TRENDS OF METAL POLLUTION EVALUATED BY GUARAPIRANGA SEDIMENT TESTEMONIAL

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Abstract — *The Guarapiranga Reservoir is one of the largest and the most threatened water source of the Metropolitan Region of São Paulo, supplying water to about 4 million people. The growth of urban sprawl into the reservoir is causing negative impacts on the water quality. Analysis of inorganic material in the sediments of rivers and lakes is an important means of pollution assessment due to they are prone to rapid changes in the composition with the water column. This project collected a 75 cm testimony with 75 fractions (1 cm each) from which inorganic materials were analyzed. Metals and organic matter in this sediment testimonial were evaluated over time using mass balance calculations. The anthropogenic impacts over the Guarapiranga reservoir are discussed.*

Index Terms — *anthropogenic impacts, metal pollution, sediment*

INTRODUCTION

Dam sediments are known as source of biogeochemical information, and can be considered as the drainage basin memoire [1, 2, 3]. This way, the sediment testimonial investigation can supply sequential information about aquatic ecosystem contamination. Additionally, sediment deposition past information provide aquatic environment basal knowledge that helps establishing much more realistic goals for impacted environment recovery [4, 3]. Inorganic and organic analysis in river and lake sediments are an important mean of pollution evaluation, once those are prompt to fast exchanges with water column. The re-dissolution of toxic contaminants available in sediments contributes to water quality deterioration that also causes aquatic biota toxic effects by tissue bioaccumulation and bi magnification in the trophic chain [5, 6, 7, 8, 9, 10]. These effects can cause public health damage especially considering the technical difficulties and high costs related to contaminants removal and in face of the water reuse as a worldwide reality [11, 12]. All around the globe, metals, semi-metals and persistent organic pollutants (POP's) high concentration have been found frequently in aquatic ecosystems sediments nearby highly industrialized and urbanized areas [13, 14, 15, 16, 17, 18]. Some elements (such as As, Be, Cd, Cr, Cu, Hg, Pb, Zn and Ni) are known to be potentially toxic to the aquatic biota [19, 20]. Nowadays it is currently adopted the Threshold Effect Level – TEL. Toxic effects are unlikely to occur below TEL values. Also, there are considered the Probable Effect Level – PEL, that upon these values adverse biologic effects are likely to occur [21].

So, in the present study it will be considered the Guarapiranga Dam that is one of the aquatic ecosystems very close Sao Paulo City, a highly industrialized and urbanized area supplying water to around 4 million people [22]. The metal and organic matter measurements in a 75 cm sediments testimony were evaluated in 75 portions. The information collected was related to a sedimentation rate, in order to estimate the past years exposition changes the Guarapiranga Dam has suffered.

LOCATION

The Guarapiranga Hydrographic Basin is located at the portion southwest from the Sao Paulo Metropolitan Region (Figure 1). The Guarapiranga Dam testimonial collection was done at the most favorable area to sediment deposition that could provide the most profound and preserved stratigraphic sequence [23]. The location of the T1 collection site can be seen in Figure 2. The location description and GPS coordinates are presented in Table 1.

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MATERIAL AND METHODS

A modified gravity sampler was used [24, 25]. After the sample collection, the sample was sliced in regularly 1 cm sub samples. To preserve the interest analytes, samples were kept at 4°C in iceboxes up to its lyophilization. Later on, each portion was grinded and sieved at 80 mesh (1 mm).

The metal and semi-metal digestion was in accordance to the EPA 3051 method [26]. Analysis of Ag, Al, As, Ba, Ca, Cr, Co, Cu, Fe, Li, Mg, Mn, Mo, K, Sb, Sc, Na, P, Pb, V, Zn was performed by ICP-OES (Spectraflame, SPECTRO Analytical Instruments GmbH, Germany). Organic matter was measured in already dried samples gravimetrically at 500°C per 6 hours [27].

TABLE I
SAMPLE STATION DESCRIPTION AND GEOGRAPHICAL COORDINATES.

Sample station description	Geographical coordinates
Most degraded area close to Formiga Island.	23° 41'45.1"S 46° 43'59.6"W

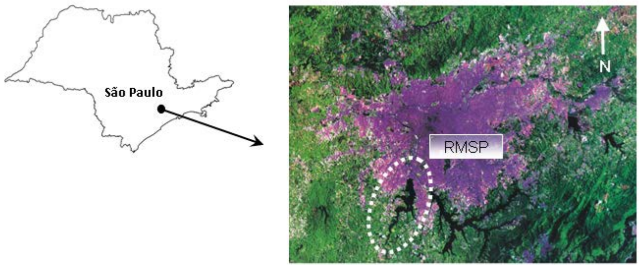

FIGURE. 1
LOCATION OF GUARAPIRANGA DAM

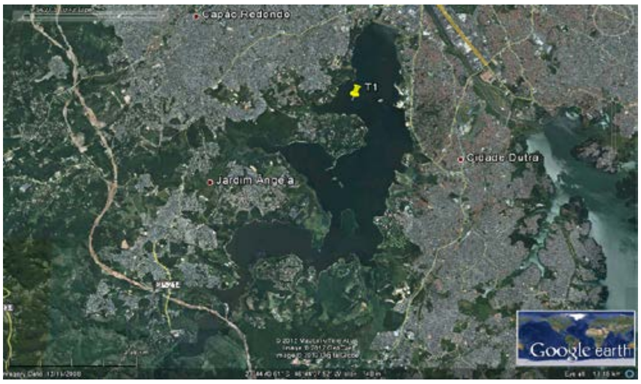

FIGURE. 2
LOCATION OF T1 COLLECTION POINT

RESULTS

Metal concentration trends

Copper, Zn and Pb sediment concentration profile is presented in Figure 3. Copper values from fractions 1 to 22 were 5 to 16 times PEL (197 mg kg^{-1}) and agree with the superficial sediment values reported by PADIAL, 2008 [21]. These results are related to the use of copper sulfate as algaecide, applied at Guarapiranga since the first bloom reported [28] in 1990. No concentration above the method limit of detection was found for Ag (< 0.8 mg kg^{-1}) and Mo (< 4.5mg kg^{-1}). Zinc values from fraction 44 (oldest) to the more recent ones presented a growing trend. At the fraction 15, TEL values were reached and zinc concentration is still increasing. The zinc anthropogenic source is related with the burning of vulcanized materials and fossil fuels in general [29, 30]. Zinc emission is almost the double when compared with lead's, according to CALLENDER and RICE [30]. Lead concentration in the sediment reached its maximum between fractions 31 and 33. The early portions presented a continuous decrease up to top. This is linked to the use of lead in fuel that occurred between 1950 and 1970 [30]. In Brazil, lead use was discontinued in 1989 and completely removed from fuel in 1992. This event can explain the decreasing Pb trend that started in fraction 31. The P, K and Mg profile is presented in Figure 4. Concerning P, it is possible to notice a small increase in its concentration from fraction 31 to 26, and more recently a significant increase in P concentration from fraction 26 to the top. This is a clear demonstration of the historical eutrophication process that the Guarapiranga Dam is going through. The sediments in the lower fraction (60 cm to the bottom) presented also an initial P value (around 1000 mg kg^{-1}) that was superior to the value from fraction 26 to 60. These earliest high values are related to the Dam fill in process. As a nutrient, P is clearly non conservative and its form and availability must be considered together with Fe. However, MOZETO et al. [31] mentioned the deepest P flux from sediments to water that can reach -7.7 mg cm $year^{-1}$ at 8.5 cm maximum. Below this depth, it is not expected any P mobility.

The majority of the elements such as Al, Ba, Ca, Co, Cr, Fe, K, Li, Mg, Na, Sb, Sc and V presented a general concentration distribution in the sediment profile, with low concentrations at the bottom, an abrupt increase up to twice the initial concentration occurring around from fraction 48 up to the top. The superficial fractions (0-2 cm) presented a small decrease in this most recent sediment, probably because of the unconsolidated material. Potassium (Figure 4), Co and Cr (Figure 5) exemplified the described behavior that is shared by the 13 of the 21 studied elements.

Arsenic average values in the Guarapiranga Dam sediment exceeded TEL (5.9 mg kg^{-1}) in almost 3 times, from the top to the fraction 28 and from fraction 35 to 50 (Figure 5). Due to an As uneven distribution that caused a larger standard deviation in fraction 17 and 28, it was not possible to state that TEL has exceeded in all the fractions from the top up to fraction 28. When As is present in a geological formation, it is frequent to reach a higher concentration level in the sediments. However, the As concentration in fractions below 55 (1.92±0.31 mg kg^{-1}) indicated that this is not applicable at Guarapiranga Dam.

Organic Matter

The organic matter OM percentage (dry matter) is presented in Figure 6. The percentage values increase from the top to the bottom. At fraction 49 and below it is observed that reaches the highest values associated with the minimum metal content, which indicates that OM and metals source changed. The most recent OM source is the local biota and the probable initial and oldest source OM is the Guarapiranga dam filling, that could be generated by roots and trees degradation [29].

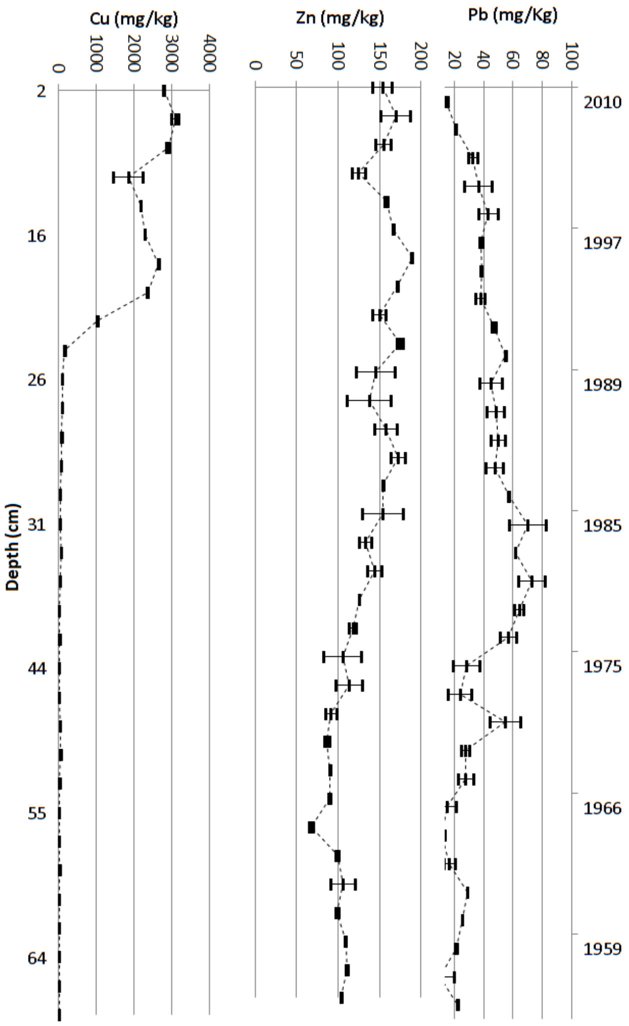

FIGURE. 3
TESTIMONIAL T1 Cu, Zn AND Pb CONCENTRATIONS (IN mg/kg)PER FRACTION WITH THE ESTIMATED TEMPORAL SCALE

Temporal trends

In order to evaluate the temporal data from a testimony, it is required to know the sediment deposition rate. In low anthropogenic activity areas, like natural lakes far from deforestation areas, Mozeto, Umbuzeiro e Jardim (2006) [29] mentioned a sedimentation rate lower than 0.1cm/year^{-1}.

In locations with high soil occupation and highly urbanized areas it is possible to find a rate from 2 to 3 cm year^{-1}. In the Promissão and Barra Bonita dams (Rio Tiete, SP), values from 1.25-1.5 cm year^{-1} and 2.0 cm year^{-1} were found, respectively [29]. In this work, the uniform sediment deposition rate of 1.25 cm year^{-1} was considered to estimate the temporal scale presented besides the metals profile. The Promissão Dam model seems to be the most similar data available with Guarapiranga Dam. Using this deposition sediment rate, it was possible to estimate the time period presented in Figures 3 to 5.

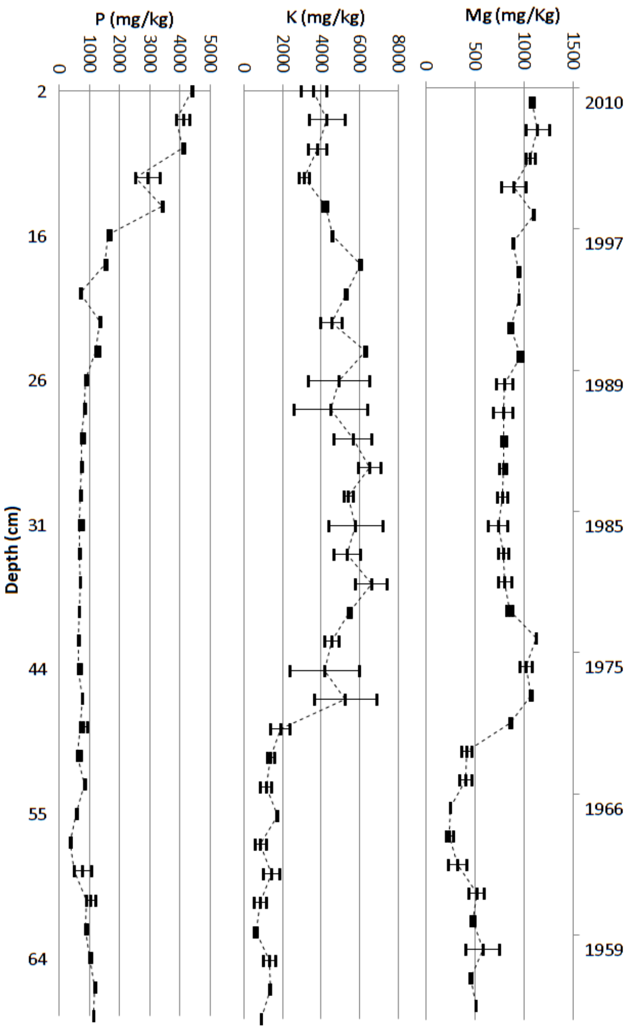

FIGURE. 4
TESTIMONIAL T1 P, K AND Mg CONCENTRATIONS (IN mg/kg)PER FRACTION WITH THE ESTIMATED TEMPORAL SCALE

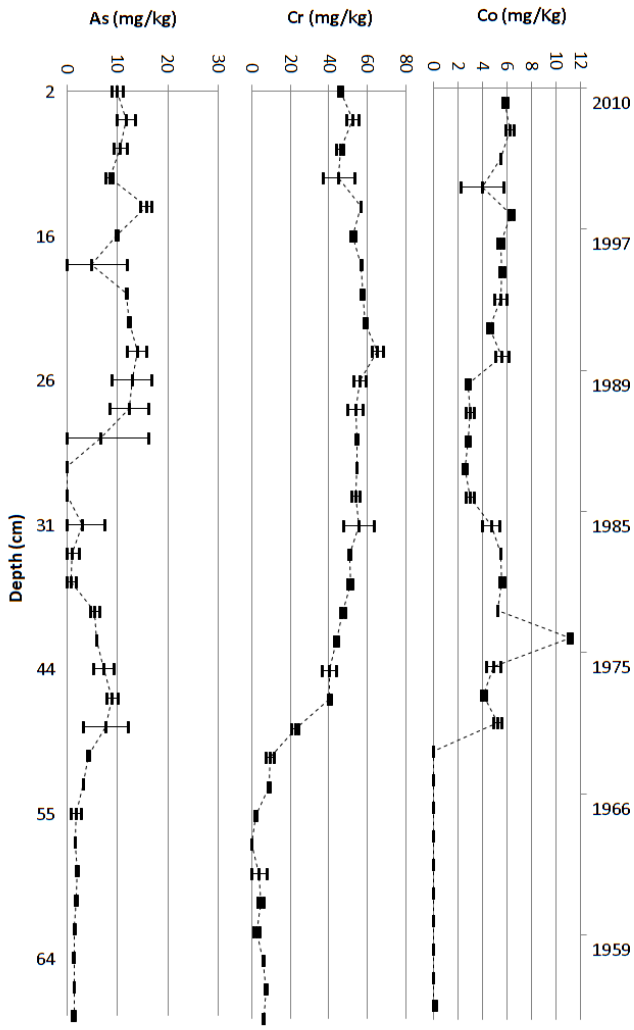

FIGURE.5

TESTIMONIAL T1 As, Cr AND Co CONCENTRATIONS (IN mg/kg) PER FRACTION WITH THE ESTIMATED TEMPORAL SCALE

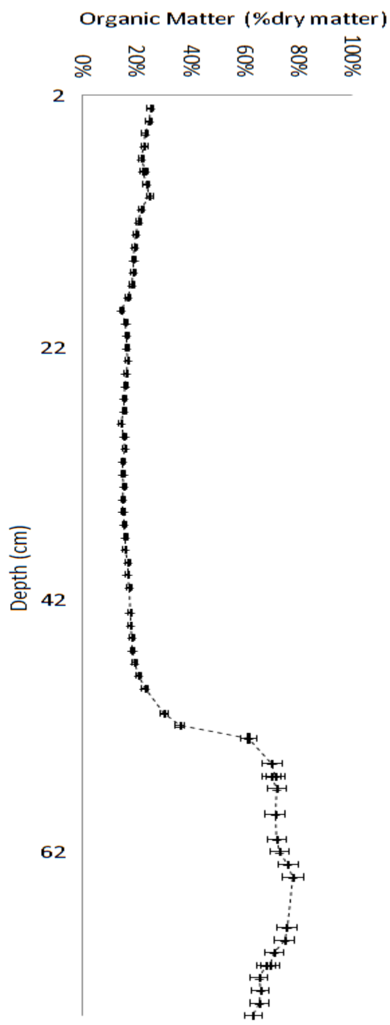

FIGURE. 6

TESTIMONIAL T1 ORGANIC MATTER (% DRY MATTER) PER FRACTION

Sao Paulo State records [32] mention the dam filling in 1906 and the urbanization starting in 1920, with a significant growth between 1950 and 1960. Social and environmental issues started in 1970 [32]. The algal blooms and the algaecide use started in 1990 and grow significantly from 1996 up to today [28]. Following this timeline, Cu, Pb, P, Cr, Co and OM values agree with the adopted model.

CONCLUSION

Sediments testimonies are useful tools that keep the environmental history from one particular site. Guarapiranga Dam use and occupation changed over time. This work proposed a timeline based in a sediment deposition model that seems to agree with the Guarapiranga Dam history and with some metals, P and organic matter profile. In the future, the ^{210}Pb and ^{226}Ra dating results will be compared with the present proposed model.

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