MAJOR AND TRACE ELEMENTS ASSESSMENT IN SEDIMENT SAMPLES FROM RIO GRANDE RESERVOIR, BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

The Rio Grande Reservoir, Southeast of the São Paulo Metropolitan Area (SPMA) supplies water for four counties (São Bernardo do Campo, São Caetano do Sul, Santo André and Diadema). It has been seriously affected by urban expansion, due to chaotic urban occupation and improper use of the surrounding areas. In this study bottom sediment samples were collected, by using a Van Veen sampler, during the dry and rainy seasons. Four sampling points were defined by using GPS and are located at the mouth of the Rio Grande and Ribeirão Pires Rivers, in the middle of the reservoir and near the catchment point of the water supply. The sediment samples were submitted to instrumental neutron activation analysis (INAA) and the following elements were determined: As, Ba, Br, Co, Cr, Cs, Rb, Sb, Sc, Se, Ta, Th, U e Zn and the rare earth elements Ce, Eu, La, Lu, Nd, Sm, Tb, Yb. Short irradiation was also performed for total Hg determination by NAA using ^{197}Hg radioisotope. This was possible due to the high Hg concentration levels in these sediments. The methodology validation was carried out by certified reference material analyses. The results obtained for multielemental concentrations in the sediment samples were compared to NASC (North American Shale Composite) values. The concentration values obtained for As and metals Cr, Hg 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

The Rio Grande Reservoir is located in the Metropolitan region of Sao Paulo and includes Santo André, São Bernardo do Campo, Ribeirão Pires and Rio Grande da Serra counties. As such, this reservoir plays a very important social function supplying both water and leisure for approximately 1.8 million people.[1,2] Fish consumption from the reservoir is also a common habit, mainly in those communities situated in the vicinity of the margins of this reservoir in the Rio Grande da Serra and Ribeirao Pires counties. These two counties also account for a

large amount of untreated sewage and industrial wastes thrown directly into the reservoir. As a result, Hg in sediments in concentrations of the order of 10 mg kg^{-1} or more can be found.

In 1982, the Rio Grande Reservoir was separated from the already highly polluted Billings Reservoir in an attempt to preserve its water quality. This separation eliminated the entrance of polluted waters from São Paulo city. However, domestic and industrial sewage from the Rio Grande da Serra and Ribeirao Pires counties continued to be thrown directly into the reservoir [1,2].

Sediments are environmental compartments with high potential of accumulation of natural and antropogenic materials. Due to this characteristic, sediments act as an excellent register, for seasonal and spatial environmental information. This characteristic differentiates it from a simple quality water evaluation [3].

Many studies have been published reporting high Hg concentrations in sediments of this reservoir, mainly in the eastern region, close to the Rio Grande da Serra and Ribeirão Pires counties [4-10], with levels many times higher than the "Canadian Council of Ministers of the Environment" oriented values (TEL – 0.17 mg kg-1 and PEL- 0.486 mg kg-1) [11].

Instrumental Neutron activation Analysis (INAA) has been extensively employed in geochemical studies due to the possibility of quantifying in only one instrumental analysis many elements at the same time with excellent precision and accuracy, without the need for previous digestion processes. The detection limits vary from 0.01 to 1 mg kg^{-1} for most elements. [4,5, 12-14]

The purpose of this study was to determine total Hg and major and trace elements (As, Ba, Br, Co, Cr, Cs, Rb, Sb, Sc, Se, Ta, Th, U e Zn and the rare earth elements Ce, Eu, La, Lu, Nd, Sm, Tb, Yb, Zn) by INAA and to compare these results with results obtained in previous studies done in this reservoir by Fávaro et al [4] for samples collected in 1998 and Bostelmann in winter 2004 [5].

2. MATERIALS AND METHODS

2.1 Sampling points and sample preparation

Four points were chosen, being two in the proximities of Rio Grande da Serra and Ribeirão Pires counties, one in the middle of the reservoir and the fourth near the catchment point of the water supply, sampled only in the second campaign. (Figure 1)

The bottom sediment samples were collected during the dry season (September 12th, 2008) and rainy season (February 4th, 2009), by using a piston corer and a Van Veen sampler. Four sampling points were defined by using GPS and are located at the mouth of the Rio Grande Rivers (discharge of contaminants – points 1 and 2), described as point 1 – near highway SP122 and point 2 near the Indio Tibiriçá highway (SP031), in the middle of the reservoir (point 3) and near the catchment point of the water supply (point 4). The samples were

previously air dried at 20-25oC in a clean recipient, ground in a mortar, passed through a 0.250 mm sieve and then homogenized before analysis.
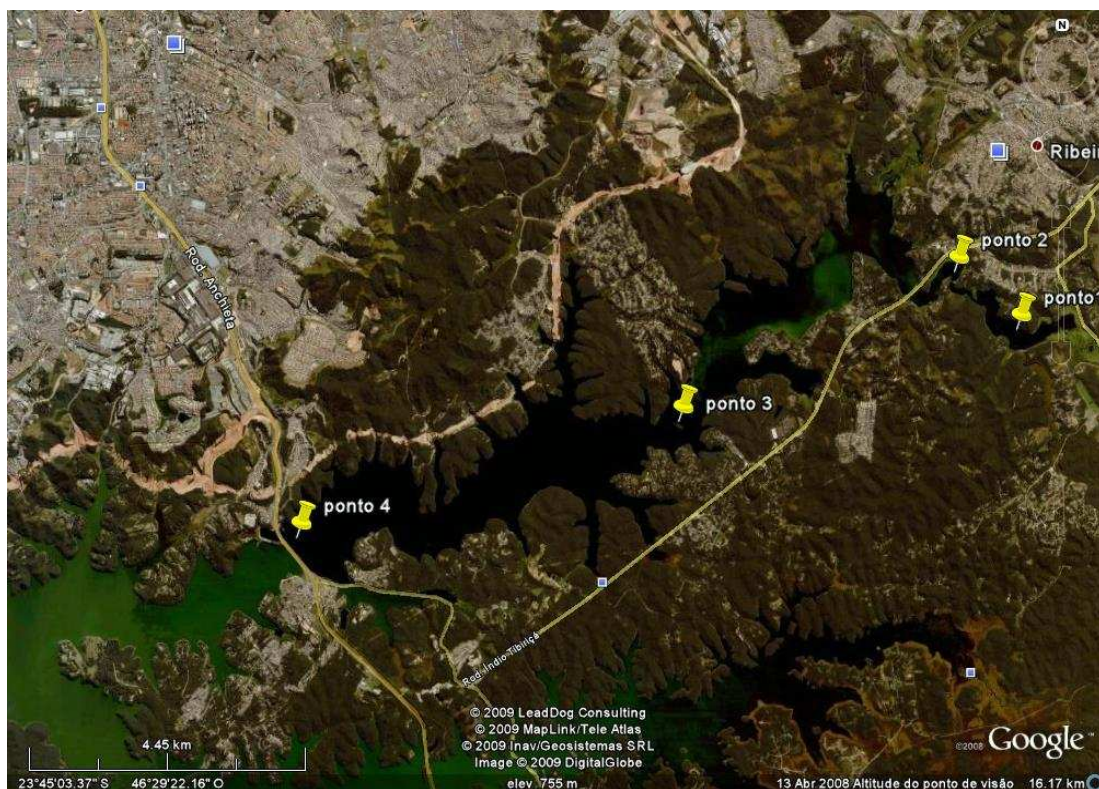

Figure 1 – Rio Grande Reservoir sampling points (1, 2, 3 and 4).

2.2 Instrumental Neutron Activation Analysis

2.2.1 Multielemental determinations

For the multielemental analysis, approximately 150 mg of sediment and 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 8 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 determined by using this methodology were As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U, Zn and the rare earths Ce, Eu, La, Lu, Nd, Sm, Tb and Yb. The analysis of the data was made by using in-house gamma ray software, VISPECT 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 WQB-3 (Lake Ontario Blended Sediment

for Trace Elements, Environmental Canada) and IAEA-405 (Trace and major elements in estuarine sediments, IAEA).

2.2.2 Total mercury determination

Approximately 100 mg of sediment samples and reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Total Hg standard was prepared pipetting 100 µl of thioacetamide solution 10 mg ml^{-1} [15] onto small sheets of Whatman No.41 filter paper and after half an hour 50µl of 90.0 mg mL^{-1} Hg standard solution was also pipetted. In this condition Hg standard was retained and stabilized in the filter paper. Sediment samples, reference materials and Hg synthetic standard were irradiated for one hour, under a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} in the IEA-R1 nuclear reactor at IPEN. Forty eight hours after irradiation the samples and standards were measured for total Hg determination. The ^{197}Hg radioisotope was used for total Hg quantification and gamma spectrometry was done as described in the item2.2.1.The methodology validation was carried out by BCR 580 (Trace elements in estuarine sediment, IRMM) reference material analysis.

3. RESULTS AND DISCUSSION

The validation of INAA analytical methodology was carried out by reference materials analysis and the results are shown at Table 1 for IAEA 405 and Table 2, for WQB-3 reference materials. Table 1 also shows the radioisotopes and gamma energy photo peak used in the present study.

Z value calculation was according to Bode [16]. If $|Z| < 3$ the individual result of the control sample (reference material) lies on the 99% confidence interval of the target value. For WQB-3 (Table 1) all the results were in the interval range except for Ce, K and Sb elements. All the results obtained for the IAEA 405 reference material were in this interval range ($|Z| < 3$), indicating good precision and accuracy of the INAA technique (Table 2). For total Hg determination in the BCR 580 reference material the results are presented at Table 3. Z values (0.36 and -0.03) were quite good, proving again the precision and accuracy of the analytical technique for this element determination.

Table 4 shows the results obtained for the bottom sediment samples analyses by INAA in the dry (winter/ September 2008) and rainy seasons (summer/ February 2009). Except for point 4 the sampling was done only in summer. No significant variation concentration for most elements analysed in the summer and winter campaigns were observed. For the elements As, Ba, Ce, Co, Cr, Cs, Eu, Rb, Sc, Th concentration variation not higher than 20% for the 2 seasons in all sampling points was observed. This behavior can be reflecting the permanency of these elements in the sediments during this period (September 2008 to February 2009), indicating that they do not suffer significant alterations with seasonal variations of the reservoir.

For Br and Zn, a considerable variation concentration between the two campaigns at point 1, in the entrance of the reservoir was observed. While the results in the dry season were 8.6 and 185 mg kg^{-1} for Br and Zn respectively, in the rainy season the results were 24.1 and 604 mg kg-1. In the other two sampling points the variation concentration was lower than 20%. For Hf and Lu elements there were variation concentrations between summer and winter at points 1

and 3. For the elements La and Sm, the results obtained were quite similar for the sampling points at the entrance of the reservoir (point 1 and 2). There was a higher concentration variation between the 2 campaigns at point 3. K was detected only in the rainy season campaign.

In general, for the other elements analyzed there was no considerable variation concentration in summer and winter in all sampling points.

When the results obtained were compared to Continental crust values [17], the elements As, Br, Ce, Cs, Hf, Lu, Nd, Sb, Sc, Ta, Tb, Th, U and Yb presented enrichment. For La, Sm and Zn enrichment was observed only at points 1 and 2. The elements Co, Cr, Eu and K, presented concentrations lower than Continental crust values.

In general, the concentrations values for most elements analyzed were higher at points 1 and 2, near the entrance of the reservoir where the domestic and industrial sewage from the Rio Grande da Serra and Ribeirao Pires counties are thrown.

Table 4 also shows the TEL (Threshold Effect Level) and PEL (Probable Effect Level) oriented values from Canadian Council of Minister of the Environment (CCME) [11]. 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.

The results for As and Cr presented concentration values higher than TEL (5.9 mg kg^{-1}, 37.3 mg kg^{-1}) and PEL oriented values (17 mg kg^{-1}, 90 mg kg^{-1}), in all sampling points in summer and winter.

Table 1 – Results (mg kg^{-1}) for the WQB-3 reference material analysis by INAA

	WQB-3		
Energy(keV)	**Found values**	**Certified values**	**Z SCORE**
^{76}As (559)	21.4 ± 1.5	18.8 ± 1.5	1.64
^{42}K (1524.58)	1.48 ± 0.07	2.03 ± 0.07	-4.49
^{140}La (328)	31.4 ± 1.5	27.5 ± 1.5	2.50
^{140}La (1596.2)	31.4 ± 1.5	27.5 ± 1.5	2.22
^{239}U (228.18)	2.4 ± 0.1	2.51 ± 0.10	-0.37
^{131}Ba (496)	458 ± 76	416 ± 66	0.42
^{141}Ce (145)	72.4 ± 1.1	60.2 ± 1.1	3.08
^{60}Co (1173)	14.8 ± 1.7	15.3 ± 1.7	-0.24
^{60}Co (1332)	15.2 ± 1.7	15.3 ± 1.7	-0.07
^{57}Cr (320)	187 ± 3	119 ± 30	2.19
^{134}Cs (795.8)	5.5 ± 0.2	5.34 ± 0.18	0.33
^{86}Rb (1076)	99.5 ± 4.5	91.4 ± 4.5	0.65
^{46}Sc (889)	31.2 ± 2.2	46.5 ± 22.0	-1.60
^{65}Zn (1115.6)	1486 ± 107	1396 ± 107	0.49
^{124}Sb (1690)	1.8 ± 0.3	3.04 ± 0.27	-3.25

Table 2 – Results (mg kg^{-1}) for the IAEA 405 reference material analysis by INAA

		IAEA 405		
Energy(keV)	Found values	Certified values	95% confidence interval	Z SCORE
^{76}As (559)	22.48	23.6	22.9 – 24.3	-1.44
^{82}Br (554)	73.1	85	60 – 110	-0.47
^{82}Br (776)	79.5	85	60 – 110	-0.22
^{42}K (1524.58)	2.27	2.49	1.77 – 3.21	-0.30
^{140}La (328)	34.16	40.4	33.1 – 47.7	-0.87
^{140}La (1596.2)	36.7	40.4	33.1 – 47.7	-0.51
^{153}Sm (103.18)	6.52	6.86	6.50 – 7.22	-0.91
^{239}U (228,18)	3.20	3.01	1.86 – 4.16	0.16
^{239}U (277.6)	2.90	3.01	1.86 – 4.16	-0.09
^{175}Yb (282)	2.90	3.04	2.19 – 3.89	-0.17
^{175}Yb (396.33)	2.78	3.04	2.19 – 3.89	-0.30
^{60}Co (1173)	13.7	13.7	13.0 – 14.4	-0.005
^{60}Co (1332)	12.9	13.7	13.0 – 14.4	-0.84
^{57}Cr (320)	89.8	84	80 – 88	1.07
^{134}Cs (795.8)	11.6	12.5	10.4 – 14.6	-0.38
^{152}Eu (121)	1.20	1.25	0.89 – 1.61	-0.14
^{152}Eu (1408)	1.41	1.25	0.89 – 1.61	0.44
^{181}Hf (133)	5.47	5.8	4.93 – 6.67	-0.38
^{181}Hf (482.2)	5.87	5.8	4.93 – 6.67	0.07
^{177}Lu (208.36)	0.50	0.468	0.283 – 0.653	0.19
^{46}Sc (889)	12.76	13.52	11.53 – 15.51	-0.38
^{233}Th (312)	13.52	14.3	12.2 – 16.4	-0.36
^{169}Yb (177.21)	2.17	3.04	2.19 – 3.89	-0.95
^{169}Yb (197.9)	2.22	3.04	2.19 – 3.89	-0,94
^{65}Zn (1115.6)	280	279	272 – 286	0.03
^{122}Sb (564)	1.54	1.81	1.62 – 2.00	-0.91
^{124}Sb(1690)	1.78	1.81	1.62 – 2.00	-0.10

Table 3 – Results (mg kg^{-1}) for total Hg in the BCR 580 reference material analysis by INAA

	BCR 580	
Found Values	Certified value	Z SCORE
134. 8 ± 4.8	132 ± 6	0.36
131.8 ± 4.4		-0.03

Regarding total Hg concentration in the sediment samples, the results far exceeded PEL value (0.486 mg kg^{-1}) in all sampling points. Total Hg was not detected at point 4 by INAA (< 1.0 mg kg^{-1}). Mainly at points 1 and 2 (entrance of the reservoir) the results were quite higher, an indicator of very high Hg pollution in this environment. There were no significant concentration differences between summer and winter campaigns in all points analyzed. These

concentrations can be very dangerous for the environment once Hg presents high potential of bioaccumulation besides the possibility of organomercurial compounds transformation (extremely Hg toxic forms).[12,18]

Regarding Zn, only the points 1 and 2 exceeded the TEL (123 mg kg^{-1}) and PEL (315 mg kg^{-1}) oriented values, in summer and winter.

Table 5 shows the results obtained in previous studies at the Rio Grande reservoir by Favaro [4] and Bostelmann [5] for the sampling points located near the catchment point of water supply (point 4).

Favaro et al [4] collected four sediment cores at the Rio Grande reservoir, in the same sampling points of this study. The samples were also analyzed by INAA in the same conditions of the present study and fraction <0.063 mm was analysed. The sampling collection was carried out in 1998.

For the elements Ba, Ce, Co, Sc, Th and Yb the concentration values were quite similar in all 3 studies and are within the analytical interval obtained by Favaro in the sediment core sample even though this collection was done 10 years ago. This probably shows that concentration of these elements are not increasing or not becoming available in the water column.

The elements Cs, Eu, La, Lu, Nd and Ta presented results similar to Bostelmann [5] in campaign of winter 2004, indicating a certain stability of these elements. For these elements the values obtained by Favaro collected 10 years ago were higher. This can be indicative that these elements are apparently inert in the lower sediment layers, which in turn lessens their availability.

Potassium and Zinc presented similar values obtained by Favaro but lower than Bostelmann [5]. However, these 2 elements normally present a wide concentration variation during different seasons of the year probably due to the soil run off.

Table 6 shows the results obtained in the present study and previous results in the point 3 (middle of the reservoir).

For the elements Ce, Cr, Sc, Ta and Th the results were quite similar in the three studies and are within the interval obtained for Favaro et al [4] in the core sample collected at this point. Again this behavior may be reflecting the permanency of these elements in the sediments along this period.

For the elements Ba, Co, Cs, La, Lu, Rb, Hf, Sm, U and Yb the concentrations were quite similar from those obtained by Bostelmann [5], indicating a recent stabilization once there were lower than those obtained by Favaro et al [4] 10 years ago. This fact can be indicative that these elements are inert in lower sediment layers, which makes their availability more difficult.

Eu, Nd, Tb and Zn presented results lower than the previous studies, especially for Nd.

For the other elements analyzed, the results obtained in the present study were quite similar than those in the past studies.

Table 4 – Sediment samples results (mg kg⁻¹) by INAA in the dry (September 08/winter) and rainy (February 2009/summer) seasons, in the samplings points (1,2 , 3, 4)

	Point 4	Point 3		Point 2		Point 1		TEL	PEL	Continental crust
	summer	winter	summer	winter	summer	winter	summer			
As	35.6 ± 1,0	18.1 ± 1,3	19.4 ± 0,6	12.2 ± 0,9	14.0 ± 0,4	10.1 ± 0,7	12.8 ± 0.4	**5.9**	**17.0**	**1.7**
Ba	503 ± 67	483 ± 45	510 ± 68	364 ± 57	425 ± 60	764 ± 69	746 ± 68			**584**
Br	19,6 ± 0,4	22,6 ± 0,9	19,2 ± 0,3	22,7 ± 0,9	17,1 ± 0,3	8,6 ± 0,4	24,1 ± 0,5			**1.0**
Ce	82,5 ± 2,5	80,9 ± 1,9	85,7 ± 2,8	87,2 ± 2,0	89,6 ± 2,7	81,4 ± 1,9	87,5 ± 2,6			**60**
Co	9,5 ± 0,4	10,5 ± 0,5	9,3 ± 0,4	14,3 ± 0,8	12,1 ± 0,5	12,0 ± 0,5	13,6 ± 0,5			**24**
Cr	101,7 ± 2,7	85,6 ± 3,3	90,0 ± 2,6	88,6 + 3,5	96,8 ± 4,2	95,9 ± 3,1	109,5 ± 2,7	**37.3**	**90**	**126**
Cs	6,0 ± 0,4	5,9 ± 0,3	6,2 ± 0,3	6,0 ± 0,4	5,1 ± 0,4	7,0 ± 0,4	6,7 ± 0,3			**3.4**
Eu	0,73 ± 0,05	0,72 ± 0,04	0,75 ± 0,05	1,09 ± 0,06	0,97 ± 0,06	1,02 ± 0,04	1,11 ± 0,05			**1.3**
Hf	5,1 ± 0,2	4,1 ± 0,1	8,0 ± 0,3	6,5 ± 0,2	7,0 ± 0,5	16,8 ± 0,3	8,3 ± 0,4			**4.9**
Hg	< 1.0	3.6 ± 0.5	6.0 ± 0.8	52.5 ± 2.0	47.7 ± 1.9	68.6 ± 2.4	59.5 ± 2.2	**0.17**	**0.486**	
K	1,49 ± 0,09	nd	1,15 ± 0,09	nd	1,11 ± 0,08	nd	1,41 ± 0,09			**2.1**
La	27,8 ± 0,6	26,7 ± 0,9	35,1 ± 0,7	35,0 ± 1,0	41,0 ± 0,8	44,2 ± 1,3	45,1 ± 0,8			**30**
Lu	0,36	0,29 ± 0,03	0,53 ± 0,06	0,40 ± 0,03	0,48 ± 0,06	0,71 ± 0,03	0,59 ± 0,06			**0.35**
Nd	20 ± 4	22 ± 3	27 ± 5	31 ± 4	38 ± 6	32 ± 4	43 ± 7			**27**
Rb	75 ± 6	71 ± 7	62 ± 6	64 ± 5	67 ± 6	78 ± 6	62 ± 5			**78**
Sb	1,9 ± 0,2	0,8 ± 0,1	1,0 ± 0,2	0,5 ± 0,1	0,8 ± 0,1	0,5 ± 0,1	1,0 ± 0,1			**0.3**
Sc	20,5 ± 0,5	18,0 ± 0,4	18,0 ± 0,4	20,1 ± 0,5	17,3 ± 0,4	17,4 ± 0,4	18,3 ± 0,6			**16**
Sm	3,3 ± 0,1	4,4 ± 0,1	5,6 ± 0,1	5,2 ± 0,1	6,1 ± 0,1	6,5 ± 0,1	6,6 ± 0,1			**5.3**
Ta	1,8 ± 0,2	2,5 ± 0,4	1,8 ± 0,2	1,7 ± 0,2	1,5 ± 0,2	2,0 ± 0,4	1,9 ± 0,2			**1.1**
Tb	nd	nd	0,4 ± 0,2	0,5 ± 0,2	0,4 ± 0,2	1,0 ± 0,1	1,3 ± 0,2			**0.6**
Th	20,9 ± 0,7	26,0 ± 0,8	20,9 ± 0,6	21,6 ± 0,5	19,2 ± 0,5	18,7 ± 0,6	18,2 ± 0,5			**8.5**
U	4,0 ± 0,4	4,7 ± 0,6	4,1 ± 0,4	4,1 ± 0,4	3,4 ± 0,4	5,3 ± 0,3	4,3 ± 0,3			**1.7**
Yb	3,3 ± 0,2	2,1 ± 0,1	2,9 ± 0,2	2,5 ± 0,1	3,1 ± 0,2	4,2 ± 0,2	3,2 ± 0,3			**2.0**
Zn	118 ± 6	107 ± 7	116 ± 6	356 ± 20	350 ± 15	224 ± 11	604 ± 26	**123**	**315**	**203**

Table 5 – Comparison of the results obtained in this study (mg kg^{-1}) with previous studies in the point 4

	Point 4 (this study)	Point 4 Favaro et al[4]	Point 4 Bostelmann [5]
	fev/09		
As	35.6 ± 1.0	8.3 (6.6 – 14)	90.7
Ba	503 ± 67	636 (493 – 82)	591
Br	19.6 ± 0.4	6.9 (4.3 – 12.4)	4.2
Ce	82.5 ± 2.5	96 (72 – 136)	96
Co	9.5 ± 0.4	8.7 (6.1 – 12.1)	8.2
Cr	101.7 ± 2.7	77 (64 – 93)	77
Cs	6.0 ± 0.4	19.2 (13.8 – 25.6)	4.8
Eu	0.73 ± 0.05	1.46 (1.10 – 2.12)	0.7
Hf	5.1 ± 0.2	15.1 (8.4 – 20.9)	7.8
K	1.49 ± 0.09	1.63 (0.96 – 2.39)	2.72
La	27.8 ± 0.6	52.6 (41.1 – 69.6)	31
Lu	0.36	0.9 (0.55 – 1.21)	0.5
Nd	20 ± 4	46 (35 – 56)	25
Rb	75 ± 6	100 (78 – 124)	113
Sb	1.9 ± 0.2	0.70 (0.53 – 0.89)	nd
Sc	20.5 ± 0.5	18.7 (16.6 – 20.1)	22
Sm	3.3 ± 0.1	10.7 (5.5 – 28.6)	4.9
Ta	1.8 ± 0.2	3.1 (2.4 – 3.8)	1.8
Th	20.9 ± 0.7	18.2 (13.8 – 21.4)	21.8
U	4.0 ± 0.4	7.7 (6.3 – 9.3)	2.1
Yb	3.3 ± 0.2	5.3 (3.3 – 7.0)	2.8
Zn	118 ± 6	92 (70 – 119)	224

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. Further, it is also important to note that sample preparation can be a factor which may influence the results. For example Favaro et al [4] and Bostelmann [5] used the fine sediment fraction (<0.063 mm) in their studies, whereas this study used the sediment fraction <0.250 mm, which according Gaudette [19] is the fraction that has higher affinity for organic matter and therefore the metals in general.

Table 6 – Comparison of the results obtained in this study (mg kg^{-1}) with previous studies in point 3 (middle of the reservoir)

	Point 3 (this study)		Point 3 Favaro et al [4]	Point 3 Bostelmann [5]
	Set/08	**Fev/09**		
As	18.1	19.4	7.8 (6.2 – 9.7)	20.8
Ba	483	510	930 (790 – 1125)	475
Br	22.6	19.2	3.6 (1.3 – 3.2)	16.4
Ce	80.9	85.7	115 (76 – 135)	88
Co	10.5	9.3	18.4 (12.0 – 23.3)	10
Cr	85.6	90	97 (84 – 104)	86
Cs	5.9	6.2	18.7 (16.5 – 19.7)	6.0
Eu	0.72	0.75	1.78 (1.26 – 2.04)	1.0
Hf	4.1	8.0	12.6 (10.5 – 14.1)	7.0
K	nd	1.15	---	1.19
La	26.7	35.1	50.3 (42.9 – 57.0)	32
Lu	0.29	0.53	0.94 (0.70 – 1.50)	0.5
Nd	22	27	56 (40 – 64)	37
Rb	71	62	108 (100 – 128)	73
Sb	nd	0.89	0.70 (0.69 – 0.75)	1.9
Sc	18	18	21.9 (20.1 – 22.8)	20
Sm	4.4	5.6	9.3 (6.6 – 10.6)	5.0
Ta	2.5	1.8	3.2 (2.4 – 4.7)	2,6
Tb	nd	0.4	1.2 (1.1 – 1.4)	0.8
Th	26	20.9	22.0 (19.1 – 23.4)	23.5
U	4.7	4.1	9.3 (7.2 – 9.8)	4.6
Yb	1.7	2.9	4.8 (4.0 – 5.3)	2.6
Zn	107	116	149 (131- 173)	146

4. CONCLUSIONS

Instrumental Neutron Activation Analysis used to determine metals and trace elements presented appropriate sensitivity for sediment monitoring, showing good precision and accuracy.

When the concentration values for As and metals Cr, Hg and Zn in the sediment samples were compared to TEL values from Canadian legislation and adopted by CETESB, it was possible to conclude that samples from points 1 and 2 (entrance of the reservoir) presented the highest values exceeding the TEL and PEL values for As, Cr, Hg and Zn. Points 3 and 4 exceeded the TEL and PEL only for As and Cr.

When the results obtained were compared to Continental crust values [18], the elements As, Br, Ce, Cs, Hf, Lu, Nd, Sb, Sc, Ta, Tb, Th, U and Yb presented enrichment. For La, Sm and Zn

enrichment was observed only at points 1 and 2. The elements Co, Cr, Eu and K, presented concentrations lower than Continental crust values.

In general, the concentrations values for most elements analyzed were much higher at points 1 and 2, near the entrance of the reservoir where domestic and industrial sewage from the Rio Grande da Serra and Ribeirao Pires counties are thrown. On the other hand, the lowest concentration values were obtained for sediments from point 4, near the catchment point of water supply.

Most of the elements analysed in this study showed lower concentrations than those of Favaro in 1998 [4] yet similar to those Bostelmann[5] 5 years ago. This can be considered that these elements becoming more inert in the sediment especially those that presented high concentration values in relation to Continental crust.

From the results obtained in the present study, mainly regarding Hg, we could verify that Hg presented concentration values 100 times higher than the PEL oriented value from CCME. This Hg can suffer methylation under appropriate conditions, biomagnifying and incur serious consequences for the biota and population of this region. Due to this it is important to conduct further monitoring studies in this reservoir.

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