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Ecotoxicology and geostatistical techniques employed in subtropical reservoirs sediments after decades of copper sulfate application

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Abstract Spatial distribution linked to geostatistical techniques contributes to sum up information into an easier-to-comprehend knowledge. This study compares copper spatial distribution in surface sediments and subsequent categorization according to its toxicological potential in two reservoirs, Rio Grande (RG) and Itupararanga (ITU) (São Paulo—Brazil), where copper sulfate is applied and not applied, respectively. Sediments from 47 sites in RG and 52 sites in ITU were collected, and then, copper concentrations were interpolated using geostatistical techniques (kriging). The resulting sediment distributions were classified in categories based on sediment quality guides: threshold effect level and probable effect level; regional reference values (RRVs) and enrichment factor (EF). Copper presented a heterogenic distribution and higher concentrations in RG (2283.00 ± 1308.75 mg/kg) especially on the upstream downstream, associated with algicide application as well as the sediment grain size, contrary to ITU (21.81 ± 8.28 mg/kg) where a no-clear pattern of distribution was observed. Sediments in RG are predominantly categorized as "Very Bad", whereas sediments in ITU are mainly categorized as "Good", showing values higher than RRV. The classification is supported by the EF categorization, which in RG is primarily categorized as "Very High" contrasting to ITU classified as "Absent/Very Low". Copper total stock in superficial sediment estimated for RG is 4515.35 Ton of Cu and for ITU is 27.45 Ton of Cu.

Keywords Ecotoxicology · Spatialization · Copper sulfate · Variogram · Geostatistics

Introduction

Physical changes in the environment mainly in warmer areas lead to changes in the hydrological cycle, and systems (precipitation patterns and evapotranspiration, among others) must be counted (Chang

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et al., 2015; IPCC, 2021). Reservoirs, being hybrid ecosystems, are not only influenced by human activities but natural factors as well, such as climate change (Chang et al., 2015). Changes in the global temperature are expected; this will concern not just the physical environment; aquatic organisms will experience changes in their metabolism and phenology (Daufresne et al., 2009). Aquatic species have different responses to natural and artificial trends or adaptations to a non-equilibrated environment (Roland et al., 2012).

One visible effect of this unbalance, due to the lack of sanitary plans, is the artificial eutrophication as a consequence of the excessive inputs of nutrients such as phosphorus and nitrogen, leading to algal bloom events and cause public health problems due to toxins in some cyanobacteria species (dos Santos Machado et al., 2022; Haiming Wu et al., 2017; Yang et al., 2020). With global warming, these algal blooms tend to become more frequent (Hou et al., 2022; Paerl & Huisman, 2008). The blooms can affect the drinking water supply processes increasing costs of chemical products employed to remediate water organoleptic properties (Ko & Sakai, 2021; Leal et al., 2018). In this context, algal bloom control before treatment process is highly important.

Copper sulfate and hydrogen peroxide application are widely used for algal bloom control around the world (Anderson et al., 2019; Hullebusch et al., 2003; Kansole & Lin, 2017; Marcelo Pompêo, 2017; Reis & Capelo, 2022; Sklenar & Horne, 1999; Zhang et al., 2022). In the USA, there are application records since 1905 (McKnight et al., 1983) as well as in Fairmont lakes, Minnesota (Hanson & Stefan, 1984), and in Canada there are also records in small springs of farms (Alberta Agriculture, 1980, *apud* Prepas & Murphy, 1988). In São Paulo, Brazil, there are records of copper sulfate applications since 1979 in Guarapiranga reservoir (Mancuso, 1987). $CuSO_4$ is responsible for increasing the regional reference value (RRV) up to 120 times (Cardoso-Silva et al., 2021; Leal et al., 2018).

Due to its wide acceptability and low cost, copper sulfate and hydrogen peroxide are some of the cheapest and quickest solution to avoid algal blooms (Leal et al., 2018; Zhang et al., 2022). Despite its natural presence in the terrestrial crust, copper is considered a toxic metal in aquatic communities (Cervi et al., 2021; Luoma & Rainbow, 2008). High copper concentrations reduce algal cell division up to 50% causing cellular lyses (Hadjoudja et al., 2009; Haiming Wu et al., 2017), and hydrogen peroxide effectively inhibits the metabolic activity and photosynthesis in a very short time (Zhang et al., 2022).

In the aquatic environment, metals, e.g., copper, tend to accumulate in sediment at the bottom of the reservoir. In certain environmental conditions, those metals can be released to the water column again. The main concern is the accumulation of metals in the aquatic environment from anthropogenic activities including fertilizers leaching, domestic and industrial sewage (Frascareli et al., 2018; Melo et al., 2019; Pedrazzi et al., 2013; Wengrat et al., 2019). Thus, sediment needs to be constantly monitored to understand transport and suspension processes in aquatic environments, from a spatial standpoint (Alexander et al., 1993; Hao et al., 2021; Melo et al., 2019) which is useful to assess the bioavailability of those potential pollutants (Cardoso-Silva et al., 2016a; b).

Sediment quality guidelines (SQGs) have been applied to characterize sediments according to its toxicity potential. The SQGs developed by the Canadian Environmental Agency present the TEL (threshold effect level) and PEL (probable effect level) (CCME, 1999), which is widely applied and recognized by the scientific community (Broce et al., 2022; Cardoso-Silva et al., 2016a, b; Leal et al., 2018; Yüksel et al., 2022). Concentrations below TEL suggest toxic effects are unlikely to occur; values above PEL indicate that the toxic effects are likely to occur; meanwhile, the toxic effect when concentrations are between TEL and PEL is uncertain. However, sediment characterization is incomplete since it does not demonstrate the metal origin. Therefore, enrichment factor is a means to measure the metal concentration increase considering another reference element in the lithosphere (D. S. Lee et al., 1994; Mohan & Krishnakumar, 2022; Pan et al., 2022). The reference element must be a metal, used to quantify the degree of pollution (P.-K. Lee et al., 1997; Passos et al., 2022; Hongchen Wu et al., 2022) to differentiate the natural or anthropogenic origin (Bern et al., 2019; Cardoso-Silva et al., 2021; Martins et al., 2021).

In order to assess the metal's toxic potential, it is necessary to evaluate the sediment quality with representative number of sampling sites that cover the area of interest. Combining traditional sampling techniques and the geostatistical approach, to plot the spatial distribution of certain element. For this purpose, it is possible to employ the kriging interpolation method (Golia et al., 2021), widely used for mining activities (Belkhiri et al., 2017; Guo et al., 2018; Jia et al., 2018) as well as in reservoir assessments (Oladosu et al., 2019; Rakhmatullaev et al., 2011) or lakes (Kostka & Leśniak, 2020) assessments and even few studies that provide the toxic potential of metals in the sediment of reservoirs (Chen et al., 2018; Leal et al., 2018). This method uses geostatistical models such as autocorrelation among a cloud of points to create predictions with specific weights for the collected points. These weights are based in the distance and its spatial autocorrelation (Baux et al., 2022; Szatmári et al., 2022).

Kriging considers the anisotropy, which is related to the spatialization of natural events, assuming that the area of interest does not present a uniformity from one point to another. This method takes into account how a given property varies in space through the variogram function (Saito et al., 2021). The difference between kriging and other interpolation methods relies how weights (properties under analysis) are distributed among all sampling sites. In addition, kriging provides unbiased estimates with minimal variance (Ferreira et al., 2013). Those weights are calculated from the spatial analysis, which is based on the experimental variogram. There are distinct types of kriging divided in linear and nonlinear models (Saito et al., 2021). Finally, due to the natural events happening in the environment and the lack of uniformity, particular events or properties cannot be mapped by simple mathematical functions (Ferreira et al., 2013).

Despite the copper pollution evidence in Rio Grande reservoir (Cardoso-Silva et al., 2021; Mariani & Pompêo, 2008), no study explored in a wide manner the sediment in these reservoirs. As far as it is known, this is one of a few studies (e.g., Leal et al., 2018) developed in subtropical reservoirs associating metal analysis, toxicological quality categorization and the kriging technique. This research presents a relevant contribution to geochemistry performed in reservoirs and results can be applied in other geographical contexts with the same or other metal contamination. It has been expected that: (a) Rio Grande reservoir (RG) with a major urban pressure, added to the lack of a proper sewage treatment system, shows higher copper concentrations in sediment than Itupararanga reservoir (ITU). (b) The sediment in ITU, located inside an Environmental Protection Area, presents copper values lower than the threshold level. (c). The management in these reservoirs led to copper accumulation since their installation originated from human applications.

The objectives of the present research are to: (1) evaluate copper concentration, its stock and its spatial distribution in surface sediments of two reservoirs; (2) assess toxicity and categorize sediments using Sediment Quality Guidelines and Enrichment Factors; (3) analyze the water quality management applied in two reservoirs, with and without copper sulfate applications.

Study area

General description

Rio Grande (23°45′46″*S* 46°29′49″*W*) and Itupararanga (23°36′49″*S* 47°20′18″*W*) reservoirs are located in the Billings–Tamanduateí subbasin and in the high course of Sorocaba river, respectively. RG belongs to Alto Tietê hydrographic basin; meanwhile, ITU, to the Middle Tietê watershed, São Paulo State, Brazil (Fig. 1). Rio Grande reservoir (RG) has been isolated from the Billings Complex, through the Anchieta dam in 1982, intended for drinking water supply to 1.2 million people from São Bernardo do Campo, Santo André and Diadema municipalities, but it also receives domestic sewage from the surrounding area (Wengrat et al., 2019). RG is at an altitude of 750 m, it has an area of 7.4 km^2, an inlet volume of 194 m^3/s, an average depth of 26.2 m and a residence time of 306 days (Cardoso-Silva et al., 2021). According to the Köppen classification, the region has a humid subtropical climate (Cwa), characterized by summer rains with an average annual precipitation of 1500 mm.

The area is dominated by the Atlantic Forest and is originally formed by dense ombrophilous forest (Copobianco & Whately, 2002). However, due to intense urbanization, the vegetation has been restricted to small patches. Anthropogenic activities occupy an average of 27% of the basin, 20% of which are considered urban areas (Bonzi et al., 2017). It is estimated that around 900,000 people live in its drainage area, most of them in irregular settlements (Bonzi et al., 2017). For the year 2017, about 75% of

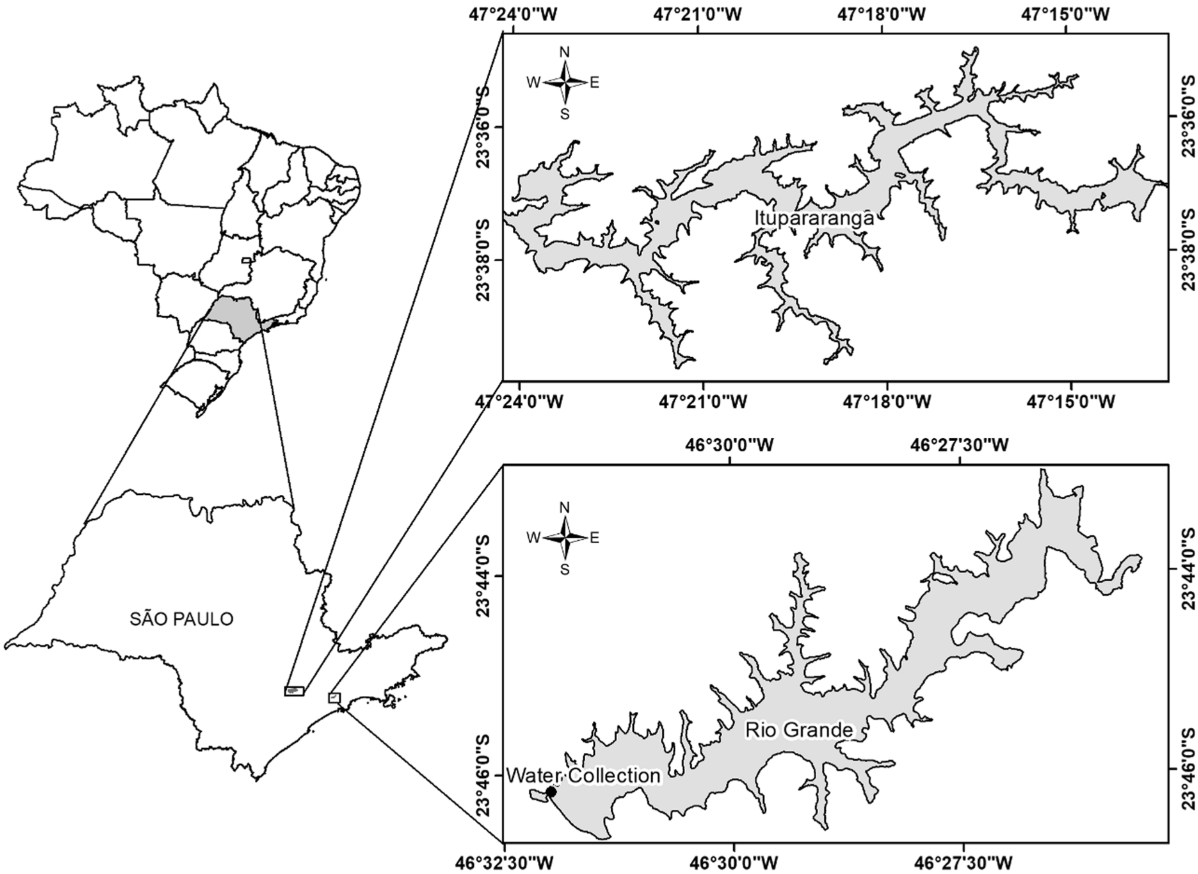

Fig. 1 Study area, Itupararanga reservoir (scale, 1:120,000) and Rio Grande (scale, 1:80,000)—São Paulo, Brazil. Itupararanga near the Metropolitan Region of Sorocaba and RG near the Metropolitan Region of São Paulo. The black point indicates the SABESP water collection site in RG

the sewage generated in the municipalities that make up the Rio Grande reservoir microbasin was collected and only 40% of this total was treated, which contributes to the eutrophication process in the region (CBH-AT, 2022). In Rio Grande reservoir (RG) (São Bernardo do Campo, SP—Brazil), copper sulfate pentahydrate has been applied since 1985 (Beyruth & Pereira, 2018) in order to control algal bloom.

Itupararanga reservoir (ITU) was built in 1912 by damming the Sorocabaçu, Sorocamirim and Una rivers; its drainage basin has a total area of 936.51 km^2 and covers Ibuúna, Piedade, São Roque, Cotia, Vargem Grande Paulista, Mairinque and Votorantim municipalities (Taniwaki et al., 2013). ITU belongs to an Environmental Protection Area (Área de Proteção Ambiental—APA) of Itupararanga since 1998, created by State Law *n*° 10.100, aiming to preserve the hydrological quality and important extensions of the Atlantic Forest Biome remnants as a wildlife refuge (Beu et al., 2011). ITU is at an altitude of 849 m, has an area of 26 km^2, a volume of 286 m^3, an average depth of 11 m and a residence time of 250 days (Cardoso-Silva et al., 2021). The region has also a humid subtropical climate (Cwa), characterized by summer rains with an average annual precipitation of 1370 mm.

In the Middle Tietê basin, where the Itupararanga reservoir is located, for the year 2016, 86.4% of the generated domestic sewage was collected and 64.6% was treated (CBH-MT, 2022). In Itupararanga reservoir (ITU) (Ibiúna, SP), there are no algicide application records for algae bloom control. Frascareli et al. (2018) evaluated three different areas in ITU and observed a spatial heterogeneity in copper distribution in sediments.

Geology and geomorphology

RG watershed is located in the Planalto Paulistano, covering part of the crystalline relief of the Planalto Paulista, according to Ross and Moroz (2011) classification, characterized by an area of granites, and some outcrops of mica schists and micaceous gneisses from the regional Precambrian formations (Ab'Saber, 2007). The most abundant minerals in the sediment, in decreasing order of importance, are such as kaolinite, vermiculite, illite, gibbsite and goethite (IPT, 2005).

In ITU, six major geological groups integrate the watershed: Massif Caucaia (9.24%), Cenozoic covers (10.64%), Embu complex (20.87%), Ibiúna Complex (48.54%), São Francisco Complex (4.24%) and São Roque Group (6.41%) (Secchin, 2012). Six shear zones are also present, covering periods from the Upper Middle Proterozoic to the Quaternary (FF, 2009). The predominant composition is monzogranites and syenogranites (Secchin, 2012). The morphological unit to which the hydrographic basin belongs is the Planalto Ibiúna/São Roque, where sharp hills and convex tops predominate (Ross & Moroz, 2011).

Material and methods

Bathymetry and morphometry

The bathymetric survey in RG was performed on April 13, 2016, and in ITU was carried out on September 21, 2017. This survey followed the method applied in (Leal et al., 2018), who navigated in a zigzag pattern through the reservoir to better describe the bottom of the reservoir. The followed track began near the dam and went upstream, maintaining a mean vessel speed of 17 km/h to reduce water disturbance. Data were collected using a Garmin Fishfinder GPSmap 421S paired to a data-log and georeferenced with Datum WGS84 and projection UTM 23S. This survey corrected its sampling error due to two previously known points located in bridges. The circuit, which covered all the extension of the reservoir, was performed in a zigzag pathway keeping a constant speed of 17 km/h to reduce the possibility of zones without data due to turbulence, the Fishfinder was placed at the stern (Bilhalva, 2013; Leal et al., 2018). This bathymetric sonar has been chosen since it is inexpensive, easy to install, manipulate and capable to storage large amount of data. It has to be considered that in ITU, additionally to data gathered in this study, another database collected by the Department of Biology from the Federal University of Sao Carlos, Sorocaba (2011), was employed. In that survey, an ecobathymeter model Bathy 500-MF® (Ocean Data), coupled to a GPS model GS20 Professional Data Mapper (Leica Geosystems), was employed. The bathymetric survey database for RG was 9,429 points, added to 4,186 additional points from the shoreline vectorization process and 47 points from the sediment sampling sites, with a total of 13,662 points. In ITU from the fish finder survey, we gathered 8,589 points, joined to the complementary bathymetric record list of 79,091 points and 28,439 points from the shoreline vectorization with a total of 116,119 bathymetric points. The benchmark used to correct water depth was 746.77 m in RG, from April 13, 2016 (SABESP, 2022), and 822,45 m in ITU from September 21, 2017 (ANA, 2022).

In order to calculate the accumulation of Cu, the morphometrical parameters were updated, throughout georeferencing and remote sensing techniques. To define the shoreline in RG and ITU was used Sentinel-2 imagery from the European Spatial Agency (ESA), of April 7th, 2016 and September 19th, 2017, respectively. The water portions were highlighted via the normalized difference water index (NDWI), which uses Band 3 (GREEN) and the near infrared (NIR) following: NDWI = (GREEN − NIR)/(GREEN + NIR) (McFeeters, 1996), both with a spatial resolution of 10 m. The vectorization was performed through a semi-automatic manner. The shoreline vector, together with the bathymetric data, was used for modeling the bottom of the reservoir, as well as for calculating the copper concentration to transform the bathymetric data into altimetry. The methodology described in Leal et al. (2018) and (Bilhalva, 2013) was followed, considering the altitude values.

The previous process resulted in a digital elevation model (DEM) applying the triangular irregular net (TIN) based in the Delauney criteria (circumscribed circumference) widely used due to its rapid interpretation and availability in geographic information system (GIS) software (Shelke et al., 2016). The sextant extension was to the DEM Sá (2018); these algorithms allowed to determine the partial slope aspect of sediment, in north–south (dY) and east–west (dX) for each pixel in the matrix, based in Horn (1981) criteria. With the UTM Datum and projection, the 2D and 3D surface area were calculated. The morphometric analysis was performed with QGIS v. 3.4.9 software and ArcGIS 10.4 software.

Sediment sampling and copper concentration assessment

Sediment sampling in RG (47 sites) was performed on November 16, 2017, and in ITU (52 sites) was on September 28, 2017. These collection sites we georeferenced (WGS84; UTM 23S) and distributed along the reservoirs to better understand the spatial variation in both study sites. Sediment sampling strategy followed the conditions employed in Leal et al. (2018). A collector-type Lenz (225 cm2) was employed, collecting 4 cm from the superficial sediment. The gathered samples were stored in collecting flasks (100 ml) completely loaded, kept in thermal bags and in the dark.

In the laboratory process, samples were dried in an oven at 50 °C and ground in a glass mortar. For near-total metal assessment (Cu and Al), the sediment was processed following the 3050B method from US EPA series SW 846 (U.S.EPA, 1996). The samples were stored at 4 °C prior to analysis of copper and aluminum by inductively coupled plasma atomic emission spectrometry (ICP-OES), using an Agilent Series 720 instrument. Analytical-grade reagents (obtained from Merck and Sigma-Aldrich) were used in all the analyses. All glassware items and equipment used to storage and processing the samples for metal assessment were left in 10% nitric acid for at least 24 h, followed by rinsing with ultrapure water. The accuracy of the data obtained was evaluated in recovery assays performed using sample solutions fortified with metals. These assays employed SpecSol® G16 V standard solutions containing 100 mg/L of the metals in 2% HNO_3. A value between 75 to 125% was considered as the acceptance criterion. The recovery efficiencies ranged from 89.67 up to 112.63%, and limits of quantification and detection were calculated according to Vogel (2000) (Table 1). The metal data were expressed as milligrams per kilogram of dry weight (mg/kg dw).

Spatial analysis and copper stock calculation

We applied the kriging interpolation method, using non-converted data (original values), to recognize and understand copper concentration distribution, using the GS + v. 7.0 software. Copper stock calculation was performed according to the equation used in Leal et al. (2018) Equation: $S = \left[\left(\frac{\mathrm{FS}}{\mathrm{Kv}} * \mathrm{SRS} * h\right) - (\mathrm{Wm})\right] * [\mathrm{Cu}] * 10^{-3}$, where FS/Kv is the ratio between fresh sediment and the container volume, SRS is the sediment surface, h is the sampler penetration, Wm is the mean water mass and Cu is the mean copper concentration in the reservoir.

The Grub test was applied to evaluate outliers. Following data normality and homogeneity was tested. A t test ($p < 0.05$) was performed to check whether mean copper concentrations were different between the two reservoirs and to evaluate whether metal concentrations were homogeneous along each reservoir. The calculations were performed using PAST 2.7 software (Hammer et al., 2001).

Enrichment factor and copper toxic potential assessment

The EFs were calculated as follows, EF = (Me/El)/(Mer/Elr), where Me/El is the ratio between the concentrations of the analyzed metal and the conservative element in the sample, and Mer/Elr is the ratio of the background values for the metal to be analyzed and the conservative element. Aluminum was used as

Table 1 Analytical recovery (AR) (%) from solutions with 0.10; 0.25; 0.50; and 1.00 mg/L and R^2 value of the calibration curves and limits of detection (LD) and quantification (LQ)

Metal	AR 0.10 mg/L	AR 0.25 mg/L	AR 0.50 mg/L	AR 1.00 mg/L	R^2	LD	LQ
Al	112.63	110.63	110.62	109.33	0.9997	0.007	0.024
Cu	105.56	101.27	89.67	90.29	0.9991	0.002	0.006

a conservative element (Förstner & Wittmann, 1981; Luoma & Rainbow, 2008), since aluminosilicates are part of the composition of the fine-grained fractions (< 63 µm, silt and clay) and are important metal-binding phases (Devesa-Rey et al., 2011). The EF categorization were labeled in five categories: absent/very low, moderate, considerable, high and very high (Table 2) according to the classification for enrichment factor described by Sutherland (2000).

This assessment was based on the Canadian Interim Sediment Quality Guidelines (ISQGs) such as TEL and PEL (CCME, 1999); simultaneously to the Regional Reference Values (RRV) for ITU (Cardoso-Silva et al., 2021) and RG (Nascimento, 2003). To categorize the ecotoxicological risk associated with sediment quality, five classes were labeled as follows: Excellent, Good, Regular, Bad and Very bad, as described in (Leal et al., 2018) (Table 3).

Results and discussion

Bathymetry and morphometry

Water depth (considering the shoreline as 0 m), in RG, varied from 0.4 to 13.2 m; in ITU from 0.35 to 22.21 m. The regions presenting the maximum values of water depth are located close to the dam in both reservoirs (Fig. 2), which agrees with the hydrographic patterns described by Sperling, 1999.

The calculated morphometric values are presented in Table 4, as well as previous studies developed in the areas. As observed, there are differences in the evaluated studies. We must consider that the bathymetry is variable, since it is influenced by weathering and sedimentation rates presented in the basin. This phenomenon of area, water depth and volume variation in RG and ITU can be assigned to seasonal characteristics, sedimentation and in specific the date when the satellite image has been taken.

Table 2 Classification for enrichment factor (EF) according to Sutherland (2000)

Classes				
absent/ very low	Moderate	Considerable	High	Very high
< 2	$2 \leq EF < 5$	$5 \leq EF < 20$	$20 \leq EF < 40$	> 40

Copper in sediment assessment

Copper mean values were significantly different between the two reservoirs and in each reservoir suggesting a heterogeneous distribution ($p < 0.05$). The spatial distribution concentrations in RG and ITU showed compartments (Fig. 3). In RG, there is a significant increasing, but disperse copper concentration in direction to the dam, this spatial heterogeneity is related to algicide application process. The company in charge of the drinking water treatment (SABESP) starts the algicide application near the dam, where the water collection for drinking water treatment occurs (Fig. 3), and continues in direction to the reservoir entrance (CETESB, 2018; Mariani & Pompêo, 2008). The Cu spatial heterogeneity can also be consequence of sediment re-suspension due to physical factors and granulometric influence, since fine-grained sediment (< 63 µm) presence increases from upstream to

Table 3 Qualitative classification of sediment according to Leal et al. (2018)

Classes	Limits/intervals	Ecotoxicological potential
Excellent	$0\ \text{mg/Kg} \leq [M] < RRV$	Region with minimal ecotoxicological potential. Basal concentrations
Good	$RRV \leq [M] < TEL$	Region with possible anthropic contamination, but with little to improbable ecotoxicological activity
Regular	$TEL \leq [M] < PEL$	Region with anthropogenic contamination of unknown ecotoxicological activity and medium occurrence probability
Bad	$PEL \leq [M] < 10{*}PEL$	Region with high ecotoxicological activity and occurrence probability
Very bad	$10{*}PEL \leq [M] < +\infty$	Region with maximum ecotoxicological effect and maximum occurrence probability

where *M* metal concentration, *RRV* regional reference value, *TEL* threshold effect level, *PEL* probable effect level, *10*PEL* ten times PEL

Cu data: RRV = 15 mg/kg; TEL = 35.7 mg/kg; PEL = 197.0 mg/kg

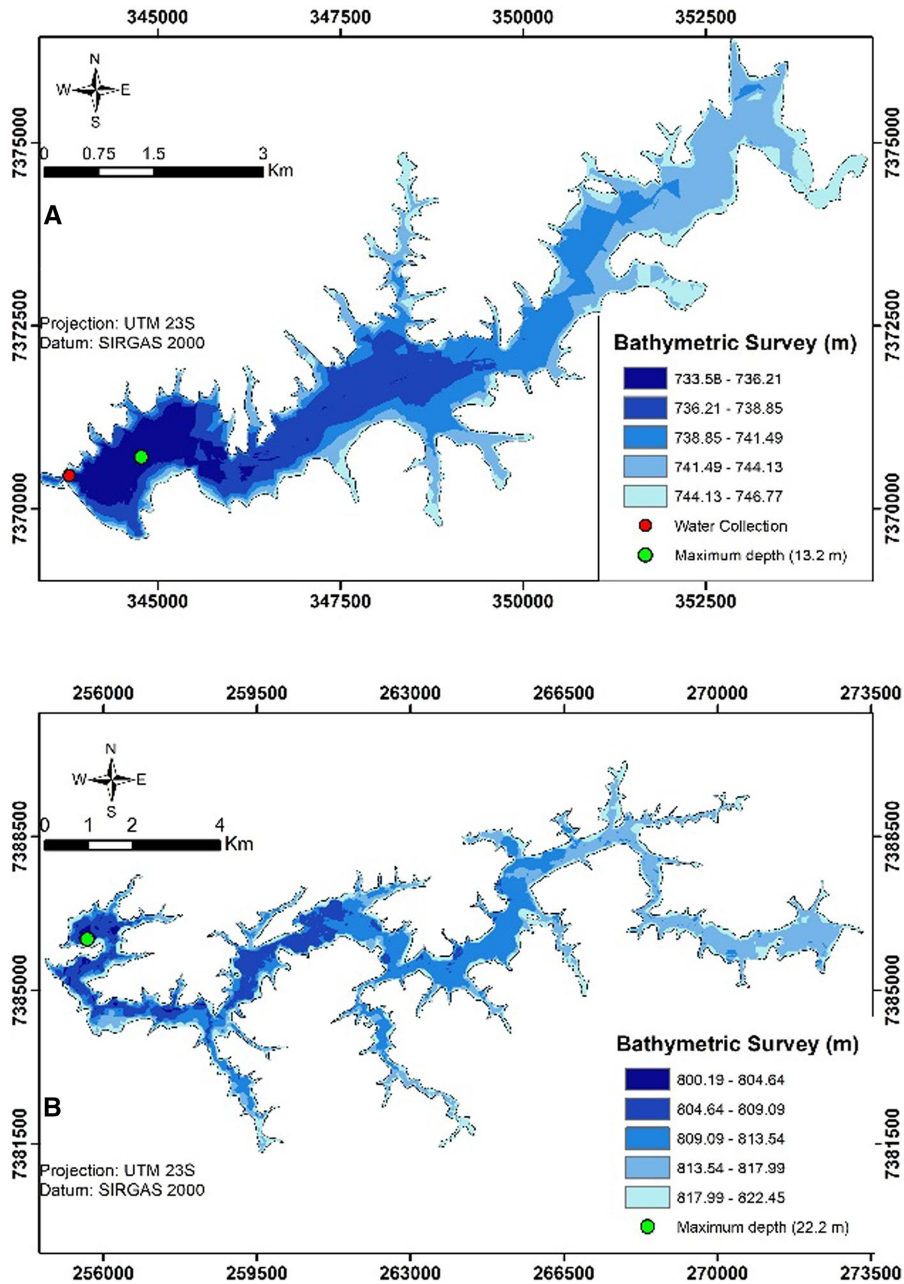

Fig. 2 Maps from the bathymetric surveys in **A** Rio Grande (Scale, 1:60,000) and **B** Itupararanga (Scale, 1:100,000). Darker colored zones represent deeper areas in the reservoirs; "Green" point shows the maximum depth in both reservoirs and "Red" point indicates the SABESP water collection. Water depth correction performed with 746.73 m in RG, and 822. 45 m in RG as benchmarks

downstream (Mariani & Pompêo, 2008; Frascarelli et al., 2018).

In ITU, there is no uniform distribution as well, the observed pattern can be associated due to the dendritic format, as well as the water flow by the reservoir tributaries in different points along the reservoir. However, areas where high copper concentrations are located close to zones intended to agriculture and urban expansion. Therefore, in geostatistical studies to evaluate contamination by metals, it is important to consider the main contamination sources, as well as the morphometry of the reservoir, whether dendritic or not, and if it predominantly follows the compartmentalization proposed by Kimmel et al. (1990).

It is possible to observe in Table 5 that the copper mean concentration in RG (2282.996 mg/kg) exceeds 12 × the PEL (197.0 mg/kg); also, the minimum concentration assessed (100.07 mg/kg) is 7 × the RRV

Table 4 Morphometric parameters from Rio Grande and Itupararanga reservoirs in a comparison with previously reported values for the reservoirs

Reservoir	Total planar area (km^2)	Sediment surface area (Km^2)	Perimeter (km)	Max. depth (m)	Mean depth (m)	Volume (hm^3)	References
	14.12	15.561	80.57	13.2	5.91	89.61	This study
	7.4	–	–	–	26.2	110	Frascareli et al. (2018)
Rio Grande	16.17	–	–	–	6	–	Wengrat et al. (2018)
	15	–	–	–	–	155	Maier et al. (1985)
	–	–	–	13	–	85	Souza et al. (2018)
	15	–	–	–	–	–	Barbieri and Godinho Orlandi (1989)
	23.28	30.949	199.61	22.21	9.19	174.83	This study
	29.9	–	–	–	7.8	260	Frascareli et al. (2018)
Itupararanga	24.48	–	–	–	7.8	–	Wengrat et al. (2018)
	–	–	–	–	–	249.58	ANEEL (2004)
	–	–	–	–	–	286	Smith and Petrere (2008)
	27.23	–	–	–	–	–	Beu et al. (2011)

value (Nascimento, 2003). Despite the high copper concentrations, a previous study suggested that Cu is not being bioavailable in RG because of the high levels of sulfide, organic matter, and the predominance of the grain size < 63 µm (Mariani & Pompêo, 2008). However, this does not mean that the metals are not exerting adverse effects. Study developed by Beghelli et al. (2016) show the bioaccumulation of Cu in a reservoir in which there are records of Cu only threefold the background.

In ITU, the copper mean concentration (21.82 mg/kg) is lower than TEL (35.7 mg/kg) value. However, the maximum concentration (56.62 mg/kg) is almost 3 × the RRV (Cardoso-Silva et al., 2021), indicating that it preserves its original characteristics, considering copper concentration in sediment, but there is evidence that are sites with copper accumulation that eventually could compromise the aquatic ecosystem.

Likewise, in Table 5, we can see that copper mean concentration, which Frascareli et al. (2018) previously reported in RG, is 21.65% higher than our data. Nevertheless, it is important to note that the authors evaluated only three sampling points, which does not necessarily indicate a decrease in copper values in the reservoir. Our research presents a much wider range of points showing more assertively the copper distribution along the reservoir. When comparing RG and Guarapiranga reservoir (GUA), which is another SABESP-managed reservoir, where copper-based algicides are applied as well, copper mean values in RG are 6.8% higher than the values in GUA (Leal et al., 2018; Marcelo Pompêo et al., 2013), which is preoccupant due to their morphometric differences (GUA is 10 km^2 bigger) indicating a higher pressure in RG. In the case of ITU copper mean concentration in sediment is similar to the values reported previously by Frascareli et al. (2018), this indicates a geogenic accumulation within the basin. When comparing RG and Paiva Castro (PC), a reservoir which presented CuSO4 applications in its main tributary (Cardoso-Silva, et al., 2016a, 2016b), the minimum copper concentration in RG is 5 × the maximum concentration in PC.

The application of copper sulfate, despite its low cost, is a palliative and controversial measure since it can promote a series of adverse effects on a variety of non-target aquatic species (Jančula & Maršálek, 2011) as many fish and aquatic invertebrate species

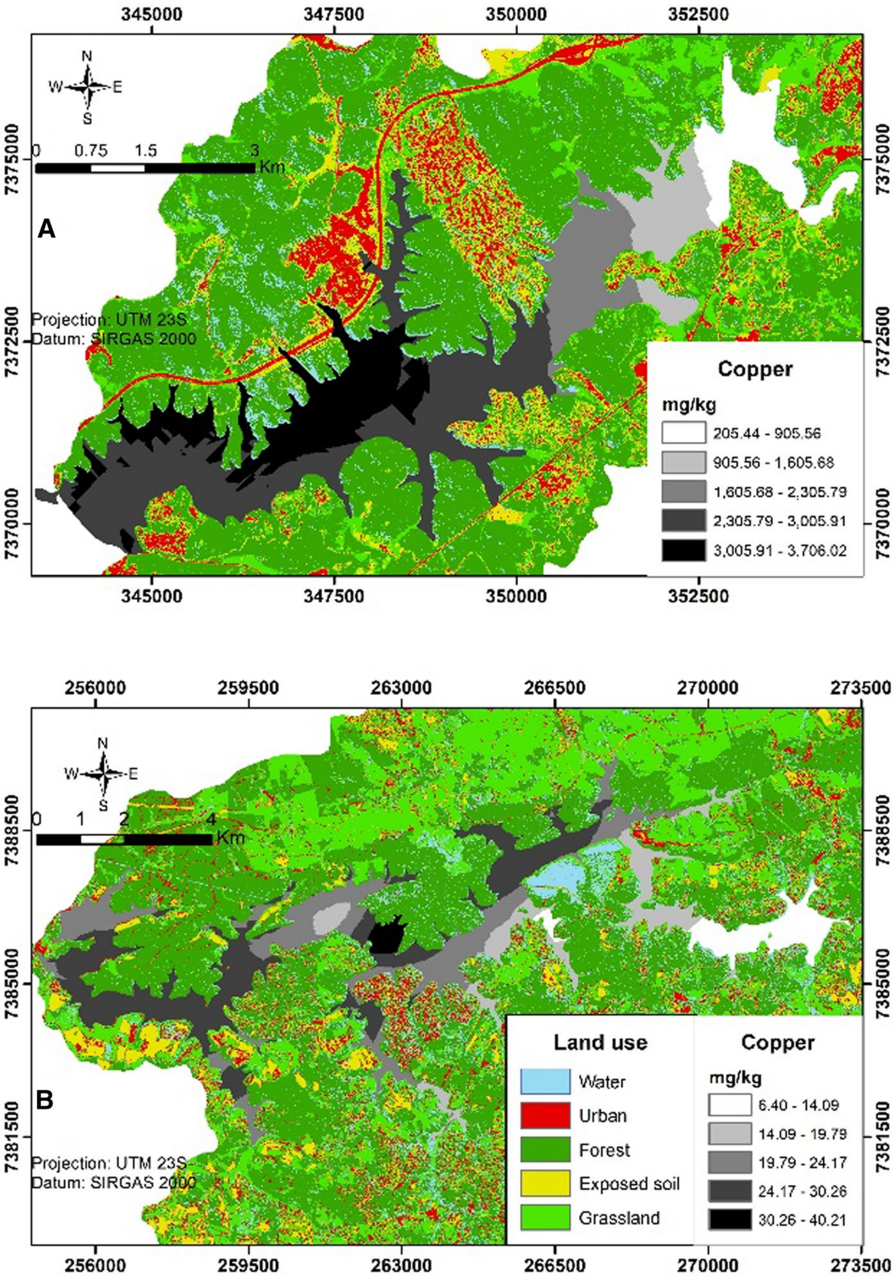

Fig. 3 Visual representation of copper concentration spatial variability in reservoirs. Land-use classification performed by maximum likelihood method **A** Rio Grande: Sentinel-2 imagery (2016/04/07) and **B** Itupararanga: Sentinel-2 imagery (2017/06/24)

(Closson & Paul, 2014; Silva et al., 2014). Besides that, repetitive copper sulfate dosing can lead to resistance of phytoplankton communities (García-Villada et al., 2004) and its application leads to cell damage releasing cyanotoxins into the water (Jančula & Maršálek, 2011).

When comparing RG with other in-land water bodies considering attributes such as inflows of domestic and industrial sewage, and agricultural pollutants, it has been observed that copper concentrations in RG are the highest, in a regional (de Andrade et al., 2018; Souza & Wasserman, 2015) or international context (Li et al., 2020; Wang et al., 2016) (Table 5), in water bodies with or without CuSO4 applications. In Daheiting reservoir—China (Li et al., 2020), for example, the maximum copper concentration (163.50 mg/kg) is very alike with the minimum values registered in RG; or Taihu lake—China (Wang

Table 5 Comparison of copper concentration in sediments in different water bodies

References	Reservoir	Mean ± SD	Range	CV	Cu-based algicide application*
This study	Rio Grande	2,282.996 ± 1,294.76	100.07–4827.57	56.71	Yes
This study	Itupararanga	21.82 ± 8.28	3.09–56.62	37.95	No
Leal et al. (2018)	Guarapiranga	1,241.64 ± 1,135.62	0–3011.99	91.46	Yes
Mariani and Pompêo (2008)	Rio Grande	1,644.1 ± 1,067.9	8.2–3582.6	64.95	Yes
Cardoso-Silva et al. (2016a)	Paiva Castro	3.9 ± 6.6	3.5–21.00	169.23	Yes
Frascareli et al. (2018)	Rio Grande	2,914.08 ± 1,704.52	–	58.85	Yes
Pompêo et al. (2013)	Guarapiranga	1,157.2 ± 1,125.6	29.2–2902.4	97.27	Yes
Frascareli et al. (2018)	Itupararanga	20.9 ± 1.51	–	7.22	No
Mozeto et al. (2014)	Ibirité—Brazil	142.05	115.8–170.8	–	Yes
de Oliveira Soares Silva Mizael et al. (2020)	Broa—Brazil	32.65 ± 1.82	–	5.57	No
Souza and Wasserman (2015)	Juturnaíba—Brazil	14.2	2.8–21	–	No
de Andrade et al. (2018)	Lago Guaíba—Brazil	78	13.8–132.1	–	Yes
Wang et al., (2016)	Lake Taihu—China	35.18	12.5–113	–	No
Li et al., (2020)	Daheiting—China	82.97 ± 14.61	33.93–163.50	17.61	No
Feng-Lan et al., (2019)	Qinggeda Lake—China	46.73 ± 6.87	30.06–59.78	14.70	No
Manoj et al., (2018)	Vembanad Wetland System—India	21.66 ± 12.45	2.88–40.92	57.48	No
Jacinthe et al., (2010)	Eagle Creek—USA	59.9	–	–	Yes
Milošković et al., (2013)	Gruža Reservoir—Serbia	10.53 ± 0.006	–	0.00005	Yes

Descriptive statistics mean, standard deviation, range (minimum–maximum), values in mg/kg and coefficient of variation (CV) expressed in (%)

*Cu-based algicide application in the reservoir or in their main tributaries at least in some period

et al., 2016) that presents areas dominated by algae as well, the maximum copper concentration (113.0 mg/kg) being above TEL values is slightly higher than the minimum copper value in RG. When comparing RG with Qinggeda lake—China (Feng-Lan et al., 2019), which shows a similar area (17 km^2) and it is located near an urban area as well, it has been observed that the maximum copper concentration (59.78 mg/kg) is half the minimum copper value registered in RG. In our research, we did not find any reservoir with Cu concentration as high as those recorded in RG, except for GUA. Therefore, further studies addressing ecotoxicological effects, including synergistic and additive effects, as well as effects on the trophic cascade, are carried out in RG. Some other reservoirs where Cu-based algicide were used reported by (Jacinthe et al., 2010) in Eagle Creek—USA and (Milošković et al., 2013) in Gruža Reservoir—Serbia. Eagle Creek presents concentrations higher than PEL but below the reported values in RG. Gruža Reservoir presents values below the TEL which are similar to ITU.

Enrichment factor

The EF categorization (Fig. 4) in ITU, copper, shows enrichment classified as "Absent/Very Low", which suggests a geogenic source. Contrasting with RG, where the EF is represented by three categories: "Considerable" 5.46%, "High" 5.62%, and "Very High" 88.92%, where we can infer that copper presence has an anthropogenic source mainly due to metal-based algicide, such as CuSO4.5H2O (copper sulfate pentahydrate).

It is worth mentioning that, similarly, as observed in the Guarapiranga reservoir (Leal et al., 2018), Rio Grande reservoir has been receiving periodically copper sulfate and hydrogen peroxide applications for almost 50 years (Pompêo, 2020). The use of hydrogen peroxide is a recommended alternative to reduce

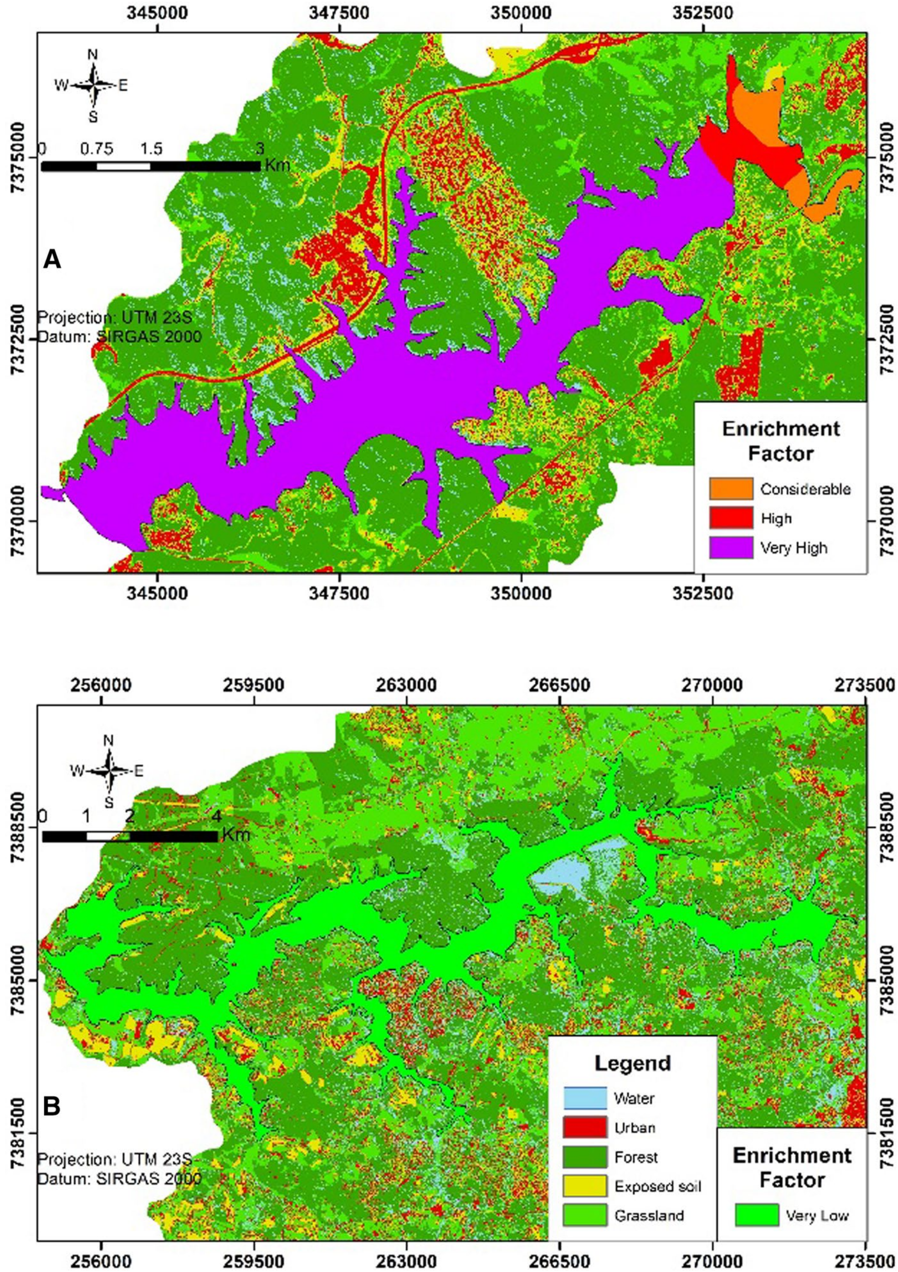

Fig. 4 Copper enrichment factor categorization in reservoirs. Land-use classification performed by maximum likelihood method **A** Rio Grande: Sentinel-2 imagery (2016/04/07) and **B** Itupararanga: Sentinel-2 imagery (2017/06/24)

impacts caused by copper present in algicides. In Table 6 are presented total values applied each year in Rio Grande reservoir. These data are worthy of comparison with CETESB registers mentioned in Leal et al. (2018) that in 2007, total copper sulfate application reached 360 Ton. It is important to consider that 25% of copper sulfate molecular mass is related to copper.

Superficial sediment potential toxicity

Figure 5 shows the sediment categorization in RG and ITU according to the methods described in the Canadian Interim Sediment Quality Guidelines (ISQG) (CCME, 1999), as applied by Leal et al. (2018). In the case of RG, the quality conditions after applying the kriging interpolation to sediment data show that all the superficial sediments are above PEL values.

Table 6 Annual total amounts of copper sulfate and hydrogen peroxide applications as algicide in Rio Grande reservoir. Source: SABESP

Year	2012	2013	2014	2015*
Hydrogen peroxide (ton)	700	226	1109	181
Copper sulfate pentahydrate (ton)	109	60	97	106

*Applications until October 9, 2015

Worse, 71.05% of the total area in the reservoir surpasses the PEL (×10) categorized as "Very Bad". In ITU occurs the opposite, the superficial sediment presents mean quality values that area classified as "Good". Considering the reservoir's total planar area, a minimum area shows concentrations above the TEL, classified as "Regular". On the other hand, 75.57% of superficial sediment was categorized as "Good", but there are concentrations above the regional reference values (RRVs) (Cardoso-Silva et al., 2021; Nascimento, 2003). This growth can be related to soil deterioration due to rapid urban expansion, deforestation and increasing agricultural areas, where artificial fertilizers and pesticides are applied, in the basin (Martins et al., 2021; Taniwaki et al., 2013).

The kriging geostatistical method was performed due to the sediment sample sites spatialization, the separation among these points was considerable, and the heterogeneity both spatial and the range of copper concentration that showed being irregular. Looking at the experimental variograms, these RG follow a Gaussian structure, while ITU, a spherical one, demonstrates the existence of a spatial correlation between the copper variability and the assessment distance, with a relevant SILL and a nugget effect, which is the result of the sample points distribution in both reservoirs. In RG, the variogram evaluation (Fig. 6A) demonstrates that there is a strong correlation due to the positive variation of copper concentrations along the reservoir, from upstream to downstream direction until the dam. In ITU (Fig. 6B), this correlation is present as well, but it is not as strong as in RG, probably due to minor variations of copper in the sediment along the reservoir.

It is possible to infer that the copper sulfate application, since the decade of 1980s, has directly influenced the very high values that surpass the international sediment patters. This copper concentration categorization in sediments is directly related to enrichment factor, because the classes "High" and "Very High" cover 94.54% of the reservoir's area, indicating artificial sources of copper, due to the geological composition of the basin (kaolinite, vermiculite, illite, gibbsite and goethite), natural accumulation at the observed scales might be unlikely. On the other hand, in ITU the copper concentration is not directly related to anthropogenic sources and the whole reservoir was classified as "Absent/Very Low". It is possible to state that.

To calculate the copper concentration total stock in superficial sediment, we used the equation proposed in Leal et al. (2018). In RG, we used the copper concentration mean values from kriging, $[Cu] = 2{,}267{*}10^{-3}$ kg (Cu)/kg(sediment), in addition to bathymetry and sediment data. From the sediment sampling, the fresh sediment, $FS = 0.1$ kg., sample height, $h = 0.04$ m., sample volume, $v = 0.0001$ m^3. From the bathymetric survey and interpolation, area $3D = 15{,}560{,}731.94$ m^3. This calculation resulted in a value of 1,411.047 Tons Cu. Considering the sedimentation rates, in RG, reported by Franklin et al. (2016), there is an accumulation of 0.4 cm/year, and considering that copper sulfate pentahydrate started being applied in 1985 according to Beyruth and Pereira (2018), in total 32 years, it results in 4,515.35 Ton Cu. This value is close to the estimation reported by Leal et al. (2018) in Guarapiranga reservoir, SP, approximately 4,540 Ton Cu.

In ITU, the mean copper concentration value from kriging was $[Cu] = 2{,}217{*}10^{-5}$ kg(Cu)/kg(sediment). From the sediment collection, fresh sediment weigh, $FS = 0{,}1$ kg., sample height, $h = 0.04$ m., sample volume, $v = 0.0001$ m^3. From the bathymetric survey and interpolation, area $3D = 30\ 949{,}264.69$ m^3. This calculation resulted in 27.45 Tons Cu.

Conclusions and final considerations

The geostatistical method applied clearly demonstrated the spatial heterogeneity and potential toxicity of copper in both reservoirs, being more perceivable in RG, which was caused by inorganic metal-based algicide to control algal blooms.

RG presented 71% of its sediment higher than PEL (×10), and the enrichment factor corroborates the

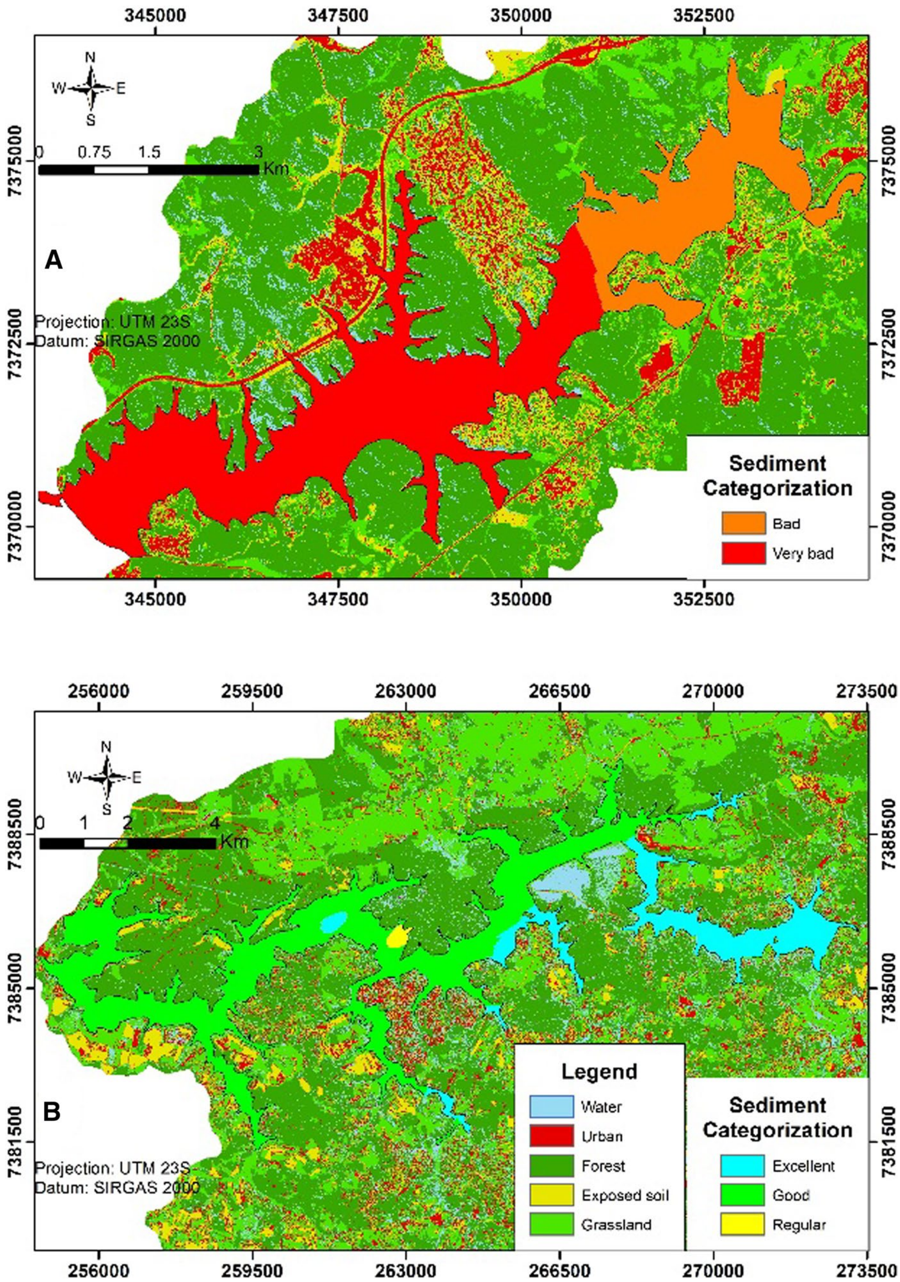

Fig. 5 Sediment quality categorization in reservoirs. Land-use classification performed by maximum likelihood method **A**) Rio Grande: Sentinel-2 imagery (2016/04/07) and **B** Itupararanga: Sentinel-2 imagery (2017/06/24)

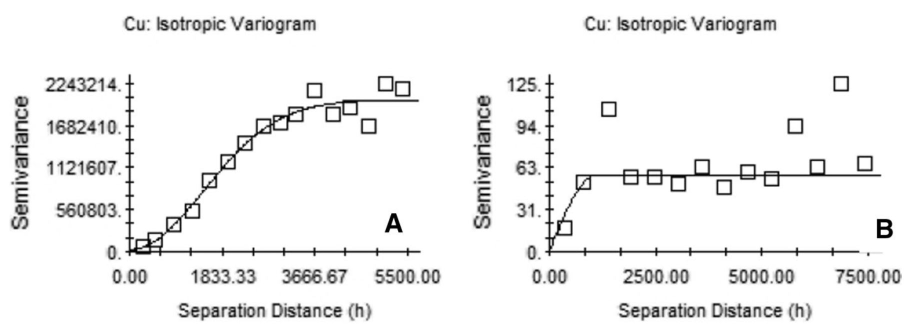

Fig. 6 Copper experimental variograms. **A** Rio Grande: Isotropic variogram type; Lag = 5500 m.; Angular tolerance = 22,5; Sill = 2,022,000; Nugget = 37,000. **B** Itupararanga: Isotropic variogram type; Lag = 7500 m.; Angular tolerance = 22,5; Sill = 57,0; Nugget = 0,1

anthropic source. Meanwhile, Itupararanga showed 75% of the sediment is higher than regional reference values; however, the enrichment factor indicates a geogenic source.

Although previous works suggest that Cu is not being bioavailable in RG, this does not mean that the metal is not exerting toxic effects on the biota. Our data suggest adverse effects, and it is possible that Cu bioaccumulation is occurring. Therefore, Cu high concentrations can promote a trophic cascade effect.

The application of copper sulfate as an algaecide is a palliative and controversial practice since Cu is recognized for its toxic character to aquatic communities. The copper sulfate application has already been banned in several European Union countries but is still being continuously applied in several other regions. Although the cost of applying this algaecide represents a lower monetary cost to the government compared to investments in sewage collection and treatment (Leal et al., 2018), the ecosystem services of the water bodies are threatened by this practice. As pointed out by Pompêo (2020), in almost 50 years of continuous copper sulfate application, under no circumstances this treatment can be considered a success. On the contrary, this palliative effort mismatches and appropriate quality management system, potentially polluting the sediments.

Our study shows the potential of using the kriging technique to reveal areas most potentially affected by a given contaminant, as well as allowing to calculate its stock. Thus, it can be contributed to risk analysis studies and the proper management of the water body. Moreover, geostatistical techniques and enrichment factor demonstrated being replicable to analyze the toxicological potential of metals in sediments and advantageous to assist decision makers.

New strategies to keep algal blooms under control must be considered; we believe that implementing proper sewage treatment systems to prevent the entrance of raw sewage is of the utmost importance.

Author contributions All authors contributed to the design of this study: IB-R performed conceptualization, investigation, formal analysis, software, data curation, writing—original draft; SC-S performed data curation, investigation, validation, writing—review and editing; MB did software; AS, VM-C and AR did data curation MP was involved in formal analysis, investigation, writing—review and editing, supervision, funding acquisition. All authors commented on previous versions of the manuscript and read and approved the final manuscript.

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Data availability Not applicable.

Declarations

Conflict of interest The authors declare no competing interests.

Ethical approval and consent to participate Not applicable.

Consent to publish Not applicable.

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