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Metal, Trace and Major Elements Assessment in a sediment profile from Lobo/Broa Reservoir by INAA, São Paulo State, by INAA

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1. Introduction

Reservoirs were built from the damming of rivers to meet the demand and expansion of the use of water, in order to regulate the water flow and maintain constant energy generation over time. However, they cause environmental, social, economic and cultural impacts due to the alteration of the natural behavior of the water system and to the appearance of conflicts related to the use of water [1]. The damming of waters forms a lentic environment, where the flow and velocity of water currents favor the deposition of suspended particles, accumulating them in the bottom of the reservoirs and resulting in sedimentation [2,3]. Sediment has been an important study tool to evaluate the quality of aquatic ecosystems, since it portrays the historical conditions of the influence of anthropogenic activities on these environments, not always detectable by the use of water variables [4]. In addition, the sedimentary profiles allow the comparison of concentrations of elements in the surface sediments (that is, of the upper layers of the sediment, recent sedimentation) with the oldest sediments, going back to the formation of the reservoir. In addition to the visualization of concentrations in the profiles, the use of a geochemical tool associated to the basal values of the sedimentary profiles provides a better way of distinguishing between the geogenic and anthropogenic concentrations [5]. Sedimentary profile analyses can also provide information that helps to understand the processes that took place during the construction of the reservoir and recent processes in the reservoir, such as significant changes in particle size, caused by the change in channel velocity, differentiation of total organic carbon (TOC) concentrations, due to flooding of the river floodplain and flooding of cultivated areas or forests, and also mineralogical changes resulting from the deposition of sediments from a new basin on-site drainage [6]. The aim of the present study was to determine the concentration and distribution of metals, trace and major elements in a sedimentary profile from the Broa reservoir (or Lobo dam) using the INAA technique. The enrichment factor (**EF**), Geoacumulation Index (***IGeo***) and **TEL** and **PEL** guideline values were used in the present study as important tools for sediment quality evaluation.

2. Methodology

2.1 Study area

The Carlos Botelho reservoir (Lobo-Broa) is located in the central region of the State of São Paulo (22 ° 15 ′ S; 47 ° 49 W), and belongs to the municipality of Itirapina. It is inserted in the Tietê-Jacaré hydrographic basin and its main tributaries are the Córrego do Lobo and the Itaqueri River, both with the most extensive wetlands. The region surrounding the Lobo/Broa reservoir is characterized by rocks from the Serra Geral formation (sandstone, basalt and diabase) and halocenic sediments (sand, gravel and clay). The land uses in the Itaqueri River basin, the main tributary of the Lobo-Broa dam, are agricultural crops and animal husbandry, with intense non-point dumping of organic and inorganic residues (fertilizers and pesticides) and metals from mining sand.

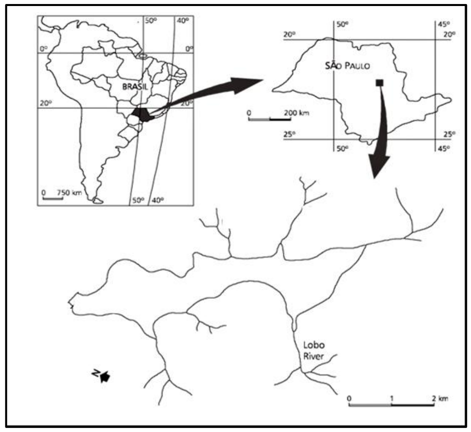

Figure1. Lobo/Broa location map (Adapted from [8]).

2.2 Sampling and sample preparation

The sediment profile was collected in 2017 by the CETESB's Sector of Sampling of Aquatic Environments. The collected profile was sliced every 2.5 cm with the aid of an extruder, from top to bottom of the profile and the fractions were packed in properly identified plastic bags. The sediment core was 50 cm long and 20 fractions were obtained in the total. The collected sediments were dried in an oven at 40°C until constant mass, macerated in agate mortar and stored in a Falcon bottle. The total fraction of the sediments (< 2mm) was analyzed.

2.3 INAA Experimental Procedure

For multielemental determination, about 150 mg of sediment (duplicate samples) and reference certified materials were accurately weighed. After that were irradiated for a daily cycle (6-7 hs), under a thermal neutron flux of 5 x 10^{12} n cm^{-2} s^{-1} in the IEA-R1 nuclear reactor at IPEN. The elements analyzed by using this methodology were As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U and Zn. Details of the analytical methodology is already described by Rocha et al. [9]. The methodology validation was verified by measuring the reference materials Lake Sediment (IAEA SL-1), Lake Sediment (IAEA SL-3) and BEN (Basalt –IWG-GIT), that presented certified concentration values for almost all elements analyzed [9]. The Zeta-score criteria was used to check the INAA technique, in terms of accuracy and precision, analyzing the certified reference materials.[10].

2.4 Enrichment Factor (EF) and Geoaccumulation Index (*IGeo*) assessment

EF and the Geoaccumulation index (*IGeo*) [11,12] are tools used for assessing pollution levels of metals in soils and sediments. In the present study, Sc was chosen as a reference element and the basement (last layer) of the sediment profile as reference values. According to Zhang and Liu [12], if 0.5<EF<1.5, the elemental concentration is probably due entirely too crustal or natural weathering origins; values above 1.5 indicate anthropogenic contributions. According to Sutherland [13], if EF<2.0 it means depletion or low enrichment; 2<EF<5, moderate enrichment; 5<EF<20, significant enrichment; 20<EF<40, very high enrichment and EF>40, extremely high enrichment. The classification of pollution levels from the *IGeo* values are: <0, baseline; 0 to 1, unpolluted; 1 to 2, moderately polluted; 2 to 3, moderately to polluted; 3 to 4, polluted to strongly polluted; 4 to 5, strongly polluted and> 5, very strongly polluted.

2.5 TEL and PEL oriented values assessment

As a criterion for quality sediment evaluation for metals, CETESB has adopted the TEL and PEL guide values, established by the Canadian Council of the Ministry of the Environment (CCME)[14] for the total concentration of As, metals and organic compounds, in order to assess possible deleterious effects on the biota. TEL (Threshold Effect Level) indicates the concentration below which there is a rare occurrence of adverse effects to biota and PEL (Probable Effect Level), the concentration above which there is frequent occurrence of these effects. TEL and PEL values for As, Cr and Zn are shown in Table 1.

3. Results and Discussion

Table 1 shows the results obtained by the INAA technique for the sediment core. According to the analysis of the Lobo-Broa reservoir sediment profile, built in 1936, therefore aged 81 years until the date of collection in 2017; it showed a clear sedimentary transition at a depth of 17.5 cm which can be considered the depth at which the reservoir had its beginning. The average sedimentation rate of this reservoir at the sedimentary profile collection site was 0.22 cm yr^{-1} [15]. At a depth of 17.5 cm there was a decrease in the sand fraction and a consequent increase in the clay fraction. From that point onwards, the % of fines increased from 84% to values above 93% and there was also an increase in TOC (Total Organic Carbon) from 11.5 to 15.2% (Table 1). These changes indicated that this profile reached the sedimentary transition from river to reservoir at this depth and, also, that this profile represents well the sedimentation history of this reservoir [15]. From the results in Table 1 it was observed that the highest concentrations of the elements As, Br, Co, Cr, Cs, Fe, Sc, Th and Zn were found in the most superficial slices, among 15 and 2.5 cm deep, which means, from the sedimentary transition (17.5 cm). In these fractions, the fines content showed an increasing variation from 84 to 98%, between depths of 15 to 2.5 cm, respectively. The highest concentration values in this range may be associated with the presence of finer sediments due to their higher capacity to absorb metals and trace elements [4]. From a depth of 20 cm to the base of the profile in 50 cm (older sediments) the elements analyzed, in general, showed a tendency of decreasing concentration. There was also a decrease in the % of fines from 52 to 32% and an increase in the % TOC from 11.5 to 24.7%. In this same interval, the elements As, Co, Fe, Sc and Zn showed stability in the concentration values, with slight variations. Some elements showed slight increases in concentration (Br, Rb, Sb, Th and U) and the elements Cr, Cs, Hf, K and Ta, showed a more accentuated tendency to increase from a depth of 20 cm to the basement of the profile. According to CETESB [15], the increase in element concentrations was due to the new sedimentary dynamics of the reservoir after the construction of the dam. The change in the post-construction water movement may have favored the deposition of finer particles in the sediment. FRASCARELI [16] evaluated the quality of surface sediments in the Lobo-Broa reservoir for metal contamination by coupled plasma optical emission spectrometry (ICP OES). The author carried out assessments with guideline values of sediment quality (VGQS), regional and basal reference values, toxicity with TEL/PEL and EF. The following concentration values were obtained: Fe (3.5 ± 0.7%); Cr (26 ± 4 mg kg^{-1}) and Zn (36 ± 6 mg kg^{-1}). Comparing the metal concentration values of the most superficial slice of the sedimentary profile analyzed in the present study (Table 1) with these values we could see that they were a little bit higher for these metals.

When the concentrations values for As, Cr and Zn were compared to the TEL and PEL oriented values, it was observed that As reached the TEL value (5.9 mg kg^{-1}) only in two superficial slices of the profile (between 7.5 and 10 cm in depth) and in the other slices, the concentration values remained below TEL, with excellent quality classification for this element. Cr concentrations with values above TEL (37.3 mg kg^{-1}) were found before the sedimentary transition, that is, and in the slices at the base of the profile, between 35 and 50 cm of depth. The sediment classification for the Cr metal was good quality. For the Zn element there was an increase in concentration from the sedimentary transition by 17.5 cm, but the concentrations remained below the TEL guide value (123 mg kg^{-1}), throughout the entire sedimentary profile, with classification of excellent sediment quality for this metal. Despite the results found for As and Cr above TEL values, these concentrations are stable throughout the sediment profile after reservoir construction, that means they are associated with the new site deposition characteristic. This suggests that such concentrations have geogenic rather than anthropogenic characteristics. Table 2 presents the results for EF and *IGeo* calculations where the concentration values of the 15 cm slice, the first slice above the sedimentary transition, was considered as baseline values for the reservoir and the Sc element as the normalizer. Values of 2.0 <FE<1.0 (sediment with low enrichment) were found only for the elements As, K and Na from the sedimentary transition. The *IGeo* values results were obtained by using the same basal values and the correction for the % of fines. Only Ba presented values of $0<IGeo<1$, classifying the sediment as unpolluted. The other elements analyzed presented $IGeo<0$, with a basal level classification, according to the classification presented in item 2.4.

Table 2. EF (2<EF<1) and *IGeo* (***0<IGeo<1***) results calculated considering the concentrations of elements in the slice corresponding to 15 cm as baseline values, Lobo-Broa reservoir

Depth (cm)	**2<EF<1**			***0<IGeo<1***
	As	**K**	**Na**	**Ba**
2.5	**1.5**	**1.7**	**2.2**	
5	**1.6**	**1.9**	**1.9**	
7.5	**1.7**		**1.7**	**0.3**
10.0	**1.6**	**2.1**		**0.9**
12.5		**1.5**		**0.3**

4. Conclusions

From the results of the present study it was possible to conclude that the Lobo-Broa reservoir presented no anthropogenic contributions for the elements analyzed by the three tools used for the sediment contamination assessment by throughout the analysis of its sediment profile.

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Table 1. Results (mg kg^{-1}) for metals, trace and some major elements determined by INAA technique, total organic carbon (TOC) and particle size composition (% of fines) of the sediment profile samples from the Lobo-Broa reservoir (BROA02800), analyzed and published by CETESB (2018); TEL and PEL oriented values

Depth (cm)	As	Br	Co	Cr	Cs	Fe (%)	Hf	K (%)	Na	Rb	Sb	Sc	Ta	Th	U	Zn	Fines (%)	TOC (%)
2.5	5.3 ± 0.8	16.8 ± 1.3	12.6 ± 0.8	49 ± 3	1.4 ± 0.3	5.6 ± 0.2	6.2 ± 0.4	1.0 ± 0.2	203 ± 6	10 ± 2	0.45 ± 0.06	20.0 ± 0.7	1.8 ± 0.2	9.0 ± 0.4	2.1 ± 0.4	65 ± 11	**98.4**	**11.3**
5	5.8 ± 0.9	17.7 ± 1.4	13.6 ± 1.1	48 ± 3	1.5 ± 0.3	5.8 ± 0.2	5.9 ± 0.7	1.1 ± 0.2	186 ± 8	10 ± 2	0.56 ± 0.08	20.8 ± 0.8	1.7 ± 0.2	9.7 ± 0.4	1.6 ± 0.4	70 ± 12	**96.0**	**10.4**
7.5	5.9 ± 0.9	17.8 ± 1.3	11.5 ± 0.9	45 ± 3	1.4 ± 0.4	5.3 ± 0.2	5.5 ± 0.5	0.5 ± 0.1	159 ± 7	n.d.	0.53 ± 0.07	19.7 ± 0.7	1.4 ± 0.1	9.3 ± 0.4	1.8 ± 0.4	65 ± 11	**98.2**	**9.7**
10.0	6.0 ± 1.0	18.3 ± 1.4	13.5 ± 1.3	44 ± 3	1.6 ± 0.3	5.5 ± 0.2	6.3 ± 0.6	1.4 ± 0.2	128 ± 9	10 ± 3	0.46 ± 0.06	22.9 ± 0.8	1.6 ± 0.1	10.5 ± 0.4	2.6 ± 0.6	69 ± 11	**97.6**	**8.2**
12.5	5.0 ± 0.4	17.5 ± 1.7	17.2 ± 0.5	57 ± 3	1.6 ± 0.3	6.2 ± 0.3	8.0 ± 0.3	1.2 ± 0.1	142 ± 7	11 ± 2	0.76 ± 0.11	28.0 ± 1.0	2.1 ± 0.5	13.4 ± 0.6	2.7 ± 0.7	67 ± 5	**93.4**	**8.5**
15	5.0 ± 0.4	21.6 ± 2.2	14.7 ± 0.5	49 ± 3	1.7 ± 0.2	6.5 ± 0.3	9.0 ± 0.4	0.8 ± 0.1	133 ± 6	6 ± 1	0.56 ± 0.10	29.0 ± 1.0	2.0 ± 0.2	11.4 ± 0.5	3.2 ± 1.1	81 ± 10	**84.2**	**11.6**
17.5	2.3 ± 0.2	12.7 ± 1.2	8.2 ± 0.3	33 ± 2	1.2 ± 0.2	3.3 ± 0.2	6.4 ± 0.2	n.d.	136 ± 9	3 ± 0	0.29 ± 0.06	13.8 ± 0.5	1.5 ± 0.2	6.3 ± 0.3	2.2 ± 0.5	41 ± 3	**67.5**	**15.2**
20	0.7 ± 0.1	7.3 ± 0.7	3.7 ± 0.1	22 ± 2	0.7 ± 0.2	1.3 ± 0.1	6.1 ± 0.3	1.1 ± 0.2	124 ± 8	5 ± 1	0.17 ± 0.03	4.5 ± 0.2	1.0 ± 0.2	3.3 ± 0.2	1.5 ± 0.6	17 ± 2	**52.3**	**11.5**
22.5	0.7 ± 0.1	7.6 ± 0.8	3.9 ± 2.2	20 ± 1	0.7 ± 0.1	1.2 ± 0.1	7 ± 1	0.7 ± 0.1	114 ± 5	9± 1	0.17 ± 0.04	4.4 ± 0.2	1.1 ± 0.2	3.0 ± 0.1	1.0 ± 0.2	26 ± 4	**65.7**	**11.0**
25	0.7 ± 0.1	7.6 ± 0.6	4.0 ± 0.7	21 ± 1	0.7 ± 0.2	1.2 ± 0.1	6.1 ± 0.8	1.1 ± 0.5	124 ± 5	11 ± 1	0.14 ± 0.02	4.6 ± 0.2	1.1 ± 0.2	3.0 ± 0.1	1.1 ± 0.2	27 ± 4	**53.9**	**11.1**
27.5	0.8 ± 0.1	8.3 ± 0.7	4.1 ± 0.1	19 ± 1	0.8 ± 0.1	1.3 ± 0.1	6.1 ± 0.7	1.3 ± 0.4	121 ± 5	6 ± 1	0.19 ± 0.07	4.5 ± 0.2	1.2 ± 0.1	2.9 ± 0.1	1.2 ± 0.2	30 ± 5	**69.4**	**13.2**
30	0.9 ± 0.1	9.8 ± 0.7	4.3 ± 0.9	23 ± 1	0.8 ± 0.1	1.2 ± 0.1	5.4 ± 0.6	n.d.	115 ± 5	6 ± 1	0.21 ± 0.03	4.7 ± 0.2	1.2 ± 0.1	3.3 ± 0.1	1.2 ± 0.3	29 ± 5	**61.2**	**17.7**
32.5	1.1 ± 0.3	9.2 ± 0.7	4.7 ± 0.1	33 ± 2	1.0 ± 0.1	1.3 ± 0.1	6.7 ± 0.5	1.5 ± 0.2	122 ± 7	10± 1	0.29 ± 0.04	6.1 ± 0.2	1.4 ± 0.2	4.0 ± 0.2	1.4 ± 0.2	26 ± 4	**56.8**	**22.9**
35	1.1 ± 0.2	5.6 ± 0.4	5.3 ± 0.2	43 ± 2	1.4 ± 0.1	1.2 ± 0.1	10.3 ± 1.0	2.0 ± 0.2	137 ± 8	10 ± 1	0.34 ± 0.04	7.4 ± 0.3	1.8 ± 0.2	4.9 ± 0.2	2.0 ± 0.2	25 ± 4	**61.3**	**15.6**
37.5	0.9 ± 0.2	4.9 ± 0.6	5.5 ± 0.4	44 ± 2	1.4 ± 0.2	1.2 ± 0.1	10.6 ± 1.1	2.1 ± 0.2	140 ± 5	10 ± 1	0.28 ± 0.12	8.0 ± 0.3	1.9 ± 0.2	5.3 ± 0.2	1.9 ± 0.2	24 ± 4	**59.7**	**14.4**
40	1.2 ± 0.2	6.2 ± 0.7	6.4 ± 0.4	52 ± 3	1.6 ± 0.2	1.2 ± 0.1	9.8 ± 0.7	2.2 ± 0.3	136 ± 7	20 ± 2	0.32 ± 0.04	10.0 ± 0.4	1.6 ± 0.2	5.9 ± 0.2	2.4 ± 0.2	26 ± 4	**46.5**	**16.0**
42.5	1.0 ± 0.3	7.7 ± 1.7	6.4 ± 0.4	55 ± 6	1.9 ± 0.3	1.1 ± 0.1	9.2 ± 1.5	1.9 ± 0.4	116 ± 4	8 ± 2	0.23 ± 0.16	10.2 ± 0.4	1.5 ± 0.1	6.0 ± 0.5	2.1 ± 0.9	26 ± 4	**48.6**	**20.6**
45	1.1 ± 0.3	9 ± 2	6.3 ± 0.2	53 ± 6	1.6 ± 0.2	1.0 ± 0.1	7.4 ± 0.4	1.5 ± 0.3	108 ± 4	9 ± 2	0.31 ± 0.05	9.8 ± 0.4	1.9 ± 0.3	5.4 ± 0.5	1.5 ± 0.2	28 ± 5	**48.2**	**22.3**
47.5	0.9 ± 0.2	11.1 ± 2.2	6.3 ± 0.2	54 ± 6	2.0 ± 0.2	0.9 ± 0.1	7.7 ± 0.7	2.9 ± 0.7	118 ± 5	5 ± 1	0.41 ± 0.04	10.1 ± 0.4	1.9 ± 0.2	5.6 ± 0.5	1.9 ± 0.3	29 ± 5	**39.4**	**21.6**
50	1.0 ± 0.3	11.1 ± 2.2	6.0 ± 0.2	51 ± 5	1.9 ± 0.1	0.8 ± 0.1	6.6 ± 0.5	2.6 ± 0.4	108 ± 6	9 ± 2	0.25 ± 0.04	9.6 ± 0.3	1.5 ± 0.1	4.9 ± 0.4	2.3 ± 0.3	23 ± 4	**32.0**	**24.7**
TEL	**5.9**			**35.3**												**123**		
PEL	**17**			**90**												**315**		

n.d – not determined; X –sedimentary transition