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Papers

Metals in the Sediments of Reservoirs: Is There Potential Toxicity?

Karen de Souza Ferreira¹

Bárbara Rani-Borges²

Gustavo Laranjeira Melo Santos³

Sheila Cardoso-Silva⁴

Lilian Rose Marques de Sá⁵

Marcelo Pompêo 600

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Abstract

Metals are important recognized for their potentially toxic character to communities, in addition to being bioaccumulative in some organisms. In this work, the concentrations of cadmium, chromium, copper, lead, mercury, and zinc in sediments from three sampling points in the Billings, Guarapiranga, and Rio Grande reservoirs (São Paulo, Brazil) between the years 2008 and 2017 were evaluated. Data were compared to regional reference values, to local legislation, and to sediment quality values: threshold effect level (TEL), probable effect level (PEL), and Sediment Assessment Criteria (CQS). Billings reservoir sediment samples had the highest number of metals with contents above the reference values and above the PEL. There were high copper concentrations in the Guarapiranga and the Rio Grande reservoirs probably due to the management system currently in use, which is based on Copper Sulphate Pentahydrate. The data analyzed here indicate that the lack of regionalized indexes with background values and toxicity criteria for sediment, specific for each of these reservoirs, is a great problem for more accurate and predictive analysis. This study shows that the current contamination levels of the reservoir sediments are reducing the water.

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¹Universidade Estadual Paulista - UNESP, Sorocaba, SP, Brazil. kferreira@unesp.br

²Universidade Estadual Paulista - UNESP, Sorocaba, SP, Brazil. barbara.rani-borges@unesp.br

³Universidade Estadual Paulista - UNESP, Sorocaba, SP, Brazil. gustavo.laranjeira@unesp.br

⁴Universidade Federal do Acre (UFAC), Rio Branco, AC, Brazil. she.cardosos@gmail.com

⁵Universidade de São Paulo - USP, São Paulo, SP, Brazil. liliansa@usp.br

⁶Universidade de São Paulo - USP, São Paulo, SP, Brazil. mpompeo@ib.usp.br

INTRODUCTION

Aquatic environments are continuously contaminated by substances of anthropic origin, especially industrial and domestic effluents. contaminants may reach several terrestrial and aquatic compartments and cause toxic effects to the biota (PEREIRA EBECKEN, 2009; HUERTA et al. 2013; LÓPEZ-DOVAL et al., 2017). Among pollutants, metals are the most relevant, as they can accumulate in chain, form harmful food complex compounds that critically affect different biological functions and, when present in water supply reservoirs and power generation, can be extremely harmful (PAUL et al., PROSHAD et al., 2018). Such events occur because metals cannot be degraded by natural processes persisting in sediments, from where they are gradually released into bodies of water (PAUL; SINHA, 2015). For this reason, many regulatory agencies consider sediment contamination as one of the main risks to the aquatic environment, since many organisms spend most of their life cycle living in sediments (SADIQ; ALAM, 1992).

The physicochemical and mineralogical properties of background sediment in aquatic ecosystems affect geochemical behavior and the bioavailability of metals for aquatic biota. In this sense, changes in the conditions of these environments play a crucial role in the processes of geochemical speciation, bioavailability, and metal toxicity (DIAGBOYA et al., 2015; LU et al., 2016). The contaminants adsorbed to the sediment represent a source of constant contamination, since the sediment is a natural reservoir for the deposition of these metals. Sediment can also be considered a transforming environment, since it interacts with the biota and organic matter and interferes in oxygen contents, which are factors that may modify the toxicity of the metals present there (SIQUEIRA; APRILLE, 2012; VOIGT et al., 2016).

are potentially toxic chemical Metals compounds with carcinogenic, mutagenic, teratogenic, and allergenic properties. They are considered harmful to the biota, therefore studying them is relevant and the control of these elements is essential for minimizing and controlling risks (MWINYIHIJA, GODECKE et al., 2012; BHUSARI, 2016). Among the metals most often found in aquatic environments that stand out for toxic levels are mercury, copper, cadmium, zinc, chromium, and lead (LUOMA; RAINBOW, 2008). Anthropic actions directly contribute to the increase in the levels of these metals in sediments (CETESB,

2016). Management companies are responsible for analyzing conditions and establishing criteria and methods to manage this problem.

The Guarapiranga, Billings, and Rio Grande reservoirs together supply drinking water for about 30% of the territory of the Greater São Paulo (SÃO PAULO, 2008), a region of high complexity where public management faces major challenges, including the problem of disposal of domestic and industrial wastewater and solid waste. Results of previous studies have shown that these three reservoirs already presented vulnerability regarding sediment toxicity levels, mainly due to the progressive deterioration of their water quality associated with urban expansion near the reservoirs (MARIANI; POMPÊO, 2008; POMPÊO et al, 2013; CARDOSO-SILVA et al, 2014). Therefore, continuous monitoring of these springs and evaluating the presence of metals in sediment are indispensable for an optimized control and management system of reservoirs.

In order to contribute to public management systems, the objective of this study is to evaluate and compare the concentrations of cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), and zinc (Zn) metals present in the sediments of São Paulo reservoirs from 2008 to 2017. This study submits the results to different criteria to evaluate sediment quality in order to observe the toxicity potential of these metals.

MATERIAL AND METHODS

Study area

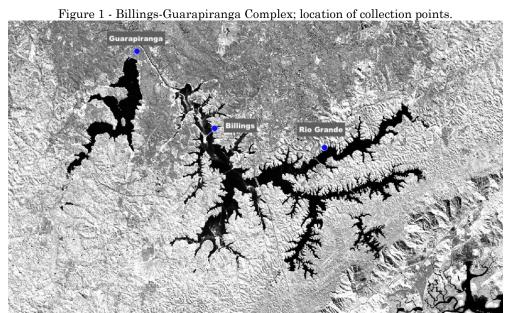
The Metropolitan Region of São Paulo (MRSP) is the largest and most urban agglomeration area in Brazil and one of the five largest in the world. It covers 39 cities and concentrates more than 21.4 million inhabitants (SÃO PAULO, 2021). The area of this study includes a water complex comprising two water reservoirs interconnected by the Taquacetuba arm, both with a large population in their surroundings, that supply about 6.4 million of habitants in the MRSP (PIRES et al., 2015; POMPÊO; MOSCHINI-CARLOS, 2012).

The Guarapiranga reservoir is supplied by a basin named after the Capivari, Monos, and Taquacetuba rivers (the latter connecting with the Billings Reservoir). Its length is approximately 630 km² covering different municipalities in the MRSP, such as Embu-Guaçu, Itapecerica da Serra, São Lourenço da Serra, Juquitiba, Embu, and São Paulo. It is

estimated that almost 800,000 inhabitants live on its shores and 60% of them are residents in the city of São Paulo (SABESP, 2008).

The Billings complex borders five municipalities of the MRSP and the southern region of the city of São Paulo. It also provides water by pumping it to the Henry Borden hydroelectric power plant in Cubatão, taking advantage of the potential of the descent of the Serra do Mar (ESCAMES, 2011).

In this study, we chose to collect data from three collection stations from the monitoring network of the Companhia Ambiental do Estado de São Paulo (CETESB), the state agency responsible for the environmental monitoring and assessment. One point is located in the Guarapiranga Reservoir (GUAR 0900) [23°40'27" S and 46°43'40" W], another in the Rio Grande Arm (RGDE 02900) [23°46'07" S and 46°32'00" W], and a third in the Billings Reservoir (BILL 02100) [23°44'57" S and 46°38'52" W (Figure 1).



Source: the authors (2021).

Laboratory sampling and analysis

In this work, we used the data collected in campaigns for the preparation of surface water quality reports of CETESB, during the dry season, autumn/winter period (between April and September) from 2008 to 2017. There were four collections in the Billings and Guarapiranga Reservoirs and six collections in the Rio Grande arm (CETESB, 2018). The metals of interest were selected and compiled either by toxicological risk or anthropic contribution.

The sampling was carried out in triplicate per sampling point with a distance of 250 m between each release. The samples of surface sediments (6 cm deep) were collected using a bottom sampler "Van Veen" with 0.020 m² of inlet. Samples were then removed from the sampler using plastic shovels, packed in plastic pots, transported to the laboratory under refrigeration, and kept at $4 \pm 2^{\circ}$ C until drying (ANA, 2011). The sediment samples were previously dried at 103-105°C in an oven; for mercury, this process was performed at a

temperature below 60°C, so that there would be no loss by volatilization. After this process, the samples were crushed and sieved in a sieve of 2 mm to homogenize before the determination of metals using optical emission spectrometry with plasma (ICP-OES) following the protocol 3051A United States Environmental Protection Agency) – USEPA (2007a) For mercury, the method used was USEPA 7473 (2007b) by thermal decomposition - atomic absorption spectrometry (TDA-AAS).

Data analysis

Criteria for assessing sediment quality

The concentration values of metals in the sediment samples were compared with the guiding values, threshold effect (TEL), probable effect (PEL) of Canadian Council of Ministers of the Environment (CCME, 2001), and Sediment Evaluation Criteria (CQS) (CETESB, 2008), the Conselho Nacional do Meio Ambiente (Conama) Resolution No. 454/2012, which nationally guides the maximum concentrations in class 1

and 2 water bodies for sediments to be dredged (BRASIL, 2012) and regional reference values (VRR) for the Alto Tietê (NASCIMENTO; MOZETO, 2008). Tables 1 and 2 show information on TEL, PEL, CQS, Conama No. 454/12, and VRR. The guiding CQS values were based on toxicological variables that classify sediments into five classes (excellent, good, regular, poor and very poor) toxicity acute/sublethal assays with the amphipod Hyalella azteca and reverse mutation assay (known has ames test), which were formulated from the relationship of biological

effects and the cause-effect relationship at various stages of life. The bioavailability and toxicity of the metals in the sediment were also taken into account (CETESB, 2004).

According to CCME's (2001) guide values adopted in TEL, the probability of the adverse effect on organisms occurring is practically ruled out, while in pel this adverse effect is probably certain. Therefore, intermediate values to TEL and PEL are in a "transition zone," in which the effects of toxicity in organisms are uncertain. For values below VRR, they only indicate a natural contribution resulting from the weathering that occurs in the basin.

Table 1 - Guidance of sediment toxicity in relation to probable effect values, threshold effect, regional reference values for the Tietê River Basin for the analyzed metals and reference values established by CONAMA for Water Bodies Class 1 and 2. PEL: probable effect; TEL: threshold effect; VRR: Regional Reference Values; Cadmium (Cd); chromium (Cr); copper (Cu); lead (Pb); mercury (Hg); and zinc (Zn).

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Metal	TEL	PEL	VRR	CONAMA Class 1	CONAMA Class 2
			mg kg-1		
Cd	0,6	3,5	0.22 ± 0.08	0,6	3,5
Cu	35,7	197	18 ± 6	35,7	197
\mathbf{Cr}	37,3	90	36 ± 7	37,3	90
Hg	0,13	0,7	0.14 ± 0.05	0,17	0,48
Pb	35,5	91,3	61 ± 7	35	91,3
Zn	123	315	82 ± 14	123	315

Source: the authors (2021).

Table 2 - Qualitative classification of sediments in relation to the presence of the metals analyzed is defined according to the values of probable effect (PEL), threshold effect (TEL), regional reference values (VRR), and their classification colors. Cadmium (Cd); chromium (Cr); copper (Cu); lead (Pb); mercury (Hg); and zinc (Zn).

Makal	Qualitative of sediments (mg kg ⁻¹)							
Metal	VERY GOOD	GOOD	REGULAR	BAD	VERY BAD			
Cd	< 0,24	0,24 - 0,6	0,60 - 3,50	3,5 - 35	> 35			
Cu	< 18	18 - 35,7	35,7 - 197	197 - 1970	> 1970			
Cr	< 30	30 - 37,3	37,3 - 90	90 - 900	> 900			
$_{ m Hg}$	< 0,13	0,13-0,16	0.16 - 0.70	0.7 - 7	> 7			
Pb	< 35,5	35,5 - 61	61 - 91,3	91,3 - 913	> 913			
Zn	< 82	82 - 123	123 - 315	315 - 3150	> 3150			
classification	< VRR	> VRR < TEL	> TEL < PEL	PEL - 10x PEL	> 10x PEL			

Source: the authors (2021).

Statistical analysis

Statistical processing was performed by principal component analysis (PCA). PCA was used to assist in understanding the distribution and geochemistry of metals over time and space. Statistical analyses were developed with Logies data using the software PAST 3.0 (HAMMER et al., 2001).

In the preparation of the PCA, the year 2016 was excluded from the analysis because there was no sampling in two of the three reservoirs. This occurred due to the transposition of waters from the Taquacetuba arm (Billings Dam) to Guarapiranga for the public supply during the water crisis in the metropolitan region of São Paulo (CETESB, 2016). For metals that had

unrealized years (NR), the average between the subsequent two years when available was recorded.

RESULTS

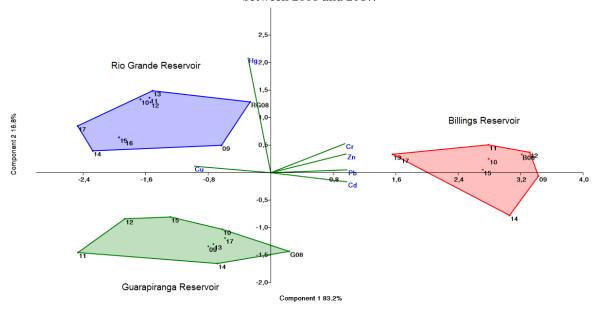
Table 3 shows the results of the metal analyses in the sediments from 2008 to 2017 in the Billings, Guarapiranga, and Rio Grande reservoirs. The high concentrations of copper in Guarapiranga and Rio Grande reservoirs stand out. Also, the Rio Grande has the highest copper concentrations and the lowest coefficient of variation compared to those of Guarapiranga. However, the rest of the Billings complex also

presents worrying concentrations of various other metals. In addition to Cu, there are Hg values above the VRR, which is suggestive of probable toxic effects to biota, mainly in the Rio Grande reservoir.

Table 3 - Concentrations of metals in the surface sediments of Billings, Guarapiranga, and Rio Grande reservoirs between 2008 and 2017. The values are colored according to the qualitative classification of sediments in relation to the presence of the metals analyzed. Levels are defined according to the values of probable effect, threshold effect, and regional reference values (blue: very good; green: good; yellow: regular; orange: bad; red: very bad). NR: Not realized; SD: Standard deviation; CV: Coefficient of variation; maximum and minimum values for each metal are highlighted in bold. The values presented as <0.1 and <0.5 are below the detection threshold.

37	Billings (mg kg ⁻¹)							
Year	Cd	Cu	Cr	Hg	Pb	Zn		
2008	NR	220	237	0,62	112	493		
2009	3,76	191	176	0,42	149	470		
2010	3,13	191	178	0,68	99,5	465		
2011	3,71	234	211	0,86	79,4	568		
2012	4,05	198	189	0,77	129	496		
2013	1,68	98,9	216	0,88	53,2	238		
2014	3,37	215	183	0,14	105	486		
2015	3,13	216	169	0,51	94,4	493		
2016	NR	NR	NR	NR	NR	NR		
2017	1,5	163	124	0,9	75,5	378		
Mean	2,4	173	168	0,6	90	409		
SD	1,5	72	67	0,3	42	169		
CV	63	42	40	54	46	41		
Year		Guarapiranga (mg kg ⁻¹)						
Tear	Cd	Cu	Cr	Hg	Pb	Zn		
2008	NR	1.859	72,9	0,14	77,8	119		
2009	1,11	2.525	56,7	0,16	NR	138		
2010	4,34	2.269	59,1	0,32	38,5	130		
2011	0,4	1.885	37,4	0,19	35,6	92		
2012	0,3	2.257	50,1	0,32	48,7	132		
2013	0,92	3.991	64,4	0,14	62,8	160		
2014	0,53	916	61,5	<0,1	75,4	99		
2015	0,81	4.295	60,3	0,31	48,3	157		
2016	NR	NR	NR	NR	NR	NR		
2017	1,01	4.326	56,8	0,18	78,8	152		
Mean	0,94	2.432	52	0,21	47	118		
SD	1,26	1.430	20	0,09	29	47		
CV	134	59	39	42	63	40		
37	Rio Grande (mg kg ⁻¹)							
Year	Cd	Cu	Cr	Hg	Pb	Zn		
2008	NR	3.129	84,8	4,43	62,3	335		
2009	1,29	4.596	75,1	1,77	NR	NR		
2010	0,56	2.448	75,8	7,64	50,8	101		
2011	0.88	5 620	83,1	7,21	48,3	120		
2012	0,88	5.639	00,1	1, <u>41</u>	10,0			
2012	0,94	4.317	72,1	7,21	NR	117		
2012								
	0,94	4.317	72,1	7,20	NR	117		
2013	$0,94 \\ 0,92$	4.317 4.436	$72,1 \\ 74,2$	7,20 9,47	NR 50	117 122		
$2013 \\ 2014$	0,94 0,92 0,54	4.317 4.436 4.923	72,1 74,2 41,5	7,20 9,47 2,59	NR 50 48,7	117 122 107		
2013 2014 2015	0,94 0,92 0,54 0,42	4.317 4.436 4.923 5.824	72,1 74,2 41,5 68,4	7,20 9,47 2,59 2,52	NR 50 48,7 52,5	117 122 107 114		
2013 2014 2015 2016	0,94 0,92 0,54 0,42 <0,5	4.317 4.436 4.923 5.824 5.866	72,1 74,2 41,5 68,4 52,7	7,20 9,47 2,59 2,52 2,76	NR 50 48,7 52,5 59,4	117 122 107 114 120		
2013 2014 2015 2016 2017	0,94 0,92 0,54 0,42 <0,5 0,46	4.317 4.436 4.923 5.824 5.866 5.796	72,1 74,2 41,5 68,4 52,7 47,1	7,20 9,47 2,59 2,52 2,76 4,71	NR 50 48,7 52,5 59,4 46,7	117 122 107 114 120 99,7		
2013 2014 2015 2016 2017 Mean	0,94 0,92 0,54 0,42 <0,5 0,46	4.317 4.436 4.923 5.824 5.866 5.796 4.697	72,1 74,2 41,5 68,4 52,7 47,1	7,20 9,47 2,59 2,52 2,76 4,71	NR 50 48,7 52,5 59,4 46,7	117 122 107 114 120 99,7		

Figure 2 - Principal Component Analysis (PCA) of cadmium, chromium, copper, lead, mercury, and zinc concentrations in the surface sediments of Billings (B), Guarapiranga (G), and Rio Grande (RG) reservoirs between 2008 and 2017.



Source: the authors (2021).

DISCUSSION

Considering the mean concentrations of metals in relation to the values provided for by the CONAMA Resolution no. 454 (BRASIL, 2012) for sediments in class 1 and 2 waterbodies, the three reservoirs exceed the legal values established for toxic metals (Table 1). The Guarapiranga reservoir complied only regarding zinc; in the Billings reservoir, chromium is the element that stands out the presenting almost twice concentration allowed for class 2; in the Rio Grande reservoir, copper presented concentration up to 30 times higher than that established by the resolution, and this shows the great potential of contamination of the biota. These high values were observed by Silva et al. (2017), with 24,350 mg Kg⁻¹ and Frascareli *et al*. (2018), 2,914 mg Kg⁻¹ also occurred in the Rio Grande reservoir.

The evaluation of sediment quality by the guide values TEL and PEL indicated that in the Billings reservoir, the sediment was classified as regular or poor for all metals, which was easily observed based on the color criterion (Table 3). The Guarapiranga and Rio Grande reservoirs presented a similar pattern, with bad quality for copper and good for lead and zinc, while the other metals (Cd and Cr) were classified as regular or bad.

The high levels of Cu are noteless, but Hg values are also worrisome, especially in the Rio

Grande reservoir. In addition to the values above the PEL, exerting probable toxic effects on the biota, the anaerobic conditions typical of the hypolimnion of the Rio Grande reservoir (MARIANI; POMPÊO, 2008) may favor the methylation of Hg. In these conditions, Hg can cross any cell barrier (CRESPO-LÓPEZ et al., 2021) and can be biomagnified, that is, its concentrations could tend to increase at each trophic level. This is worrying from the point of view of environmental and public health because fish consumed in the region may eventually present concentrations above those recommended by the World Health Organization and reach fish consumers. Hg is among the ten most toxic chemicals according to public health guidelines (WHO, 2017). It is a teratogenic element and exposure to it, even in small amounts, may lead to irreversible deleterious consequences on the central nervous system (CRESPO-LÓPES et al., 2021).

Copper is generally present in reservoir sediments at large concentrations due to the applications of the algicide copper sulfate (CuSO₄.5H₂0), used in the control of phytoplankton flowering (PADOVESI-FONSECA; PHILOMENO, 2004). In São Paulo reservoirs, the application of CuSO₄ has been occurring since the late 1970s. In recent decades, hydrogen peroxide has also been used as an alternative in the management of algae growth, especially cyanobacteria (CETESB) 2008; POMPÊO et al. 2013), which could decrease the amount of CuSO₄ applied.

However, the Cu contents observed in Guarapiranga and Rio Grande reservoirs sediments are high.

In Rio Grande, copper concentration values were 136 to 326 times higher than the regional reference values (VRR) for Alto Tietê (using the maximum and minimum concentration values and the value of 18 as the VRR value) (Table 2). In the Guarapiranga reservoir, the values were between 51 and 240 times above the VRR; and, in the Billings reservoir, where there is no constant application of the algicide, the values were 5.5 to 12.2 times above the VRR. In general, higher Cu concentrations are observed in the dam region, a site of crude water collection, both in Guarapiranga (LEAL et al., 2018, POMPÊO et al. 2013) and in Rio Grande (MARIANI; POMPÊO, 2008). These higher concentrations in the dam region are worrisome since this is the place where water is captured for public supply.

Even in the Billings reservoir, where there are no applications of CuSO₄, only in four years, Cu values were below the PEL, evidencing a great potential of contamination to the biota because concentrations such as those observed in this study have the potential to be a serious threat to microbial communities in the sediment, benthic macroinvertebrates, and fish (BEGHELLI et al. 2016; YANG et al. 2018; SUTCLIFFE et al. 2018; XIA et al. 2019).

ofThe presence metals at high concentrations in sediments can be a strong indicator of anthropic interference possibly resulting from the release of industrial sewage and land occupation around the basin (KORB; SUERTEGARAY, 2014). As the PCA figure shows (Figure 2), there is a tendency to increase Cu levels in Guarapiranga and Rio Grande reservoirs. Considering that both have a similar treatment and management systems based on the use of copper sulfate, they may exert a great influence on the concentration of this metal in the sediment. In the Billings complex, the origin of high metal concentrations is probably associated with the sporadic reversal of the waters of the Pinheiros River, a procedure that aims to regulate the flow and prevent floods in the State capital. The metals Cu, Cd, Hg, and Zn presented concentrations above the PEL, suggesting that the sediment may be a potential toxicity risk to the biota. Values above the PEL were previously found for Cu by Mariani & Pompêo (2008) $(1,644 \pm 1,067 \text{ mg Kg}^{-1})$ and Leal et al. (2018) $(1,241 \pm 1,135 \text{ mg Kg}^{-1})$ in Rio Grande and Guarapiranga, respectively.

Regarding Cd, Pb, and Zn, the most worrisome reservoir is Billings, as it has concentrations at levels close to or above the TEL. CSQ qualifies this sediment as regular or poor. For the other reservoirs, the concentrations of these metals are classified as good and eventually regular in one-off years.

Thus, it is evident that the type of management carried out in the reservoir may contribute to the increase in sediment toxicity, such as the eventual transposition of the Pinheiros River, the application of chemicals, or even the lack of supervision of irregular land occupation around springs (FRANKLIN *et al.*, 2016; PADOVESI-FONSECA; PHILOMENO, 2004; ALVIM *et al.*, 2015).

It is also notable that, based on the results of the PCA, there is a gradient between the reservoirs: Billings has the lowest sediment toxicity potential, although it is classified as poor, for all metals in most years studied. It is followed by Guarapiranga, with poor quality for Cu and regular for the other metals in most years. The Rio Grande reservoir is considered the potentially most toxic as for Cu (very bad quality in all years) and Hg, which has a poor and poor quality throughout the study period, respectively. These results are in accordance with Silva (2013), comparative studies on the reservoirs of the Rio Grande arm of Billings, Guarapiranga, and Paiva Castro. The results of acute toxicity tests of water with Daphnia similis suggest that the Rio Grande arm is potentially more toxic than the other reservoirs studied. On the other hand, the tests of acute sediment toxicity, also with D. similis, were more significant regarding the toxic potential of the Rio Grande sediment, which is considered toxic in all seasons and collection periods, followed by Guarapiranga and at last by Paiva

Another aspect that should also be taken into account are the routine applications of CuSO₄, the death of microalgae, and the subsequent lysis of the cell wall, causing the release of metabolites in water, such as cyanotoxins (POMPEO, 2017). Cyanotoxins are secondary metabolites produced by cyanobacteria and are in various classes with different mechanisms of action and characteristics of their own. They may cause numerous damage to water quality, human health and animals (MANCINI et al., 2010; SÁ et al., 2010; BORTOLI; PINTO, 2015; FONSECA et al., 2015; MACHADO et al., 2016; REGO et al., 2020). Sonobe, Lamparelli e Cunha (2019) indicating that these episodes of toxic blooms may be more frequent if there is no control of the entry of organic matter into the spring. Thus, due to the potential risks that the presence of cyanobacteria in water bodies poses, the main preventive measure should be the control of disordered growth. This is because the enrichment of aquatic ecosystems is important especially with regard to nitrogen and phosphorus. These elements are the main responsible for the intense growth of phytoplankton, particularly cyanobacteria. Thus, it is important to discuss the adoption of new forms of management of the São Paulo reservoirs, which in general prevent the growth of potentially toxic cyanobacteria and are not routinely used to control their growth.

Regarding temporal analysis, in this study, the reservoirs did not present a sudden change in sediment quality. There was not enough variation to reflect changes in ecotoxicological risk compared to the period analyzed. In the Billings reservoir, the quality varied between regular and poor despite the good classification for Pb and Hg in 2013 and 2014, respectively. In the Guarapiranga reservoir, the concentrations were between good and regular, with the exception of Cd in 2010 (bad) and Hg in 2014 (very good). In the Rio Grande reservoir, the quality variation did not present a regularity in the classification of quality in the same way as it occurred for the other reservoirs. There was an improvement in concentrations of Pb and Zn, worsening for Hg and regular for Cd. The results obtained make it clear that in the Rio Grande and Guarapiranga reservoirs, due to the systematic application of Cu-based algicides, this element had its concentrations increased in the Rio Grande and Guarapiranga reservoirs over time: two to three times the values of the initial concentration, respectively. Secondly Leal et al. (2018), in more than 40 years of routine applications of copper sulfate in Guarapiranga, 4,530 tons are estimated to be applied to the reservoir solely related to the Cu element.

Finally, factors such as high concentrations of organic matter and pH can modify sediment toxicity, act as metal complexing phases, and decrease the bioavailability of these contaminants in the medium (USEPA, 2005; MARIANI & POMPÊO, 2011). The particle size of the sediment may also favor or not the adsorption of metals; the smaller the grain size, the larger the contact surface and the complexation levels (LUOMA; RAINBOW, 2008).

FINAL CONSIDERATIONS

The systematic application of copper sulfate as a control solution of photosynthesizing

organisms, which grow greatly due to the high rates of organic load in the Rio Grande and Guarapiranga reservoirs, has been increasing the level of the potential toxicity of sediments of these environments and putting this chemical compound in evidence. Supporting managers with reliable data on the levels of sediment contamination by metals is essential. They should base their decisions on data generated through constant monitoring of reservoirs, which can help in the decision-making process for the most appropriate management of water resources.

As observed in this work, the comparison of sediment metal concentrations' toxicity and quality guiding values suggest that the biota is at risk, but an integrative view of these data is also necessary because the aquatic environment is dynamic, and many factors can interact with metals and interfere with the availability of metals to the water column and thus may negatively affect the biota.

The irregular occupation and the release of effluents into the reservoirs seem to be largely responsible for the loss of quality of the studied springs, which intensifies the responsibility of management companies. To ensure an efficient management, it is essential to establish regionalized values and criteria for sediments and to draft and implement public policies that aim adequate sanitary sewage disposal and supervision of occupation in the vicinity of the springs. In doing so, water resources providers of the MRSP will be safeguarded from the pressure of continuous population growth. Therefore, it is essential to have a balance in the management of water resources, so that it meets each other's environmental, public health, and the various uses of this resource.

In addition, laboratory and even *in situ* experiments with toxicity tests using various organisms and with the sediment of these reservoirs should be routinely carried out in order to evaluate the potential toxicity levels of these sediments not only based on quality guides and concentrations.

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AUTHORS' CONTRIBUTION

Karen de Souza Ferreira conceptualized, researched the literature, analyzed the data and wrote. Bárbara Rani-Borges carried out the bibliographical research, analyzed the data and wrote. Gustavo Laranjeira Melo Santos carried out the bibliographical research, analyzed the Cardoso-Silva wrote. data and Sheila Curatorship wrote, revised and edited the data. Lilian Rose Marques de Sá curated, drafted, revised and edited the data. Marcelo Pompêo managed the projects, supervised, curated data, wrote, revised and edited.



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