

METAL ASSESSMENT IN SEDIMENTS FROM THE GUARAPIRANGA RESERVOIR

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ABSTRACT

The study of the distribution of metals in sediments is very important from the point of view of environmental pollution once the sediment concentrates metals in aquatic systems and represents a relevant contamination monitor. The analysis of sediments has been used to evaluate the quality of aquatic systems in relation to the concentration of metals. This study aimed to assess sediment contamination by metals in the Guarapiranga Reservoir. Sediment and water samples were analyzed by ICP OES (Inductively Coupled Plasma Optical Emission Spectrometry) for As, Cd, Cr, Cu, Ni, Pb and Zn and by CV AAS (Cold Vapor Atomic Absorption Spectrophotometry) for Hg. The sediment samples results were compared to TEL (Threshold Effect Level) and PEL (Probable Effect Level) guidance values and RRV (Reference Regional Values). Geoaccumulation Index (I_{geo}) was calculated to evaluate metals pollution degree using reference values established for metals and metalloids in sediments from the Upper Tietê Basin and E_H -pH diagrams were applied to explain chemical forms and bioavailability of toxic metals in sediment samples. In general, most of the analyzed elements exceeded TEL values and Cr, Cu and Zn exceeded RRV guidelines. The high concentrations of Cu found in this reservoir can be explained by the frequent application of $CuSO_4$ algicide, mainly at sampling site S-03. The I_{geo} indicated moderated polluted sediments by Zn and moderately to extremely polluted sediments by Cu, especially at S-03, in agreement with the TEL, PEL and RRV values comparison. These results may indicate potential risk of the reservoir water quality.

1. INTRODUCTION

The Guarapiranga Reservoir is one of the main water supply in the São Paulo Metropolitan Region (SPMR), which is considered the largest and most populous Brazilian urban area, covering 8,000 km² of extension, with a population of almost 21 million inhabitants. The major challenge faced by local government is the constant search for public water supply solutions, mainly when it comes to provide sufficient water quality for its population [1-3]. The Reservoir watershed is located southwest of SPMR, in an area of approximately 63,911 hectares (639.11 km²), contributing with 20% of the water provided to the region, which represents a water supply for about 3,7 million people [3-5].

During the 1970s, there was an uncontrolled urban occupation in this region, causing environmental impacts and compromising the quality of water. In the following years, despite the efforts applied to protect the area, the problems were not fully solved. Guarapiranga Reservoir environmental impacts are caused especially due to untreated sewage discharge and

diffuse pollution, which represents all types of waste that are released and collected inappropriately, and discharged into the water bodies [1].

Sediment is a complex matrix of aquatic ecosystems and can be defined as the layer of mineral and organic particles frequently of thin granulometry. It is found at the bottom of the water bodies and often becomes a repository for many of the more toxic chemicals that are introduced into surface waters, especially toxic metals and organic compounds that can be transferred to the organisms that inhabit the region. Contaminated sediments represent a hazard to aquatic life through direct toxicity as well as to wildlife and human health through bioaccumulation in the food chain. For this reason, sediment has been used to assess the quality of aquatic environments, regarding the concentration of metals [6-8]. In this sense, the aim of this study was to assess sediment contamination by metals and metalloids in the Guarapiranga Reservoir.

2. MATERIALS AND METHODS

2.1. Sampling and Sample Preparation

Surface water and sediment samples were collected at three sites along the reservoir in three consecutive weeks during two sampling campaigns (March/April and September 2016) with the support of the Environmental Agency of the State of São Paulo (CETESB). The sampling site S-01 has Embu-Guaçú river as tributary, which receives treated sewage from the Embu-Guaçú county. S-02 suffers influence of the Billings reservoir waters transposition to Guarapiranga. S-03 is located near the State Company of Water Supply (SABESP) water supply catchment point and has presented anthropic contribution, due to frequent application of copper sulfate algicide to control algae proliferation in the reservoir. Guarapiranga Reservoir also has several polluted tributaries due to untreated sewage compromising water quality, especially for water supply [9].

Water samples were collected using a Van Dorn bottle and sediment samples by a Van Veen sampler, stored in pre-cleaned (HNO_3 10% solution) polyethylene containers. Direct measurements of Redox Potential (ORP) and pH were performed *in situ* using a pH/ORP sensor (Mettler Toledo), following CETESB guidelines of sampling [10]. Sediment samples were previously dried at 40°C in a ventilated oven until constant weight, ground in a mortar, homogenized and passed through a 2-mm sieve (US EPA, 2001). Sampling sites are shown in Fig.1 and the geographical positions and description of each sampling site are presented in Table 1.

2.2. Chemical Analysis

Approximately 0.5 g of total fraction samples (< 2 mm) and certified reference material Sandy Clay Soil (CRM 049 Sigma) were digested with 10 mL HNO_3 in a microwave digestion oven (CEM MDS-2100), according to EPA 3051A method [11]. After digestion sediment samples were transferred by filtration to 50 mL volumetric flasks, where the content was completed using ultrapure water. All reagents were of analytical grade. Digested sediment and water samples were analyzed for As, Cd, Cr, Cu, Ni, Pb and Zn using ICP OES (Thermo Cientific

ICAP 6300 DUO) and for Hg CV AAS (Perkin Elmer FIMS 100). Analytical quality control was performed by CRM Sandy Clay Soil analysis for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in sediment samples, whose measured and certified values were in agreement. Relative Error (RE) was between 1 and 19% for both campaigns. For water samples, the standard addition method was applied and analyte recovery was between 80 and 120%.

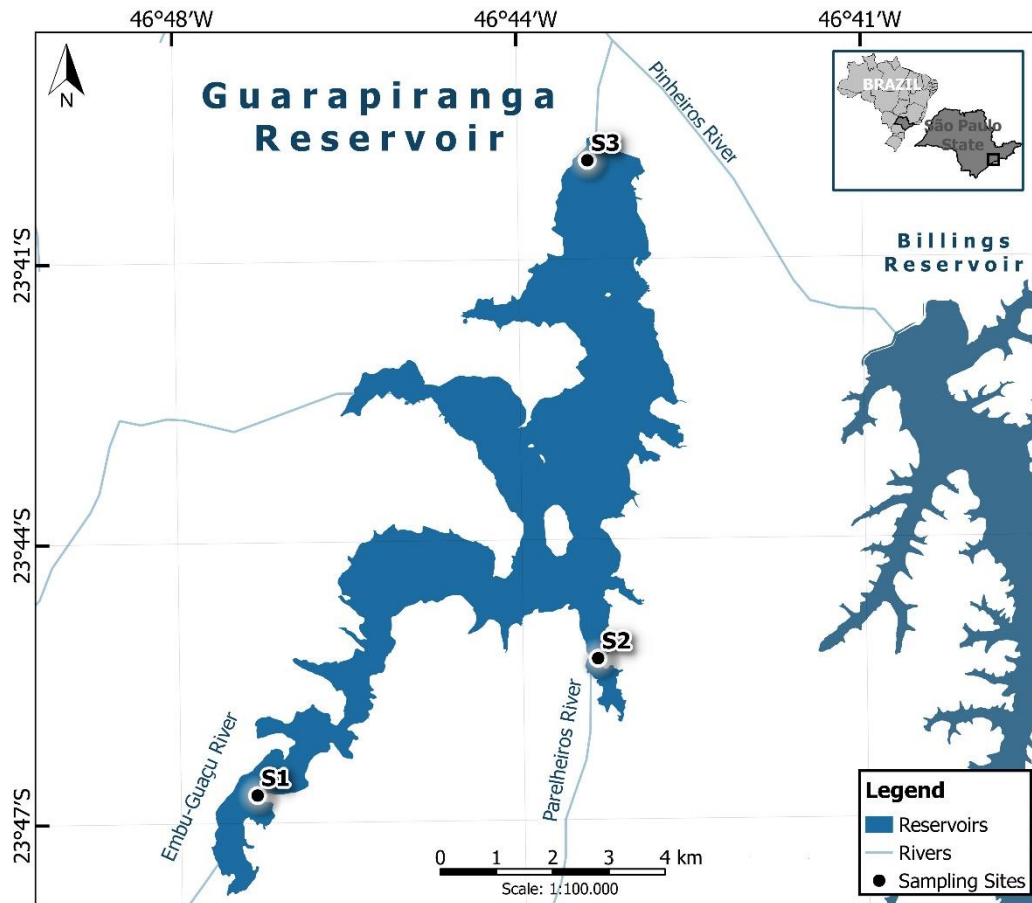


Figure 1: Sampling sites located at the Guarapiranga Reservoir.

Table 1: Description and geographical positions of the sampling sites

Site	Location	W	S
S-01	Tributary of the Embu-Guaçu River, about 2 km upstream of the Rodoanel bridge	46°47'12"	23°46'32"
S-02	In the middle of the Parelheiros River tributary, in the Balneário São José neighborhood	46°43'37"	23°45'15"
S-03	Left shore next to the SABESP's water catchment point in the reservoir	46°43'40"	23°40'27"

3. RESULTS AND DISCUSSION

Table 2 presents sediment samples results for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn, compared to guidance values established from the Canadian Council of Ministers of the Environment (CCME) for aquatic life protection, TEL (Threshold Effect Level) and PEL (Probable Effect Level) and RRV (Regional Reference Values) for the Upper Tietê Basin, that were used to assess the area's contamination degree [12-13]

In the first campaign, occasional adverse effects on aquatic biota for all sampling sites and probable adverse effects on aquatic biota were expected, due to the high concentrations of Cu, especially for S-03. For the elements As, Cr, Ni, Pb and Zn, occasional adverse effects on aquatic biota, at least for one sampling site, was expected.

For the second campaign, all sampling sites demonstrated potential adverse effects on aquatic biota, due to the presence of Cr, Pb and Cu, and probable adverse effects on aquatic biota, due to the high concentration of Cu in S-03. For the elements As, Ni and Zn, occasional adverse effects on aquatic biota at least for one sampling site was expected. Cd and Hg results did not exceed TEL values for both campaigns.

Cr and Zn concentrations exceeded RRV for all sampling sites, except the results for S-03 in campaign 1. Cu results exceeded RRV for all sampling sites, especially in S-03, where the highest values were found. As, Cd, Hg, Ni and Pb values did not exceeded RRV for both campaigns, except Ni value for S-03 in campaign 2 and Cd value for S-03 in campaign 1. In general, it was not observed significative variations in metal and metalloids concentrations among the three consecutive samplings, for both campaigns, except for Cr, Cu, Pb and Zn elements, mainly for S-03.

Metal and metalloids concentrations in surface water samples are shown in Table 3. The results presented for S-02 and S-03 were reported by CETESB [9]. Water results for the studied elements were below the detection limits of the analytical techniques applied (ICP OES and CV AAS), except Cr in the first campaign, and Cu in both campaigns.

CETESB has been evaluating sediment quality since 2002 to improve the assessment of aquatic ecosystems quality. Currently, the monitoring site used by CETESB for sediment quality assessment is next to the SABESP's water catchment site in the reservoir. Besides that, there is a monitoring site for water quality located in the middle of the Parelheiros River tributary and both sites coincide with the samplings sites of this study, S-03 and S-02, respectively. In 2015, the Guarapiranga Reservoir was considered polluted by chemical substances, according to Sediment Quality Criteria (SQC) of CETESB, as well as observed in previous years, indicating highly polluted sediments, with metal and metalloids concentrations virtually constant in relation to historical data. Furthermore, the reservoir was classified as super eutrophic and eutrophic for S-02 and S-03, respectively, which indicates a highly eutrophic environment [9,14-15].

Pompêo *et al.* [16] performed a study in the Guarapiranga Reservoir to assess sediment quality regarding Cd, Cu, Cr, Ni and Zn levels. The results indicated contamination by Cu in sediments, due to application of copper sulfate algicide. The authors concluded that the metals analyzed are not bioavailable for assimilation by aquatic biota and therefore, there is no probable toxicity. However, water column oxygenation may allow metals bioavailability, which can affect reservoir water quality.

Guimarães [17] found concentrations above PEL values for Cu in Guarapiranga sediment, especially in sites next to SABESP's catchment point. Cr, Pb and Zn results exceeded TEL values in the Embu-Guaçu River tributary and Cr, Cu, Ni, Pb and Zn results exceeded TEL values in the Parelheiros River tributary, indicating possible adverse effects on aquatic biota. Furthermore, Enrichment Factor (EF) and I_{geo} indexes showed significative enrichment for Zn in relation to Guarapiranga soil values, which indicates moderately polluted sediments, according to I_{geo} classification, which is an evidence of anthropic contribution.

Table 2: Metals concentration ($mg\ kg^{-1}\ dw$, $n = 3$) in Guarapiranga reservoir sediments compared to TEL, PEL and RRV

Element	Site	Mean among samplings	Range	Mean among samplings	Range	^[12] TEL ($mg\ kg^{-1}$)	^[12] PEL ($mg\ kg^{-1}$)	^[13] RRV ($mg\ kg^{-1}$)
		Campaign 1		Campaign 2				
As	S-01	11.8	10.8 - 12.3	12.9	11.7 - 14.4	5.9	17	23
	S-02	10.3	7.21 - 12.9	7.01	6.69 - 7.39			
	S-03	2.92	< 2.00 - 6.76	4.34	3.23 - 5.47			
Cd	S-01	< 0.50	-	< 0.50	-	0.6	3.5	0.22
	S-02	< 0.50	-	< 0.50	-			
	S-03	0.38	< 0.50 - .63	< 0.50	-			
Cr	S-01	54.2	49.9 - 57.0	51.9	43.5 - 57.9	37.3	90	36
	S-02	44.7	34.4 - 51.3	37.8	31.9 - 43.3			
	S-03	23.9	7.91 - 46.5	52.2	36.3 - 65.5			
Cu	S-01	38.8	32.0 - 49.5	39.1	38.6 - 40.0	35.7	197	18
	S-02	275	156 - 420	54.5	37.3 - 72.2			
	S-03	1583	42.5 - 4567	2099	728 - 3430			
Hg	S-01	0.10	< 0.10 - 0.13	< 0.10	-	0.17	0.49	0.14
	S-02	0.11	< 0.10 - 0.16	< 0.10	-			
	S-03	< 0.10	-	0.13	< 0.10 - 0.21			
Ni	S-01	21.3	18.7 - 23.4	17.1	16.5 - 18.0	18	35.9	23
	S-02	16.4	11.6 - 23.7	11.6	11.2 - 12.2			
	S-03	17.1	10.3 - 22.8	29.2	19.9 - 34.0			
Pb	S-01	40.5	31.2 - 55.1	41.4	38.7 - 43.9	35	91.3	61
	S-02	41.3	35.9 - 44.6	41.1	38.9 - 44.2			
	S-03	24.9	9.67 - 52.6	37.1	30.5 - 49.8			
Zn	S-01	150	110 - 202	142	128 - 165	123	315	82
	S-02	86.5	46.0 - 116	84.1	73.8 - 94.4			
	S-03	67.8	31.4 - 136	129	102 - 145			

dw = dry weight.

Table 3: Metal and metalloids concentrations (mg L⁻¹) in the Guarapiranga Reservoir water samples

(mg L ⁻¹)		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Campaign 1	S-01	-	-	-	-	< 0.0002	-	-	-
	¹⁹ S-02	-	< 0.0007	0.03	0.01	< 0.0002	< 0.02	< 0.009	< 0.02
	¹⁹ S-03	< 0.01	< 0.0007	0.03	0.03	< 0.0002	< 0.02	< 0.009	< 0.02
Campaign 2	S-01	< 0.01	< 0.0007	< 0.02	0.01	< 0.0002	< 0.02	< 0.009	< 0.02
	¹⁹ S-02	-	< 0.0007	< 0.02	0.02	< 0.0002	< 0.02	< 0.009	< 0.02
	¹⁹ S-03	< 0.01	< 0.0007	< 0.02	0.06	< 0.0002	< 0.02	< 0.009	< 0.02

n = 3 (S-01); n = 2 (S-02 and S-03).

Metals solubility is controlled by pH and E_H conditions. In bottom sediments, there is a sufficient supply of sulfur. The combination with low pH and moderate to high redox potential status presents the most favorable conditions for the solubilization of many metals, which may induce mobility and bioavailability of toxic metal cations [18].

Redox potential and pH results in sediment samples are presented in the Table 4. Only two results are presented since there are only data for two samplings of each campaign. Redox potential results were corrected to the reference electrode used for direct measures performed *in situ* [19].

Table 4: E_H and pH values in sediments from three sampling sites located at the Guarapiranga Reservoir

Site	Campaign 1				Campaign 2			
	Sampling 1		Sampling 2		Sampling 1		Sampling 2	
	pH	E _H (mV)	pH	E _H (mV)	pH	E _H (mV)	pH	E _H (mV)
S-01	6.60	-10.0	6.93	148.0	6.57	60.2	6.10	229.1
S-02	6.76	-67.0	6.48	156.6	6.52	-80.0	6.10	147.0
S-03	6.96	92.0	6.40	86.1	7.20	94.0	6.48	85.1

E_H-pH diagrams are practical and useful tools for understanding geochemical element behavior. These diagrams depict the dominant aqueous species and stable solid phases on a plane defined by the E_H and pH axes [20]. In this study, E_H and pH diagrams were applied to explain chemical forms and bioavailability of the potentially toxic metals (Cr, Cu, Ni, Pb and Zn) analyzed in the Guarapiranga sediment samples.

The E_H-pH diagram assessment demonstrated that Cu, Ni and Zn elements were present predominantly as ionic forms (Cu⁺, Cu²⁺, Ni²⁺, Zn²⁺), and for the elements Pb and Cr, the ionic complex forms (PbOH⁺, CrOH²⁺) were predominantly present in the two campaigns. Sediment samples presented reduction environment conditions, with E_H values between 300 and -100 mV. According to zones of potential redox conditions ORP process explain that Cr, Cu, Ni, Pb and Zn elements were dissolved in the sediment matrix [18].

The Geoaccumulation Index (I_{geo}) is a common approach that can be applied to evaluate trace metals and metalloids pollution in surface sediments. This index was proposed by Muller [19] and has been widely used in contamination studies since then. The I_{geo} was calculated for metals using the following expression:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 \cdot B_n} \right) \quad (1)$$

Where:

Log₂ - base 2 logarithms.

C_n -element content in sediment sample.

B_n -element content in the geochemical reference values used (background).

The factor 1.5 is employed to minimize possible variations of the background values due to lithogenic variations in the sediment [22]. In this study, reference values for metals and metalloids in sediments from the Upper Tietê Basin were used as geochemical background reference for the I_{geo} calculations. These regional guidelines are more adequate to evaluate the studied aquatic ecosystem, instead of global references [13].

Geoaccumulation Index is categorized into seven classes, composing a qualitative scale of pollution based on the numerical value of the index, as shown in Table 5. According to the classes established for I_{geo}, the analyzed sediment samples can be considered moderately polluted by Zn and moderately to extremely polluted by Cu, especially at S-03, in agreement with the TEL, PEL and RRV values comparison.

Table 5: Classification of pollution levels according to Geoaccumulation Index [21]

I _{geo}	I _{geo} -class	Description of sediment quality
> 5	6	Extremely polluted
4-5	5	Strongly to extremely polluted
3-4	4	Strongly polluted
2-3	3	Moderately to strongly polluted
1-2	2	Moderately polluted
0-1	1	Not polluted to moderately polluted
0	0	Not polluted

Table 6: I_{geo} values for sediment samples using reference values established for metals and metalloids in sediments from the Tietê River Basin as background values [13]

Element	Campaign 1			Campaign 2		
	S-01	S-02	S-03	S-01	S-02	S-03
As	-1.55	-1.75	-3.56	-1.42	-2.30	-2.99
Cd	-0.40	-0.40	0.20	-0.40	-0.40	-0.40
Cr	0.01	-0.27	-1.17	-0.06	-0.52	-0.05
Cu	0.52	3.35	5.87	0.54	1.01	6.28
Hg	-1.07	-0.93	-2.07	-2.07	-2.07	-0.69
Ni	-0.70	-1.07	-1.01	-1.01	-1.58	-0.24
Pb	-1.18	-1.15	-1.88	-1.14	-2.98	-1.30
Zn	0.29	-0.51	-0.86	0.20	-0.55	0.07

4. CONCLUSIONS

The concentration values for the elements As, Cd, Cr, Cu, Hg, Ni, Pb and Zn obtained in the sediment samples can be an important and useful tool to assess the contamination degree by metals and metalloids in this reservoir. In general, the concentration results for the elements As, Cr, Ni, Pb and Zn exceeded TEL values for most of the sampling sites and the high concentrations of Cu, mainly at S-03 exceeded PEL values. When using regional guidelines, Cr, Cu and Zn concentrations exceeded RRV for most of the sampling sites. The highest values of Cu element were found at S-03. The Geoaccumulation Index for Guarapiranga sediment samples demonstrated moderated polluted sediments by Zn and moderately to extremely polluted sediments by Cu, especially at S-03, in agreement with the TEL, PEL and RRV values comparison. The E_H -pH diagram assessment showed that Cr, Cu, Ni, Pb and Zn elements were present predominantly as ionic forms and dissolved in the sediment matrix. It should be noted that Cu is frequently used as an algicide in the reservoir, as $CuSO_4$, which explain the high concentration of this metal, mainly in S-03. These results may indicate potential risk of the reservoir water quality.

ACKNOWLEDGMENTS

The authors thank to CETESB (Companhia Ambiental do Estado de São Paulo) for sample collection and analysis and CNEN (Comissão Nacional de Energia Nuclear) and CNPq for financial support.

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