

Assessment of metals and trace elements in sediments from Rio Grande Reservoir, Brazil, by neutron activation analysis

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Abstract The Rio Grande Reservoir, Southeast of the São Paulo Metropolitan Area, supplies water for four counties (about 1.6 million people). 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 during the dry season and rainy season. Four sampling points were defined and located at the mouth of the Rio Grande and Ribeirão Pires Rivers (points 1 and 2), in the middle of the reservoir (point 3) and near the catchment point of the water supply (point 4). Samples were submitted to instrumental neutron activation analysis and some metals, trace and rare earth elements were determined. The methodology validation according to precision and accuracy was carried out by reference material analyses. The results obtained were compared to earth crust values and also with results already published in the literature. The enrichment factor in relation to earth crust values using Sc as reference element was calculated and a strong enrichment was found for the elements As, Br, Sb, Th, U and Zn. A strong anthropogenic influence was observed for some elements, mainly in the points located in the entrance of the reservoir that receives domestic and industrial effluents from the rivers that reach the reservoir.

Keywords Metals · Trace elements · Sediments · INAA · Rio Grande reservoir

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 socio-economic role supplying both water and leisure for approximately 1.8 million people [1, 2]. Fish consumption from the reservoir is also a common practice, mainly in those communities situated in the vicinity of the margins of this reservoir in the Rio Grande da Serra and Ribeirão Pires counties. These two counties also account for a large amount of untreated sewage and industrial wastes thrown directly into the reservoir.

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 Ribeirão Pires counties continued to be thrown directly into the reservoir [1, 2].

Sediments are environmental compartments with high accumulation potential of natural and anthropogenic 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].

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

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precision and accuracy and without the need for previous digestion processes. The detection limits varied from 0.01 to 1 mg kg⁻¹ for most elements [4–9].

In the present study, bottom sediment samples were collected during the dry season (September 2008 and July 2009) and rainy season (February 2009 and January 2010) in four sampling points at the Rio Grande reservoir and INAA was applied for multi-elemental characterization. These results were compared to earth crust values and also with results already published in the literature. The enrichment factor in relation to earth crust values using Sc as the reference element was calculated to assess the levels of sediment contamination by metals and other trace elements.

Materials and methods

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 (Fig. 1). The bottom sediment samples were collected by using a Van Veen sampler. The sampling points were defined by using GPS and are located at the mouth of the Rio Grande River (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 20–25 °C in a clean recipient, passed through a 2.00 mm sieve, ground in a mortar and then homogenized before analysis.

Instrumental neutron activation analysis

For the multi-elemental analysis, approximately 150 mg of sediment (duplicate samples) and reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Single and multi-element synthetic standards were prepared using pipettes with convenient aliquots of standard solutions (SPEX CERTI-PREP) onto small sheets of Whatman No. 41 filter paper. Sediment samples, reference materials and synthetic standards were irradiated for 8 h under a thermal neutron flux of 1012 n cm⁻² s⁻¹ in the IEA-R1 nuclear research reactor at IPEN. Two series of counting were made: the first, after 1 week decay and the second, after 15–20 days. Gamma spectrometry was performed using a Canberra HPGe detector and associated electronics, with a resolution of 0.88 and 1.90 keV for ⁵⁷Co and ⁶⁰Co 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 performed by using in-house

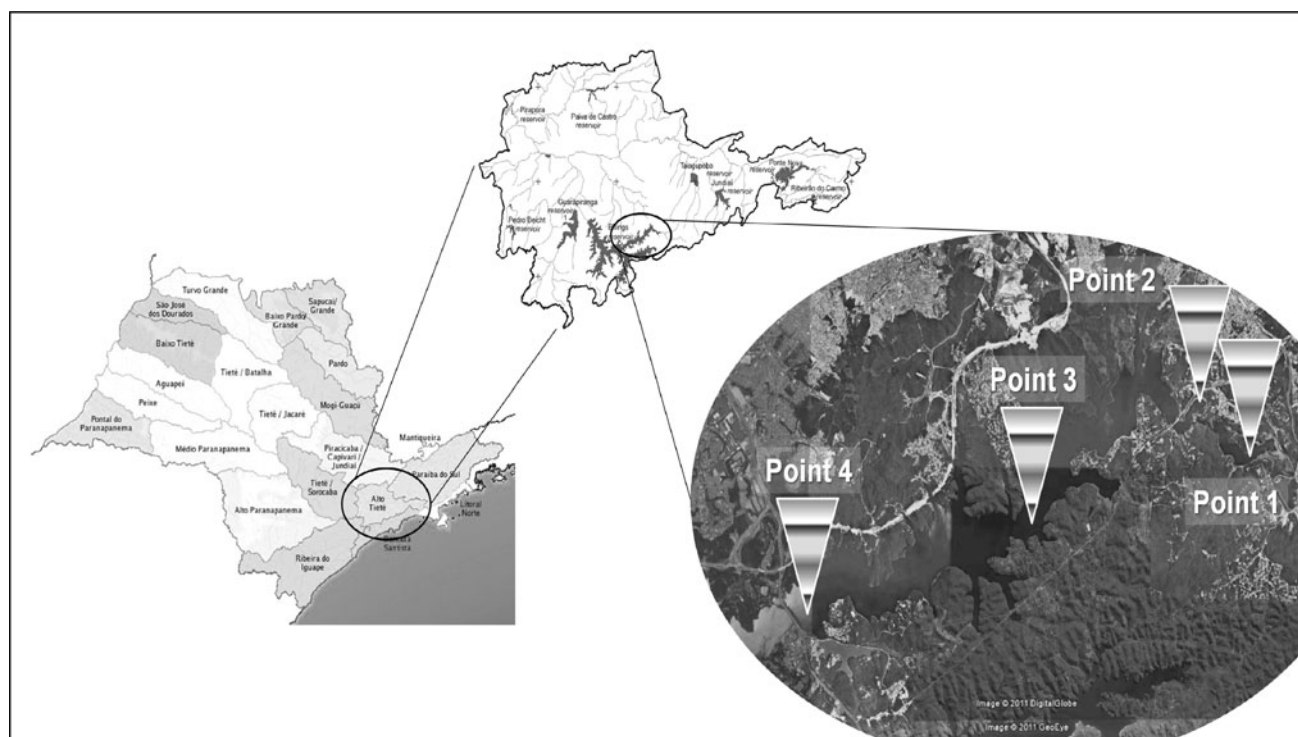


Fig. 1 Location of the Rio Grande Reservoir and sampling points (1, 2, 3, and 4)

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 validation of methodology according to precision and accuracy was verified by measuring the reference materials Buffalo River Sediment (NIST SRM 8704), Soil 7 (IAEA) and BEN (Basalt–IWG-GIT). Details of the analytical methodology are described at Larizzatti et al. [9].

Granulometric analysis and total organic carbon

The sediment granulometric analysis was carried out according to CETESB norm L6.160 [10], based on the Wentworth sieving and sedimentation principles. By this method the sand fraction is constituted of particles ranging from 2.0 to 0.063 mm (coarse sand from 1.0 to 2.0 mm); silt diameters from 0.063 to 0.0004 mm and clay, diameters <0.0004 mm.

For TOC determination the Gaudeth method was employed [11] where the sediment sample is dried at room temperature, ground and passed through a 35 mesh sieve and then treated with $K_2Cr_2O_7$ in highly acid media in order to oxidize all organic matter. The TOC is determined by titration return of $K_2Cr_2O_7$ that did not react.

Results and discussion

Table 1 shows the granulometric analysis, TOC, humidity and depth for the sediments from the reservoir.

The results for granulometric analysis indicated that practically all sampling points presented high content of fine grain, characterizing a clay texture environment, where due to the great surface area, presenting high adsorption capacity of organic matter and metals [3, 12]. These analyses concluded that the sediments are predominantly clayish, with the exception of point 1 in September 2008 and point 2, July 2009 that presented a texture with higher proportions of sand. This is probably due to sediment revolving since the location of the sampling points 1 and 2 are relatively shallow and the reservoir subject to strong winds. This reservoir is located at the top of Serra do Mar, suffering high incidence of winds. However, the correlation between high clay percentages with the humidity results presented correlation scores greater than 0.87 in all sampling points. This could indicate that these points are excellent locations for sedimentary deposition which consequently accumulate organic matter and also metals due to sedimentation deposition of anthropogenic origin.

The results obtained by INAA for Buffalo River Sediment, Soil 7 and BEN-Basalt reference materials analyses were analyzed for precision and accuracy by using the

Table 1 Granulometric analysis, TOC, humidity and depth for the sediment samples from the Rio Grande Reservoir

		Sand (%)	Silt (%)	Clay (%)	TOC (%)	Humidity (%)	Depth (m)
Point 1	Sept/08	34.3	40.5	25.2	2.8	52	1.8
	Feb/09	1.0	44.3	54.7	4.6	78	3.5
	July/09	3.2	51.2	44.9	5.6	82	3.7
	Jan/10	7.8	55.8	36.4	5.1	77	4.4
Point 2	Sept/08	25.4	26.5	48.1	4.4	70	3.5
	Feb/09	14.6	33.6	51.8	4.3	78	3.7
	July/09	59.5	22.2	18.3	2.2	63	4.1
	Jan/10	8.9	43.9	47.2	4.7	81	4.6
Point 3	Sept/08	0.5	30.7	68.8	3.9	81	6.8
	Feb/09	9.2	33.7	57.1	4.3	77	8.2
	July/09	1.4	33.7	64.9	5.9	82	8.8
	Jan/10	0.9	33.4	65.7	3.9	80	8.2
Point 4	Feb/09	0.8	48.7	50.5	4.5	85	11.2
	July/09	2.7	60.9	36.4	3.5	79	11.6
	Jan/10	1.2	52.7	46.0	3.9	80	12.0

Z scores according to [13], namely if $|Z| < 3$, the individual result of the control sample (reference material) lies within the 99% confidence interval of the target value. In this study, all Z-score values for the three reference materials analyzed were in this interval range ($|Z| < 3$) indicating good precision and accuracy of the INAA technique.

Table 2 presents the results obtained for the sediment samples by INAA in the dry (winter: September 2008; July 2009) and rainy seasons (summer: February 2009; January 2010) in four sampling points at the Rio Grande Reservoir. In general, no significant variation in concentration levels for most elements analyzed in the summer and winter campaigns were observed in all sampling points. For most elements concentration variation not higher than 25% for the two seasons in all sampling points was observed. This behavior can be reflecting the permanency of these elements in the sediments during this period and throughout the reservoir (September 2008–January 2010 and all four points), indicating that they do not suffer significant alterations with seasonal variations of the reservoir.

For Br and Zn, a considerable variation concentration between the four campaigns at point 1, at the entrance of the reservoir was observed. While the results were 8.6 and 224 $mg\ kg^{-1}$ for Br and Zn respectively in the dry season (Sept/08), in the rainy season (Jan/10) the results were 32 and 492 $mg\ kg^{-1}$. In the other three sampling points no significant variation concentration for these elements was observed in the summer and winter seasons.

However, Zn showed a large reduction in its average concentration along the reservoir, decreasing to values from 400 to 500 $mg\ kg^{-1}$ in points 1 and 2, to about

Table 2 INAA sediment sample results (mg kg⁻¹)

	Point 1				Point 2			
	Sept/08	Feb/09	July/09	Jan/10	Sept/08	Feb/09	July/09	Jan/10
As	10.1 ± 0.7	11.6 ± 0.4	9.5 ± 0.4	7.6 ± 0.4	12.2 ± 0.8	12.6 ± 0.9	10.8 ± 0.5	10.7 ± 0.7
Ba	600 ± 48	554 ± 40	576 ± 32	433 ± 69	522 ± 59	539 ± 40	583 ± 37	570 ± 60
Br	8.6 ± 0.4	24 ± 2	31 ± 5	32 ± 3	17 ± 2	17.1 ± 0.2	9.8 ± 0.4	21 ± 2
Ce	89 ± 2	88 ± 2	113 ± 8	107 ± 7	99 ± 5	93 ± 4	113 ± 7	101 ± 6
Co	12.0 ± 0.5	13.2 ± 0.3	12.5 ± 0.3	10.5 ± 0.2	12.8 ± 0.3	12.0 ± 0.3	8.7 ± 0.2	12.8 ± 0.3
Cr	82 ± 3	100 ± 3	91 ± 2	82 ± 3	87 ± 3	91 ± 2	95 ± 3	85 ± 3
Cs	7.0 ± 0.3	5.9 ± 0.3	5.7 ± 0.4	6.2 ± 0.4	5.1 ± 0.3	4.9 ± 0.3	3.7 ± 0.3	5.1 ± 0.3
Eu	1.02 ± 0.03	1.09 ± 0.05	1.1 ± 0.1	1.2 ± 0.1	1.02 ± 0.08	0.96 ± 0.05	0.95 ± 0.09	1.04 ± 0.08
Fe (%)	4.1 ± 0.2	6.6 ± 0.2	7.82 ± 0.08	6.61 ± 0.06	8.3 ± 0.1	7.51 ± 0.06	5.55 ± 0.06	7.40 ± 0.06
Hf	16.8 ± 0.2	8.2 ± 0.2	6.4 ± 0.3	10.3 ± 0.4	6.5 ± 0.1	7.1 ± 0.2	11.4 ± 0.6	7.3 ± 0.2
La	44 ± 1	44.5 ± 0.5	51.4 ± 0.9	47 ± 2	41 ± 2	41.0 ± 0.5	51 ± 1	43 ± 2
Lu	0.71 ± 0.03	0.56 ± 0.06	0.46 ± 0.07	0.60 ± 0.08	0.51 ± 0.09	0.48 ± 0.05	0.64 ± 0.08	0.52 ± 0.07
Na	1026 ± 26	1389 ± 28	1479 ± 30	1298 ± 51	1273 ± 45	1236 ± 31	1101 ± 21	1116 ± 63
Nd	32 ± 3	35 ± 3	34 ± 3	35 ± 5	31 ± 4	34 ± 4	33 ± 3	31 ± 5
Rb	65 ± 5	64 ± 4	73 ± 6	73 ± 7	72 ± 6	60 ± 5	71 ± 7	58 ± 4
Sb	0.63 ± 0.08	1.2 ± 0.1	0.98 ± 0.06	0.94 ± 0.05	1.02 ± 0.05	1.20 ± 0.08	0.65 ± .05	0.88 ± 0.06
Sc	17.3 ± 0.4	16.9 ± 0.5	16.5 ± 0.6	16.3 ± 0.5	17.5 ± 0.7	17.0 ± 0.4	15.6 ± 0.7	17.2 ± 0.7
Sm	6.49 ± 0.08	6.4 ± 0.1	6.5 ± 0.1	7.0 ± 0.2	4.9 ± 0.1	5.8 ± 0.1	7.3 ± 0.2	5.7 ± 0.2
Ta	1.9 ± 0.2	1.7 ± 0.1	2.2 ± 0.3	1.7 ± 0.2	1.9 ± 0.2	1.5 ± 0.1	1.6 ± 0.1	1.9 ± 0.2
Th	18.7 ± 0.6	17.4 ± 0.5	18.2 ± 0.7	15.8 ± 0.6	20.3 ± 0.7	19.0 ± 0.6	19.8 ± 0.8	18.7 ± 0.8
U	5.3 ± 0.3	4.6 ± 0.4	4.6 ± 0.3	4.8 ± 0.5	4.6 ± 0.5	4.8 ± 0.5	4.8 ± 0.3	4.9 ± 0.6
Yb	4.3 ± 0.1	3.3 ± 0.2	3.4 ± 0.2	3.8 ± 0.3	2.8 ± 0.2	3.2 ± 0.2	4.8 ± 0.4	3.1 ± 0.3
Zn	224 ± 11	596 ± 31	545 ± 17	492 ± 20	422 ± 18	357 ± 26	389 ± 13	438 ± 13

	Point 3				Point 4			
	Sept/08	Feb/09	July/09	Jan/10	Feb/09	July/09	Jan/10	Earth crust [14]
As	19.4 ± 0.6	17.3 ± 0.9	15.9 ± 0.6	20 ± 1	31 ± 1	24 ± 1	29 ± 2	1.7
Ba	528 ± 66	497 ± 37	483 ± 71	415 ± 50	503 ± 67	671 ± 94	545 ± 61	584
Br	20 ± 2	19 ± 3	24 ± 3	18 ± 2	20 ± 2	14 ± 1	18 ± 2	1.0
Ce	106 ± 7	93 ± 5	96 ± 6	100 ± 6	91 ± 5	97.2 ± 4.2	96.3 ± 6.0	60
Co	10.4 ± 0.2	9.3 ± 0.3	9.8 ± 0.2	9.9 ± 0.2	9.5 ± 0.3	10.2 ± 0.2	8.6 ± 0.2	24
Cr	91 ± 4	90 ± 2	75 ± 3	93 ± 3	102 ± 3	87 ± 3	99 ± 4	126
Cs	6.2 ± 0.3	5.9 ± 0.3	5.8 ± 0.3	5.7 ± 0.4	6.0 ± 0.3	5.9 ± 0.4	6.1 ± 0.4	3.4
Eu	0.90 ± 0.05	0.82 ± 0.05	0.85 ± 0.06	0.93 ± 0.06	0.73 ± 0.03	0.71 ± 0.04	0.69 ± 0.06	1.3
Fe (%)	8.4 ± 0.4	7.6 ± 0.18	8.16 ± 0.07	8.32 ± 0.07	8.26 ± 0.08	7.69 ± 0.09	8.12 ± 0.07	4.32
Hf	4.8 ± 0.2	7.6 ± 0.2	6.8 ± 0.3	4.6 ± 0.2	5.1 ± 0.2	8.1 ± 0.3	5.5 ± 0.2	4.9
La	36.2 ± 0.6	34.6 ± 0.4	34 ± 1	35 ± 2	29 ± 2	31 ± 1	27 ± 1	30
Lu	0.36 ± 0.06	0.55 ± 0.05	0.44 ± 0.06	0.40 ± 0.06	0.36 ± 0.04	0.49 ± 0.07	0.43 ± 0.06	0.35
Na	1013 ± 63	957 ± 31	908 ± 39	887 ± 52	1142 ± 46	1469 ± 59	1212 ± 66	23600
Nd	21 ± 3	31 ± 3	24 ± 2	28 ± 4	22 ± 3	21 ± 2	20 ± 4	27
Rb	71 ± 6	58 ± 4	59 ± 6	59 ± 6	74 ± 6	90 ± 7	94 ± 6	78
Sb	1.57 ± 0.07	1.36 ± 0.09	1.35 ± 0.06	1.52 ± 0.08	2.0 ± 0.1	1.60 ± 0.07	1.8 ± 0.1	0.3
Sc	18.0 ± 0.4	17.3 ± 0.5	18.2 ± 0.8	20.6 ± 0.9	19.8 ± 0.6	19.4 ± 0.9	20.7 ± 0.9	16
Sm	5.2 ± 0.1	5.4 ± 0.1	5.3 ± 0.1	5.1 ± 0.2	3.33 ± 0.03	3.78 ± 0.09	3.4 ± 0.1	5.3
Ta	2.5 ± 0.5	1.9 ± 0.1	2.2 ± 0.2	2.3 ± 0.4	1.8 ± 0.1	2.0 ± 0.2	2.5 ± 0.3	1.1
Th	24.6 ± 1.1	20.9 ± 0.5	20.2 ± 0.9	25.9 ± 0.9	20.9 ± 0.54	20.3 ± 0.8	22.9 ± 1.0	8.5

Table 2 continued

	Point 3				Point 4			
	Sept/08	Feb/09	July/09	Jan/10	Feb/09	July/09	Jan/10	Earth crust [14]
U	5.7 ± 0.6	5.5 ± 0.4	5.3 ± 0.3	5.4 ± 0.7	5.0 ± 0.5	5.1 ± 0.3	5.1 ± 0.5	1.7
Yb	2.6 ± 0.2	3.2 ± 0.2	3.1 ± 0.1	2.5 ± 0.3	2.1 ± 0.2	3.2 ± 0.2	2.4 ± 0.2	2.0
Zn	119 ± 6	112 ± 6	110 ± 4	108 ± 4	118 ± 5.9	122 ± 5	112 ± 4	65

100 mg kg⁻¹ in points 3 and 4. Br showed anomalous behavior along the reservoir (Table 2).

Hf presented an irregular behavior along the reservoir and over time, showing a great variability in concentration in the sediments, being very similar in points 3 and 4 and much higher in points 1 and 2. As, Sb and Th elements showed little variation in concentration in each sampling point, however presented a significant increase along the reservoir, from point 1 to 4 (Table 2). Co, La, Nd and Eu elements presented a decrease, but not accentuated, in concentration from points 1 to 4 and between the sampling campaigns.

In general, the concentration 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 discharged. At points 3 and 4 only the elements As and Sb presented higher concentration levels.

When the results obtained were compared to earth crust values [14], the elements As, Br, Ce, Cs, Fe, Sb, Sc, Ta, Th, U, Yb, and Zn presented enrichment. For Hf, La, Lu, Nd, and Sm the enrichment was observed only at points 1 and 2. The elements Ba, Co, Cr, Eu and Na, in general, presented concentrations lower or similar to earth crust values.

Table 3 Comparisons of the results obtained for the sediment samples at the Rio Grande reservoir by INAA in this study and literature [4, 5]

	Point 3 (this study) mean (min.–max.)	Point 3 Favaro et al. [4] mean (min.–max.)	Point 3 Bostelmann [5]	Point 4 (this study) mean (min.–max.)	Point 4 Favaro et al. [4] mean (min.–max.)	Point 4 Bostelmann [5]
As	18.2 (15.9–20.0)	7.8 (6.2–9.7)	20.8	28 (24–31)	8.3 (6.6–14)	33.3
Ba	481 (415–528)	930 (790–1125)	475	573 (503–671)	636 (493–845)	591
Br	20.3 (18.2–24.1)	3.6 (1.3–3.2)	16.4	17 (14–20)	6.9 (4.3–12.4)	6.9
Ce	99 (93–106)	115 (76–135)	88	95 (91–97)	96 (72–136)	96
Co	9.9 (9.3–10.4)	18.4 (12.0–23.3)	10	9.4 (8.6–10.2)	8.7 (6.1–12.1)	8.2
Cr	87 (75–93)	97 (84–104)	86	96 (87–102)	77 (64–93)	77
Cs	5.9 (5.7–6.2)	18.7 (16.5–19.7)	6.0	6.0 (5.9–6.1)	19.2 (13.8–25.6)	4.8
Eu	0.88 (0.82–0.93)	1.78 (1.26–2.04)	1.0	0.71 (0.69–0.73)	1.46 (1.10–2.12)	0.7
Fe (%)	8.1 (7.6–8.4)	n.d.	8.1	8.0 (7.7–8.3)	6.2 (1.55–8.64)	7.1
Hf	6.0 (4.6–7.6)	12.6 (10.5–14.1)	7.0	6.2 (5.1–8.1)	15.1 (8.4–20.9)	7.8
La	35 (34.0–36.2)	50.3 (42.9–57.0)	32	29 (27–31)	52.6 (41.1–69.6)	31
Lu	0.44 (0.36–0.55)	0.94 (0.70–1.50)	0.5	0.43 (0.36–0.49)	0.9 (0.55–1.21)	0.5
Nd	26 (21–31)	56 (40–64)	37	21 (20–22)	46 (35–56)	25
Rb	62 (58–71)	108 (100–128)	73	86 (74–94)	100 (78–124)	113
Sb	1.45 (1.35–1.57)	0.70 (0.69–0.75)	1.9	1.8 (1.6–2.0)	0.70 (0.53–0.89)	n.d.
Sc	18.5 (17.3–20.6)	21.9 (20.1–22.8)	20	20.0 (19.4–20.7)	18.7 (16.6–20.1)	22
Sm	5.3 (5.1–5.4)	9.3 (6.6–10.6)	5.0	3.50 (3.33–3.78)	10.7 (5.5–28.6)	4.9
Ta	2.2 (1.9–2.5)	3.2 (2.4–4.7)	2.6	2.1 (1.8–2.5)	3.1 (2.4–3.8)	1.8
Th	22.9 (20.2–25.9)	22.0 (19.1–23.4)	23.5	21.4 (20.3–23.0)	18.2 (13.8–21.4)	21.8
U	5.5 (5.3–5.7)	9.3 (7.2–9.8)	4.6	5.1 (5.0–5.1)	7.7 (6.3–9.3)	2.1
Yb	2.9 (2.5–3.1)	4.8 (4.0–5.3)	2.6	2.6 (2.1–3.2)	5.3 (3.3–7.0)	2.8
Zn	112 (110–119)	149 (131–173)	146	117 (112–122)	92 (70–119)	224

n.d not determined

Table 3 presents the results for the sediment samples obtained in the present study in comparison with other published studies, developed at the Rio Grande Reservoir. The locations of sampling points were very similar to this study (points 3 and 4) [4, 5].

In the published study by Fávoro et al. [4] the sediment samples were collected in 1998 and bottom and sediment profiles were analyzed. Bostelman [5] analyzed bottom sediment samples which were collected in 2004. In both studies the sediment samples were analyzed by INAA. Comparing all the results (Table 3) it can be verified that the results obtained in this study were very similar to the Bostelman's results for most elements. In both studies, As, Br and Sb presented higher concentration values than those obtained by Fávoro et al. [4]. This could be indicative that these elements may be entering the reservoir due to anthropogenic contribution of the region.

The Fávoro study [4] presented higher levels for the elements Co, Cs, Hf, Ta and U and for rare earths Eu, La, Lu, Nd, Sm, and Yb. The Ce, Cr, Ba, Sc, and Th elements presented similar results in the three studies, just with small punctual variations which are indicative that their concentrations have become more stable in the reservoir over the past 13 years.

The Enrichment factor (*EF*), defined as a double ratio normalized to a reference element (*RE*), is an index used as a tool to evaluate the extent of metal pollution and has been used for some time [15, 16] to assess, anthropogenic metal contamination in the environment, especially in sediments [15–18]:

$$EF = ([M]/[RE]_{\text{sed}})/([M]/[RE]_{\text{ref}}) \quad (1)$$

Fe, Al and Sc are generally used as reference elements for normalization purposes [15–18]. In the present study Sc was chosen as a reference element and earth crust values as reference values for sediments [17].

According to Zhang and Liu [19], if $0.5 < EF < 1.5$, the elemental concentration is probably entirely due to crustal or natural weathering origins; values above 1.5 indicate anthropogenic contributions. The higher the *EF* value the more severe the anthropogenic contribution.

The element As presented an *EF* ranging from 5 to 6 in points 1 and 2 and from 8 to 13, at points 3 and 4. For Br, the *EF* ranged from 7.9 to 31.5 at points 1 and 2 and from 11.6 to 21.1, points 3 and 4. The *EF* for Zn at points 1 and 2 ranged from 3.1 to 8.7 and decreased to around 1.3 at points 3 and 4. The same behavior was observed for the elements Sb, Th and U. As a conclusion, a strong anthropogenic influence was observed for As, Br, Th, U and Zn elements, mainly in the points located in the entrance of the reservoir (points 1 and 2) that receives domestic and industrial effluents from the rivers that reach the reservoir.

Conclusion

Multi-element analysis such as INAA allows the evaluation of several elements of interest at one time and without sample destruction. Equivalent analysis for other procedures would take very a long time and sometimes would be less precise. However, other analytical techniques such as atomic absorption spectrometry and inductively coupled plasma-optical emission spectrometer are suitable methods for elements that cannot be detected by INAA such as toxic metals Cd, Pb and Hg and some other heavy metals. In this study, most element concentration variations not higher than 25% for the 2 seasons in all sampling points were observed. This behavior can be reflecting the permanency of these elements in the sediments during this period (September 2008–January 2010), indicating that they do not suffer significant alterations with seasonal variations of the reservoir. In this study anthropogenic and non-anthropogenic trace elements were identified by *EF* and the results compared with earth crust values. The obtained *EF* for trace elements showed an anthropogenic influence for the elements As, Br, Sb, Th, U and Zn mainly at points 1 and 2 that receives domestic and industrial effluents from the rivers that reach the reservoir. At points 3 and 4 (catchment point of water supply) the *EF* higher than 8 for As and 4 for Sb were found. This conclusion calls attention for the presence of these elements in this reservoir in concentration much higher than earth crust values and particularly higher than those obtained by Fávoro et al. [4] in samples collected 13 years ago. This behavior could indicate that these elements are being deposited in the reservoir due to anthropogenic contributions with serious consequences since this reservoir supplies water for more than 1 million inhabitants and offers fish as a food source for those living near its shores.

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