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Metals and Trace Elements Assessment in a Sedimentary Profile from the Billings Reservoir, Taquacetuba Branch, São Paulo State

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1. Introduction

The Billings reservoir is located in the Southeast of the São Paulo Metropolitan Region (RMSP), in the municipalities of São Bernardo do Campo and São Paulo, and belongs to the Alto Tietê Water Resource Management Unit. The dam has an irregular shape, subdivided into 8 sub-units, called branches: Rio Grande, Rio Pequeno, Capivari, Pedra Branca, Taquacetuba, Bororé, Cocaia and Alvarenga [1,2]. The Taquacetuba branch is an important water source as it can reverse water to the Guarapiranga reservoir, for the RMSP public supply. The Taquacetuba branch is approximately 5 km long and is located in the municipalities of São Bernardo do Campo and São Paulo. The Taquacetuba region is mostly covered by well-preserved native vegetation or at an advanced stage of regeneration [1,2]. Since 2015, the monitoring of the Environmental Company of the State of São Paulo (CETESB) was expanded and intensified in the forming arms of the Billings dam, including the Taquacetuba branch, which were considered as short-term solutions by the São Paulo State government for reinforcement of the supply of the Alto Tietê and Guarapiranga Systems.[3] This study aimed to evaluate the concentration and distribution of the elements As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, K, Na, Rb, Sb, Sc, Ta, Th, U and Zn, present in a vertical profile of sediments collected in the Billings Dam, Taquacetuba branch, using the Instrumental Neutron Activation Analysis (INAA) technique. The Enrichment Factor (**EF**) and the Geoaccumulation Index (***IGeo***) tools were used for the assessment of anthropogenic pollution levels in sediments. Sediment quality evaluation in relation to toxic metals (Cr and Zn) and metalloid As was performed by comparison to the guideline values of Environmental Canada (TEL and PEL) and adopted by CETESB. This study was carried out in partnership with CETESB, in continuation of sediment quality assessment studies from supply reservoirs in the São Paulo State, developed by the LAN research group (IPEN – CNEN/SP).

2. Methodology

2.1 Sampling and sample preparation

A vertical profile of sediments was collected in 2016 by specialized technicians from the Aquatic Environment Sampling Sector of CETESB [4]. The geographic data of the collection point, profile depth and number of fractions are described in Table I. The collected profile was cut every 2.5 cm with the aid of an extruder, towards the top of the profile, during sampling collection and the fractions were packed in properly identified plastic bags. The collected sediments (fraction < 2mm) were dried in an oven at 40°C until constant mass, macerated in an agate mortar, sieved in a 120 mesh and stored in Falcon tubes.

Table I. Data of the sediment profile sampling point, Taquacetuba reservoir

Reservoir (Code CETESB)	Geographical coordinates of the sampling point	Date of sample collection	Number of fractions (profile depth, cm)
Taquacetuba (BITQ 00100)	23° 50"41'' 46° 39'20''	6/1/2016	21 (53)

2.2 INAA analytical technique

About 150 mg of sediment samples (duplicate) and certified reference materials (standards) were weighed and placed in polyethylene bags. Sediment samples and standards were irradiated during a daily cycle (6-7 hours) under a thermal flux of neutrons from 1 to 5 x 10^{12} n cm^{-2} s^{-1} in the IEA-R1 nuclear research reactor, at IPEN. Two series of counting were carried out: the first after one week decay and the second after 20 days. The measurements of the induced gamma-ray activity were performed in a gamma-ray spectrometer with a hyperpure Ge detector, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co, respectively. The elements determined were: As, Ba, Br, Co, Cr, Cs, Fe, Hf, Rb, Sb, Sc, Ta, Th, U and Zn. The uncertainties of the results were calculated by error propagation. The validation of the methodology was verified by measuring Lake Sediment (IAEA SL-1), Lake Sediment (IAEA SL-3) and BEN (Basalt-IWG-GIT) certified reference materials, with certified concentration values for almost all analyzed elements.

2.3 Sediment quality evaluation

The enrichment factor (EF) [5] and geoaccumulation index (*IGeo*) tools [5,6] were used to assess the levels of anthropogenic pollution for the analyzed elements, from the river-reservoir sedimentary transition, according to the equations (1) and (2), respectively:

$$EF = ([element]/[Sc])_{sample}/([element]/[Sc])_{background\ sample} \qquad (1)$$

$$IGeo = log_2((C_i / \%fines_i) / (1{,}5 * (Bg/ \%fines_{Bg})) \qquad (2)$$

3. Results and Discussion

Figure 1 shows the concentration variation as a function of depth of the elements determined by INAA. According to CETESB [4], changes in texture and TOC (total organic carbon) were verified for this sedimentary profile, which defined a depth of 27.5-30 cm as the transition between pre and post- dam, that is, the time when the reservoir began and there were changes in the dynamics of local sedimentation, as a result of the damming of the river. From these considerations for the elements analyzed by INAA from the sedimentary transition the elements presented, in general, two kinds of behavior: concentration increase for the elements As, Br, Co, Cr, Fe, Sb, Sc, Th, U and Zn, behavior which coincided with the increase in the % of fines to values above 90%, and decrease in concentration for Ba, Cs, Hf and Rb. These last elements showed, from the sedimentary transition to the basement of the profile (older sediments), an increase in concentration. The EF was calculated by using Sc element as a normalizer and the 25 cm depth concentration values as baseline values, based on the river-reservoir sedimentary transition. Values of 1<EF<2 (depletion or low enrichment) were obtained for the elements As, Fe, Hf, Sb and Zn; 2<FE<3 (moderate enrichment) for Br, Co and Cr and baseline values for the others elements analyzed (Table II). The *IGeo* values were also calculated using as basal values the concentration values for the elements in the slice corresponding to 25 cm in depth and taking into account the % of fines, according to equation (2)[4,5]. Values of $0<IGeo<1$ (unpolluted) were obtained only for the elements Br and Cr (Table II). For all other elements analyzed, *IGeo* <0 (basal level) were obtained. Comparing the values of As, Cr and Zn with the guiding values TEL and PEL, to verify the sediment quality from the sedimentary transition, it was verified that: **As**, it greatly exceeded the TEL value (5.9 mg kg^{-1} - poor quality); **Cr**, exceeded the PEL value (90 mg kg^{-1} – bad quality); and **Zn**, with values lower than TEL (123 mg kg^{-1} – good quality), throughout the sedimentary profile.

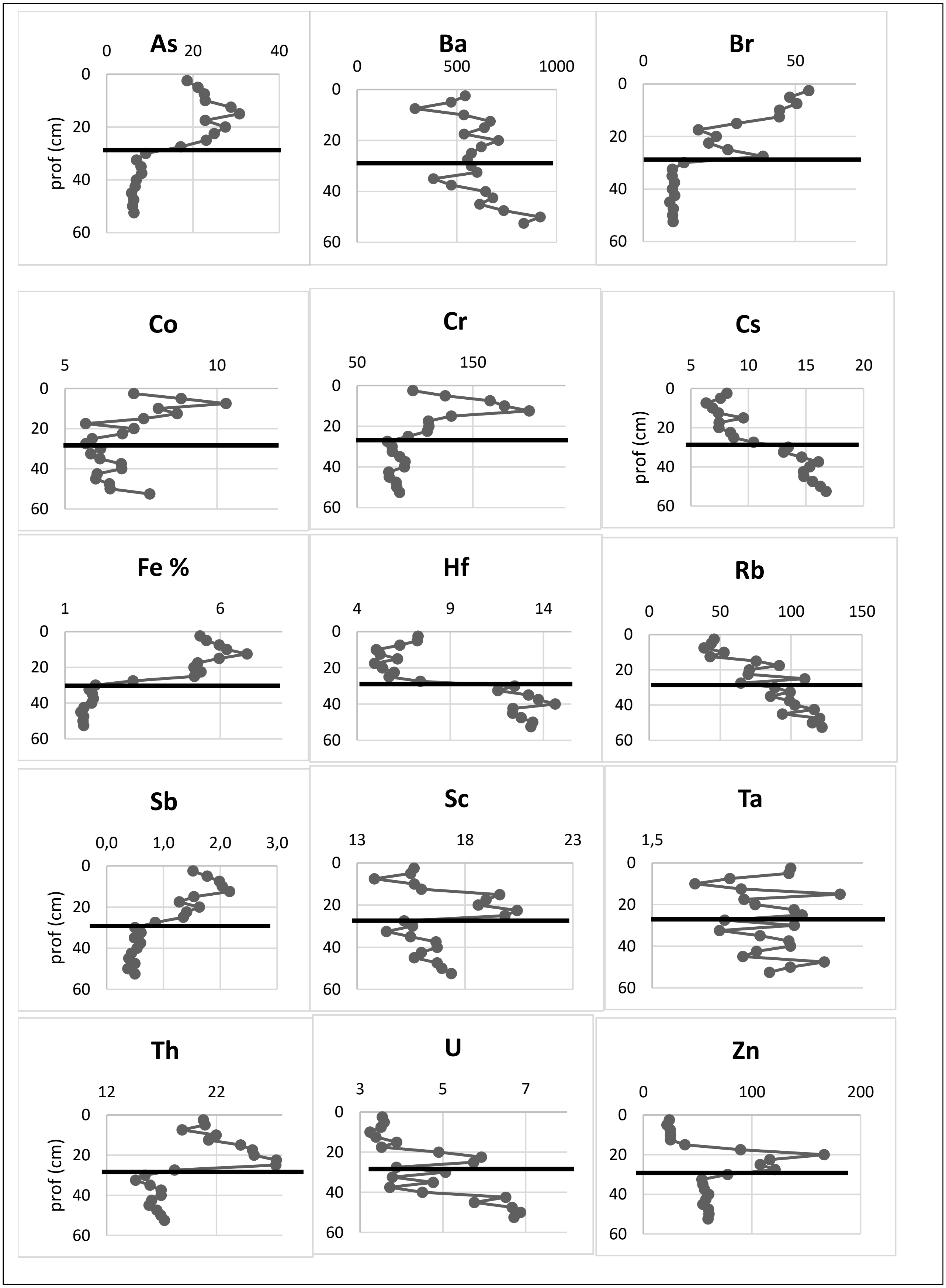
As
Ba
Br
Co
Cr
Cs
Fe %
Hf
Rb
Sb
Sc
Ta
Th
U
Zn
prof (cm)
0
20
40
60

Figure 1: Concentration distribution of the elements (mg kg^{-1}) determined by INAA along the sedimentary profile of the Billings reservoir – Taquacetuba branch (sedimentary transition – 27.5 cm).

Table II. Results from EF (**EF>1.5)** and ***0<IGeo <1***, for the elements determined by INAA

	FE > 1.5								***0<IGeo<1***	
Depth (cm)	**As**	**Br**	**Co**	**Cr**	**Fe**	**Hf**	**Sb**	**Zn**	**Br**	**Cr**
2.5		**2.5**	**1.6**			**1.6**			**0.3**	
5		**2.2**	**1.9**	**1.7**		**1.7**	**1.7**		**0.1**	
7.5		**2.6**	**2.5**	**2.5**	**1.7**	**1.6**	**2.1**		**0.3**	**0.2**
10.0		**2.0**	**1.7**	**2.4**	**1.5**		**1.9**			**0.2**
12.5	**1.6**	**2.0**	**1.8**	**2.6**	**1.6**		**2.0**			**0.4**
15										
17.5										
20								**1.7**		

4. Conclusions

The present study showed the importance of analyzing the sedimentary profile, as it provides information on the distribution history of the elements present in reservoirs, distinguishing the superficial (newer) sediments from the older ones, and the anthropic concentrations, based on their constructions. The present study contributed with concentration values for important elements from an environmental point of view, in a sediment profile of the Billings reservoir, Taquacetuba branch. According to the EF evaluation tool, low enrichment was observed for As Fe, Hf, Sb and Zn; moderate enrichment for Br, Co and Cr and baseline values for the other analyzed elements. For the *IGeo* tool, unpolluted classification was obtained only for the elements Br and Cr and baseline classification for the others analyzed elements taking into account the granulometric composition (texture) of the sediment core. In the comparison with the guiding values TEL and PEL, it was found that As and Cr presented poor sediment classification and Zn, good quality, from the sedimentary transition to the top of the sediment profile analyzed.

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