Point **SG02** showed enrichment of the elements Ba, Cs, Hf, Sc, Ta, Th, U and REE (La, Lu, Ce, Eu, Sm, Yb). The elements Co, Cr, Nd and Rb were depleted and Tb is of the same order of magnitude of NASC values. This point is located at the entrance of the Embu-Guaçu River, which receives treated and non-treated clandestine domestic sewage. According to CETESB, this point also shows no register of metal contamination and industries in the vicinity [20].

Point **SG03** showed enrichment for the elements Cs, Hf, Ta, Th, U and REE (La, Ce, Eu, Sm, Yb). The elements Co, Cr and Rb were depleted and Nd, Sc and Tb are of the same order of magnitude of NASC values. This point is situated near the entrance of the Palhereiros River, which crosses the entire southern region of São Paulo County and carries domestic and industrial non-treated sewage to the Guarapiranga reservoir. This point also receives backup waters from the Billings reservoir, from the Taquacetuba tributary. According to CETESB

[20] in the sediments from this point normally show Cu, Pb and Cd metals with Cu concentration in waters between 0.01 and 0.05 mg kg^{-1} (higher than those established by CONAMA resolution).[21] In this point there are some small industries nearby.

According to CETESB, points SG01, SG02 and SG03 present high concentration of P and N due to the presence of domestic sewage.

Point **SG04** (middle of the reservoir) does not present a history of metal contamination in the monitoring programs developed by CETESB, but it is possible to find Cu, Pb and Cd, as well as, N and P. This point presented enrichment for the elements Cs, Hf, Sc, Ta, Th, U and REE (Ce, La, Nd, Sm); Ba, Co, Cr, Lu, Rb, Tb and Yb were depleted and Eu of the same order of magnitude when comparing the results from Table 3 to NASC values.

At point **SG05**, the concentrations of Ce, Cs, Eu, Hf, La, Nd, Sc, Sm, Ta, Th and U exceeded NASC values. The concentration for the elements Ba, Co, Cr, Lu, Rb, Tb and Yb were lower than NASC values. This point is near the catchment point of water supply from SABESP [22] and according to CETESB [20], high Cu and lower Zn, Cd and Pb concentrations can be found in the sediments. High As and U concentrations can also be found. In the present study this was observed for these elements: 12.7 and 7.5 mg kg^{-1} for As and U, respectively. This point supplies water for 3.8 million people living in São Paulo southern region. [22]

The results obtained for the elements As, Cr and Zn for all samples in the present study (Table 3) were compared to TEL (Threshold Effect Level) and PEL (Probable Effect Level) oriented values from Canadian Council of Minister of the Environment (CCME) [19].

Points SG02, SG03, SG04 and SG05 presented As, Cr and Zn concentrations higher than TEL values but lower than PEL values. Point SG01 presented Cr and Zn concentrations higher than TEL values but lower than PEL values. None of the points analyzed presented concentration values higher than PEL values, and such no occurrence of adverse effects on the biological community should be expected according to CCME.

All the points presented U concentrations much higher than NASC values. In the past there was an industry that manipulated U in the vicinity of the Guarapiranga reservoir which can explain these high U contents in all sampling points.

It is important to consider that metals in sediments are correlated to their textural composition and organic matter content. Thus, any given metal can be stabilized in a clay sediment and high OM content and less stable in sandy sediment. According to Gaudette [23] the fine fraction and organic matter content show higher affinity for metals in general. In this study, points SG4 and SG05 showed the highest clay + silt, 98.9 and 98.4%, and high OM content (59 and 58 g dm^{-3}), respectively. In general, these two points presented higher concentration values for most elements analyzed (As, Br, Ca, Ce, Cr, Fe, Sb, Sc, Ta, Th and Zn). Point 1 showed the highest OM content (109 g dm^{-3}) and clay percentage (65.4%). Point SG01 showed higher concentration values for Ba, Rb, U and light rare earth elements (Ce, La, Eu, Nd and Sm).

The samples of this study were collected in April 2009, autumn season. Therefore, a new sampling in other seasons is intended, in order to assess the influences of different weather conditions upon the aquatic system, at the same sampling points, and to obtain additional data so as to make possible an efficient environmental monitoring of the Guarapiranga reservoir.

4. CONCLUSIONS

The determination of metals and trace elements by way of Instrumental Neutron Activation Analysis (INAA) appears to be appropriate for sediment monitoring as its sensitivity, precision and accuracy are very reliable.

Points SG02, SG03, SG04 and SG05 presented As, Cr and Zn concentrations higher than TEL values but lower than PEL values. Point SG01 presented Cr and Zn concentrations higher than TEL values. None of the points analyzed presented concentrations values higher than PEL values, and thus no occurrence of adverse effects on the biological community should be expected according to CCME. It should again be noted that point SG05, located near the SABESP water supply catchment point, did not exceeded the PEL values for these elements.

All points presented U concentrations much higher than NASC values. In the past there was an industry that manipulated U nearby the Guarapiranga reservoir which can explain these high U concentrations in all sampling points.

In general, sampling points SG04 and SG05 (near SABESP water supply catchment point) presented higher concentration values for most elements analyzed (As, Br, Ca, Ce, Cr, Fe, Sb, Sc, Ta, Th and Zn). These points present the highest clay and silt composition, 98.9 and 98.4%, and high OM content (59 and 68 g cm^{-3}), respectively.

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