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Paleolimnological evidence of environmental changes in seven subtropical reservoirs based on metals, nutrients, and sedimentation rates

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ABSTRACT

Paleolimnological research can shed light on a broad range of environmental concerns; however, such studies are scarce in reservoirs. To address this lack of knowledge, a paleolimnological investigation was conducted to determine historical changes in sedimentation rates (SR), using ^{210}Pb geochronology, and concentrations of nutrients and metals (Cr, Cu, Ni, Pb, Zn, Al, Mn, Fe) in seven subtropical reservoirs (São Paulo, Brazil). Sediment cores were collected in the dam areas. Increasing SR was observed in all reservoirs and was mainly attributed to eutrophication and changes in land use and occupation. Considering the total nitrogen and/or phosphorus, the sediment could be considered polluted at the Broa, Barra Bonita, Salto Grande, and Rio Grande reservoirs. Decreasing values were observed for Pb when the use of tetraethyl lead as an additive in gasoline was forbidden (1990). According to the applied indices, no significant enrichment, contamination, or ecological risk for metals were registered, except at the Rio Grande reservoir. At this reservoir, a moderate enrichment of Mn was observed since 1999, which was mainly associated with municipal wastewater and erosive processes, as indicated by a significant correlation between Mn and SR ($r = 0.73$, $p < 0.0001$). A very high enrichment of Cu was observed. The accumulation of Cu in this reservoir peaked in 2006 to 6183.0 mgCu/kg, a value 412-fold higher than the background. Even during a period before intense industrialisation, concentrations of Cu were 49-fold higher than background levels. The increase of Cu in bottom sediments could be attributed to vertical migration according to a series of complex mechanisms; however, further research will be needed to improve the understanding of Cu dynamics. This work makes an important contribution to understanding the paleolimnology of reservoirs, and the findings could also be applied in other contexts, since the impact of metal contamination in water bodies is a global-scale problem.

1. Introduction

Paleolimnology can provide important information about the dynamics of ecosystems, establishing reference conditions for water bodies and enabling the assessment of current impacts (Smol, 2008; Hollert et al., 2018; Stivrins et al., 2018). It can also provide important ecological information in the absence of long-term monitoring data (Bennion and Battarbee, 2007; Smol, 2008; Stivrins et al., 2018). Although viable, there has been little application of paleolimnological techniques to reservoirs, so the sediments of these ecosystems have rarely been used to track environmental changes (Shotbolt et al., 2006; Tse et al., 2015). This is because reservoir sediments are more susceptible to disturbances due to fluctuations in the water level, making historical reconstruction more complex (Shotbolt et al., 2006). However, the stratigraphy of undisturbed sediments can be observed in deeper reservoir areas, providing long-term environmental information that

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can be used in management programs (Tse et al., 2015) and to improve the understanding of ecological processes.

Various proxies can be used to reconstruct past environmental conditions (Smol, 2008). For example, metals, nutrients, and sedimentation rates (SRs) may be viable proxies, especially for urban reservoirs that are highly susceptible to the impacts of rapid urbanisation and industrialisation. Metal pollution in aquatic ecosystems is of great concern and is an increasing global problem (Kucuksezgin et al., 2008; Väänänen et al., 2018) . Metals, such as chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn), are of considerable environmental interest due to their toxicity, persistence, bioavailability, biomagnification in the food chain, and potential threat to ecological systems and human health (Luoma and Rainbow, 2008). Information about the dynamics of metals in aquatic ecosystems can be obtained using paleolimnological studies, as shown by Cardoso-Silva et al. (2016a), Korosi et al. (2018), Lintern et al. (2018), Thienpont et al. (2019), and Soares-Silva et al. (2020).

Analyses of macronutrients, such as phosphorus, nitrogen, and carbon, in sediments can shed light on eutrophication processes, although caution is required in interpreting the data (Boyle, 2001). It is important to consider these three main elements because under eutrophic conditions, phosphorus released from the sediment may often be intense, even if external loading is low, because of high internal loading that does not reflect the trophic state in the water column (Cardoso-Silva et al., 2018). However, nitrogen is considered a superior indicator of primary aquatic productivity (Dai et al., 2007), enabling the assessment of anthropogenic impacts. Carbon can provide important information about the diagenetic processes affecting organic matter (OM), and together with concomitant analyses of nitrogen and phosphorus, it can indicate the origins of the material (Meyers, 1994) and possible contamination by phosphorus (Cardoso-Silva et al., 2018).

The SR can also be used as an important proxy to understand environmental processes and to assess urbanisation impacts. Sedimentation processes affect the metabolism of the aquatic ecosystem, which in turn influences the regeneration of nutrients in the epilimnion, the removal of particulate matter to the bottom, and control of the supply of nutrients to the benthic community (Bloesch and Uehlinger, 1986). The SR is closely related to the hydrologic flow pattern and the topography of the basin, which affects the hydrodynamic regime (Navas et al., 2009). SRs are specific for each water body and depend on the nature of the river basin but can be influenced by anthropogenic activities, which may result in increased erosive processes and SRs associated with eutrophication (Moss et al., 2003; Scharf et al., 2010). The transport and deposition of eroded sediments can directly affect adjacent urban settlements, for example, by reducing the storage capacity of surface reservoirs (Rahmani et al., 2018). The ^{210}Pb dating technique is of great importance for studying sedimentation processes, since it can provide both geochronological information and accurate SR data, using cores of sediment younger than 150 years (Moss et al., 2003).

Long-term records of the chemical states and ecological conditions of reservoirs are absent in many regions worldwide, including tropical and subtropical areas in Brazil. This can complicate the implementation of effective and realistic environmental remediation strategies. Furthermore, the lack of information for aquatic ecosystems in tropical and subtropical areas hinders international access to information, thus restricting the understanding of processes and phenomena on a global scale.

The present paleolimnological study was undertaken to fill this knowledge gap, with the following goals: 1) elucidate temporal changes in SRs using ^{210}Pb geochronology and determine of metal and nutrient concentrations in seven subtropical reservoirs in São Paulo State; 2) propose background values for Cr, Cu, Ni, Pb, Zn, Mn, Al, and Fe; 3) investigate metal contamination and toxicity potential by analysing different indices and using empirical sediment quality guidelines; 4) evaluate quality gradients and spatial heterogeneity in the reservoirs.

The hypothesis was that the metal concentrations and SR would exhibit increases over the course of time because anthropogenic impacts have increased in the watersheds of the reservoirs. The data obtained shed light on natural and anthropogenic changes in reservoirs during the recent past. The findings represent an important contribution of paleolimnology to the understanding of subtropical reservoir environments.

2. Materials and methods

2.1. Study area

Sediment cores were obtained at seven reservoirs in São Paulo State, Brazil: Broa (sampled on June 11, 2015), Barra Bonita (June 18, 2015), Salto Grande (June 25, 2015), Itupararanga (September 10, 2015), Igaratá (September 24, 2015), Atibainha (October 1, 2015), and Rio Grande (Billings Complex) (October 8, 2015) (Fig. 1). The Broa reservoir was the smallest of the seven reservoirs and is impacted by inputs of untreated domestic sewage, resulting in high trophic levels (Tundisi et al., 2015; Frascareli et al., 2018). This reservoir was also found to be affected by metals originating from fishing boats, fuel use, and paint residues (Frascareli et al., 2018). The Barra Bonita, Salto Grande, and Itupararanga reservoirs are impacted by intensive agricultural activities along their margins, as well as by sewage inputs from urban areas (Buzelli and Cunha-Santino, 2013; Fonseca and Matias, 2014; Frascareli et al., 2015; Tundisi et al., 2015). The Salto Grande reservoir basin is also affected by a petrochemical complex, whose emissions can affect the water quality of this vital water source, including contamination by metals (Leite et al., 2004).

The Igaratá, Atibainha, and Rio Grande reservoirs are used for public water supply. Degradation of the Igaratá reservoir is less severe compared to the other reservoirs, with it currently being classified as oligotrophic (Frascareli et al., 2018). The Atibainha is the fourth of five reservoirs in the Cantareira cascade multisystem, which is the primary source of drinking water for the São Paulo metropolitan region (Cardoso-Silva et al., 2017; Pompêo et al., 2017). The type of land use around the Atibainha watershed has a major impact on the water quality of this reservoir (Vieira and Vieira, 2016; Cardoso-Silva et al., 2017). Eutrophication has recently intensified, resulting in the reservoir being classified as oligo-mesotrophic (CETESB, 2017; Cardoso-Silva et al., 2017). The Rio Grande reservoir, in the Billings Complex, lies within an extensive urban area in the metropolitan region of São Paulo in the Alto Tietê basin. Its watershed is affected by the release of untreated effluents that escalate the process of eutrophication in the region. In recent decades, this reservoir has been subjected to constant applications of copper sulphate and hydrogen peroxide in attempts to control the growth of phytoplankton (Mariani and Pompêo, 2008).

A gravity corer was used to collect three sediment cores from the dam area of each reservoir, except in the case of the Igaratá reservoir, where the sampling site was near the Dom Pedro highway. The point of sediment collection should represent, as far as possible, an 'average' accumulation of material for the entire watershed (Birks and Birks, 2006; Smol, 2008). Therefore, the samples were collected in the deepest areas of the reservoirs (the limnetic regions), where sedimentation was higher and less prone to bioturbation or other mixing processes (Smol, 2008).

Each core was sectioned at 2 cm intervals, and the samples were stored in sealed plastic bags. The plastic bags were kept in thermal bags until laboratory analyses were performed. For each reservoir, one core (Core 1) was used for the determination of organic matter (OM), particle size, and nutrients. Another core (Core 2) was used for metal determination and geochronological analysis. A third core (Core 3) was preserved at −15 °C. The core slices were numbered in ascending order, from the top of the core to the bottom. The cores had a total depth ranging between 20 and 36 cm. The sampled depths and general morphometric characteristics of each reservoir are described in Table 1. For details about the spatial heterogeneity of metals and nutrients in the surface sediments of these reservoirs, see Frascareli et al. (2018).

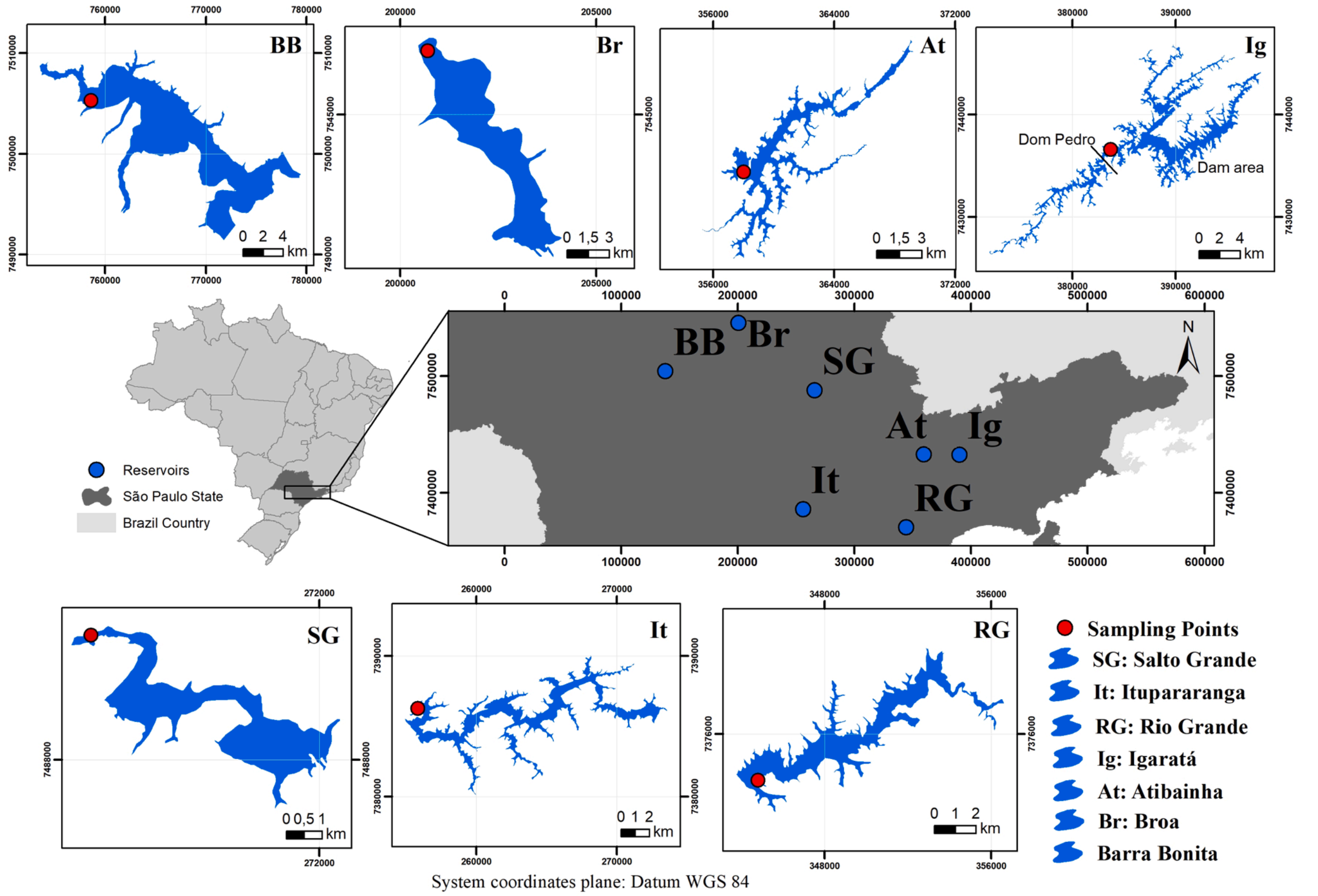

Fig. 1. Locations of the reservoirs in São Paulo State, Brazil. The sediment cores were obtained in the dam areas, with the exception of the Igaratá reservoir, where the core was obtained near the Dom Pedro highway

Table 1
Morphometric characteristics of the reservoirs.

	Area (km^2)	Mean depth (m)	Altitude (m)	Volume m^3/s	Residence time (days)	Rainfall (mm)	Sampled depth (m)
Broa	6.8	3.2	770.0	22.0	20-40	1461.0	13.0
Barra Bonita	367.0	10.2	480.0	3743.4	20	1562.0	22.6
Salto Grande	10.6	10.0	530.0	106.0	30	1313.0	11.0
Itupararanga	26.0	11.0	849.0	286.0	250	1370.0	14.8
Igaratá	55.0	22.5	844.0	1236.0	228	1592.0	24.7
Atibainha	21.8	4.8	787.0	104.0	105.8	1642.0	17.0
Rio Grande	7.4	26.2	750.0	194.0	306	1498.0	11.7

2.2. Laboratory analyses

2.2.1. General characteristics of the sediments and analysis of nutrients (Core 1)

The sediments were dried in a forced aeration oven at 50 °C until a constant weight, followed by grinding using a glass mortar and pestle. For texture analysis, 30 g portions of the dry sediment were placed in plastic vials, with the addition of analytical grade H_2O_2 for prior degradation of OM. The grain size of the sediment was determined by the laser diffraction method, using a Mastersizer 2000 analyser (Malvern Instruments, UK) at the laboratory of the Dynamic Air Company – São Paulo. The OM content was determined by the loss on ignition (LOI) method, which involves combustion of the OM in an oven at 550 °C (Meguro, 2000). The organic carbon (C_{org}) content was estimated from the OM value, presuming that the OM contained 58% carbon by weight (Meguro, 2000). Another portion of the sediment was used for analysis of the total Kjeldähl nitrogen (TN) (APHA, 2002) and total phosphorus (TP) (Andersen, 1976), as described by Pompêo and Moschini-Carlos (2003).

2.2.2. Geochronology and metal analyses (Core 2)

After the sediments had been dried and ground, portions were sent to the Radioisotope Service of the Research, Technology, and Innovation Centre of the University of Seville (Spain) for geochronological analysis. The samples were stored for at least 20 days in containers sealed against the entry of air to allow gaseous ^{222}Rn to reach secular equilibrium within the ^{238}U decay series. Estimates of the ^{210}Pb concentrations were made using alpha-spectrometry (Alpha Analyst, Canberra). Analytical grade reagents were obtained from Merck (HNO_3, HF, and HCl) and Panreac (ascorbic and boric acids). Deionised water (resistivity of 18.0 MΩ cm) was obtained from a Millipore system. The digestion procedure was based on the US EPA 3050 method (USEPA, 1996), modified by Laissaoui et al.(2013). The generated spectra were analysed using Genie 2000 software, applying decay corrections to calculate the activities of ^{210}Po and ^{209}Po. High chemical yields (>50%) were achieved in the alpha particle spectrometry. The quantification limit was determined by measuring several blank samples over a 3-day background count time. The vertical profiles of ^{210}Pb and ^{226}Ra were employed in a constant rate of supply (CRS) model (Appleby and Oldfield, 1978) to create an age-depth model and estimate the SRs for each core. This model is widely used for this purpose, providing a consistent mathematical approach for modelling the dilution and concentration of unsupported ^{210}Pb in aquatic systems prone to changes in SR. The SR was expressed as centimetres per year of dry weight (cm/y dw). Reservoir core parameters for CRS age model dating are described in the supplementary material (Table SM 1).

A second aliquot of sediment was used for metal analysis (in duplicate), according to USEPA method SW-846 3050B (USEPA, 1996). The samples were stored at 4 °C prior to analysis of Cr, Cu, Ni, Pb, Zn, Mn, Al, and Fe by inductively coupled plasma atomic emission spectrometry (ICP-AES) using an Agilent Series 720 instrument. Analytical grade reagents (obtained from Merck and Sigma-Aldrich) were used in all analyses. All glassware and equipment used for the storage and processing of the samples for metal analysis were left in 10% nitric acid for at least 24 h and rinsed 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 and 125% was considered as the acceptance criterion. The recovery efficiencies ranged from 79.8 to 116.9%. The metal data were expressed as milligrams per kilogram of dry weight (mg/kg dw).

2.3. Metal background values, enrichment factors, and pollution load indices

The obtained metal concentrations were compared to background values, with the enrichment factors (EFs) and pollution load indices (PLIs) being used to assess the level of contamination in the sediment. The background values were the average concentration of the elements in the bottommost sample of the cores (Mahiques et al., 2009). The EFs were calculated as follows:

$$EF = \frac{\frac{Me}{El}}{\frac{Mer}{Elr}} \tag{1}$$

where *Me/El* is the ratio between the concentrations of the analysed metal and the conservative element in the sample, and *Mer/Elr* is the ratio of the background values for the metal to be analysed and the conservative element. Aluminium was used as a conservative element (Förstner and Wittmann, 1981; Luoma and 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 classifications are shown in Table 2.

The PLI was calculated according to Equation (2) (Tomlinson et al., 1980):

$$\mathrm{PLI} = (C_f^1 \times C_f^2 \times C_f^n)^{1/n} \tag{2}$$

where *Cf* is the ratio between the concentration of the metal of interest and the corresponding background value. Table 1 shows the classification of the index and the corresponding interpretation.

Table 2
Classifications for enrichment factor (EF) (Sutherland, 2000), pollution load index (PLI) (Tomlinson et al., 1980), and ecological risk index (RI) (Håkanson, 1980).

Index	Classifications				
EF	Absent/very low <2	Moderate 2≤EF<5	Considerable 5≤EF<20	High 20≤EF<40	Very high >40
PLI	Present >1	Absent <1	-	-	-
RI	Low <150	Moderate 150≤RI<300	Considerable 300≤RI<600	Very high >600	-

2.4. Ecological risk

The ecological risk associated with the sediment was assessed using the ecological risk index (RI) (Håkanson, 1980) and empirical sediment quality guidelines (SQG), considering the threshold effect level (TEL), a value also known as the interim sediment quality guideline (ISQG), and the probable effect level (PEL) (CCME, 1999). The RI was calculated as follows:

$$\mathrm{Ei} = \mathrm{Tix}\ C_i/C_0 \tag{3}$$

$$RI = \sum_{i=1}^{n} E_i \tag{4}$$

where ***Ei*** is the ecological risk for a given contaminant, ***Ti*** is the toxic response factor for a given substance (Cd: 30; As: 10; Pb, Cu, Ni: 5; Cr: 2; Zn: 1) (Håkanson, 1980), ***Ci*** is the metal content in the sediment, and C_0 is the background value. The RI classification categories are listed in Table 1 (Håkanson, 1980).

The Canadian SQG system is widely used to assess the quality of sediments (Hübner et al., 2009). In this model, there is a range of values for each contaminant, where a value exceeding a specific concentration (PEL) indicates that a toxic effect is likely to occur. Likewise, effects are unlikely to occur at concentrations below the ISQG. At values between the ISQG and PEL, toxic effects can occur (CCME, 1999). The values obtained for ISQG and PEL are in the supplementary material (Table SM 2).

2.5. Statistical analyses

Basic descriptive and multivariate statistical analyses were performed for the entire dataset. Before statistical analysis, the data were transformed using their logarithms (base 10). The student's *t*-test ($p < 0.05$) was used to evaluate differences between the means. Relationships between the chemical and physical variables were first evaluated using Pearson's correlation. The relationships for the different reservoirs and metal concentration values were determined using a centred and standardised matrix containing the concentration values for each sample. Principal component analysis (PCA) was used for data ordination (Legendre and Legendre, 1998). The calculations were performed using PAST 2.7 (Hammer et al., 2001) and Origin software packages.

3. Results and discussion

3.1. General characteristics of the sediments and analysis of nutrients

The sediments from all reservoirs displayed uniform coloration, with no clear variation according to depth. The silt and clay fractions (<63 μm), which provide important binding sites for metals (Chapman et al., 1999; Cardoso-Silva et al., 2016b), were only predominant in the sediment from the Broa reservoir (60.04 ± 19.15%) (Table 3). The sediments could be considered organic with LOI values > 10% (Ungemach, 1960) (Table 3).

3.2. Sedimentation rate and dating with ^{210}Pb

Figures 2a and 2b present the vertical profiles obtained for the unsupported ^{210}Pb geochronological analyses and SRs, respectively. Dating did not cover the early years of the Salto Grande (1949) and Itupararanga (1912) reservoirs but covered a period before Brazil's industrialisation in the 1950 s. The vertical profile for the Rio Grande core showed an exponential decay trend of unsupported ^{210}Pb, implying that the SR did not change significantly during the sampled period. Conversely, the profiles for the Itupararanga and Igaratá sediment cores revealed

Table 3
Descriptive statistics for parameters of the sediments from seven reservoirs in São Paulo State (Brazil).

		Broa	Barra Bonita	Salto Grande	Itupararanga	Igaratá	Atibainha	Rio Grande
LOI (%)	**Min**	19.7	8.6	17.5	3.6	5.8	13.6	42.5
	Max	28.47	20	36.9	60.6	14.5	91.1	13.2
	Mean	23.1	14.2	22.3	17.8	11	19.6	20.2
	SD	2.4	3.4	5.8	15.5	2.3	31.6	8.2
	CV	10.5	23.8	25.9	87.3	20.5	113	40.7
Grain size <63 μm (%)	**Min**	38	20.2	19.1	16.1	25.7	15.9	30
	Max	86.7	39.4	27.5	47.1	65.3	41	82.3
	Mean	60	22.8	31	29.6	45.2	28.4	48.9
	SD	19.2	3.9	12.2	11.5	15.2	10.3	17.7
	CV	31.9	17	39.5	38.8	33.6	36.4	36.2
Total phosphorus (mg/g dw)	**Min**	0.9	1.6	0.1	0.5	0.7	0.7	1.7
	Max	1.9	3.4	3.2	0.9	1.8	1.2	2.6
	Mean	1.3	2.5	2.2	0.7	1.2	1	2.1
	SD	0.3	0.6	0.8	0.1	0.3	0.2	0.3
	CV	19.5	23.5	34.5	16	22.9	17.1	12.4
Total nitrogen (mg/g dw)	**Min**	2	1.3	0.5	1.4	0.9	0.5	2.2
	Max	8.1	4.6	1.8	3.9	3.7	3.1	11.6
	Mean	5.7	2.8	1.2	2.7	2.2	1.9	6.2
	SD	1.8	1.2	0.5	0.9	0.6	1.2	2.9
	CV	31.5	42.5	46.2	33.8	27.6	62.9	46.1

SD: standard deviation; CV: coefficient of variation (%); Min: minimum; Max: maximum; LOI: organic matter (loss on ignition).

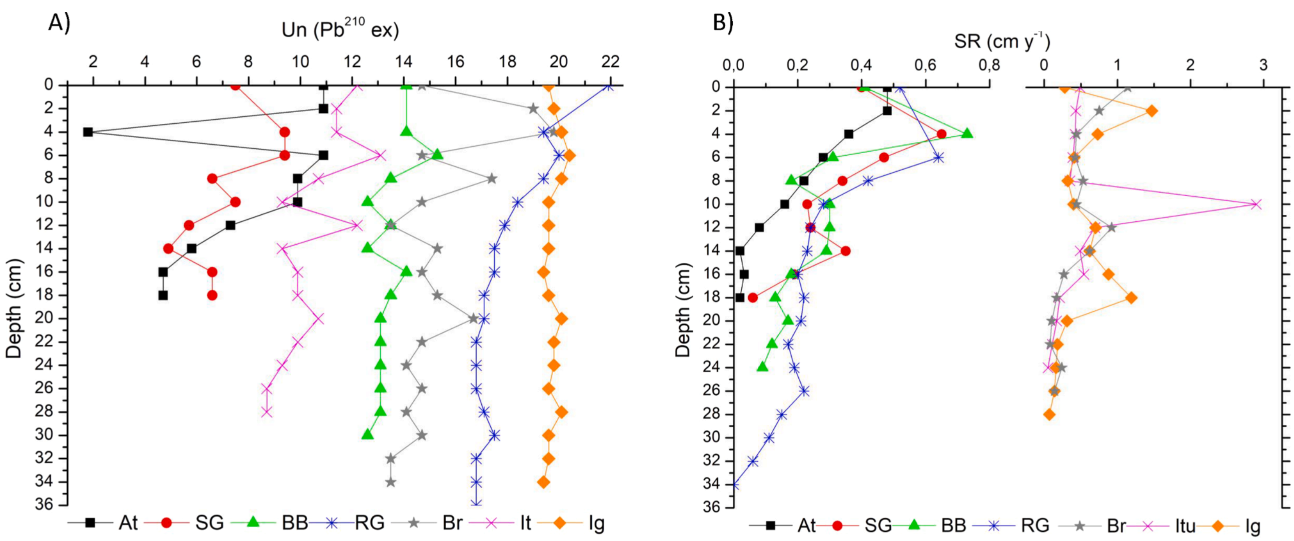

Fig. 2. Vertical profiles of unsupported ^{210}Pb (a) and vertical sedimentation rate profiles (b) for sediment cores collected from seven reservoirs in São Paulo State, Brazil. Reservoirs: Atibainha (At), Salto Grande (SG), Barra Bonita (BB), Broa (Br), Itupararanga (It), Igaratá (Ig), and Rio Grande (RG).

episodes of dilution of unsupported ^{210}Pb, which could be directly related to increases in the SR.

The various periods of intensified sediment deposition could be linked to both natural and anthropogenic processes (Fig. 2b), including land use, urban expansion along the river basins, weathering (Fávaro et al., 2007), and eutrophication (Zhang et al., 2016). Since the 1970 s, continuous urban expansion and severe transformations of soil use and occupation in the watersheds of the Barra Bonita (Buzelli and Cunha-Santino, 2013), Salto Grande (Martins et al., 2011), Broa (Tundisi and Matsumura-Tundisi, 2013), Itupararanga (Taniwaki et al., 2011), and Rio Grande (Fávaro et al., 2007) reservoirs have made these areas particularly vulnerable to siltation, which could increase the SR. At the Itupararanga reservoir, the presence of intense agricultural activities along its margins (Taniwaki et al., 2011), together with stripping of the Atlantic rainforest in the Atibainha watershed between 1989 and 2003 (Whately and Cunha, 2007), may have led to the intensification of sedimentation because of weathering. Weathering could also explain the increase in the SR at the Salto Grande reservoir, since a significant correlation ($r = 0.54$, $p < 0.10$) was found between SR and Mn in the sediment.

Increases in SR can also be linked to eutrophication, which is known to be a problem at all the reservoirs evaluated in this study, especially the Salto Grande (Zanata and Espíndola, 2002; Dornfeld et al., 2006), Barra Bonita (Buzelli and Cunha-Santino, 2013), Itupararanga (Taniwaki et al., 2011; Frascareli et al., 2018), Atibainha (CETESB, 2015), and Rio Grande (Wengrat and Bicudo, 2011; Cunha et al., 2011; Cardoso-Silva et al., 2014). Furthermore, for the Salto Grande and Barra Bonita reservoirs, the highest SRs were observed in the uppermost layers of the cores, corresponding to the 2010 s, when the local environmental agency recorded increases in eutrophication (CETESB, 2016). In addition, a significant correlation was found between SR and total phosphorus ($r = 0.59$, $p < 0.10$) for the Barra Bonita reservoir, corroborating the influence of eutrophication on SR.

The Atibainha reservoir presents interannual oscillations between oligotrophy and eutrophy (CETESB, 2015), suggesting that variations of the nutrient supply in the watershed might also increase SR. Similarly, the Broa reservoir exhibits occasional increases of nitrogen and phosphorus, leading to alternation between oligotrophy and mesotrophy (Tundisi and Matsumura-Tundisi, 2013), together with periodic blooms of cyanobacteria (*Cylindrospermopsis raciborskii*) (Tundisi et al., 2015). These phenomena affect the SR, as shown by the significant correlation between SR and total nitrogen for the Broa ($r = 0.67$, $p < 0.10$) and Atibainha ($r = 0.69$, $p < 0.10$) reservoirs.

3.3. Nutrients

Increases in TOC concentrations were observed for all reservoirs during at least some period. Although no significant differences were observed for the concentrations of TN and TP (Student's *t*-test, $p > 0.05$), variations associated with anthropogenic impacts were observed for most of the reservoirs. In the following sections data for eutrophic and mesotrophic reservoir are discussed.

3.3.1. Eutrophic reservoirs

Increases in C_{org} and TN concentrations were recorded for the Rio Grande and Barra Bonita reservoirs in the 1940–1960 s (20.0–18.0 cm) and the late 1960 s (16.0 cm), respectively (Fig. 3). In the case of the Salto Grande reservoir, a period of nearly 65 years was evaluated, with nutrient increases being recorded from 18.0 cm (approx. 1954) (Fig. 3).

The data for the Rio Grande reservoir revealed the first increases of TN and C_{org} before the establishment of the monitoring program (20.0–18 cm, 1945–1960) (Fig. 3), corroborating the evidence for eutrophication starting in the 1950 s (Wengrat et al., 2019). These nutrients and C_{org} increases were probably linked to the transfer of part of the water from the Tietê River and its tributaries to the Billings reservoir in the early 1940 s to increase the flow and consequently expand the hydroelectric generating capacity (Capobianco and Whately, 2002). Further, increases in TN and C_{org} were recorded from 12.0 cm (1992) and 8.0 cm (2006) (Fig. 3), with numerous reports of water quality degradation associated with eutrophication being recorded (Cardoso-Silva et al., 2014; CETESB, 1993, 2007). A decrease in TP concentrations, especially after the 1960 s (18.0 cm), could be attributed to the release of P due to the presence of both anoxic conditions and sulphides, which regulate the availability of Fe for the immobilisation of P onto iron oxyhydroxides. This could be explained by the fact that the Rio Grande sediments are characterised by high LOI concentrations, anoxic conditions, and the presence of sulphides (Mariani and Pompêo, 2008). In a general way, higher P loads increase the imbalance between P sedimentation and the P retention capacity of sediments, leading to P release (Hüpfer and Lewandowski, 2008).

The Barra Bonita sediment showed increases in TN and C_{org} from the start of operation of the reservoir until the early 1980 s (Fig. 3), which could be attributed to two main factors: 1) mineralisation of OM present in the recently flooded reservoir area; and 2) population growth and the consequent increase in effluent discharges in the watershed of the reservoir (Buzelli and Cunha-Santino, 2013). A decrease in nutrient levels since the 1980 s was probably linked to sanitation improvements in 1979 and 1981 (Leme-Pompeu and Mucare, 1983). Further increases

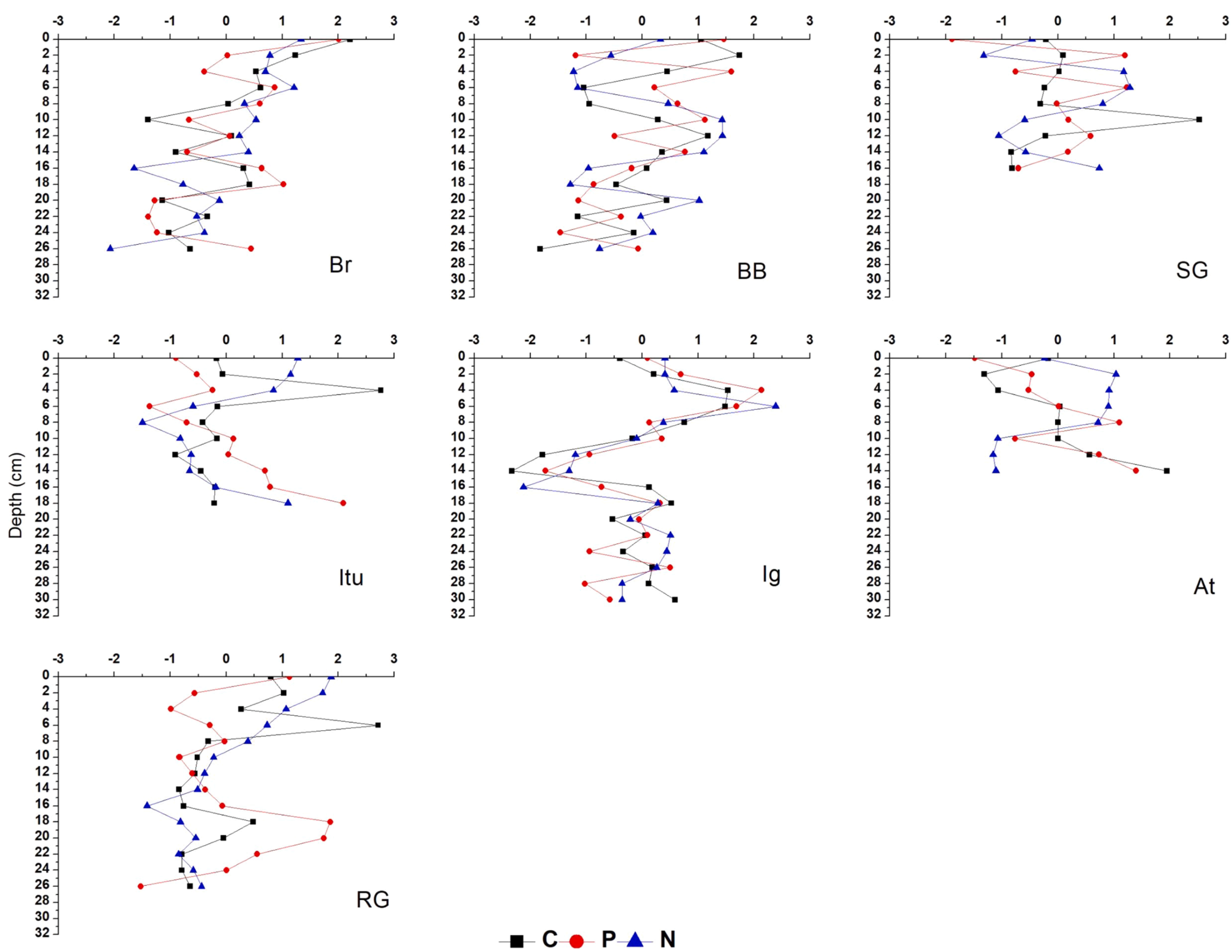

Fig. 3. Depth profiles of the C, N and P in sediment cores collected from seven reservoirs in São Paulo, Brazil. Data standardized according to Z-score.

in TN and C_{org} were observed at 4.0 cm (2011) (Fig. 3), possibly due to greater discharges in industrial and domestic effluents (Buzelli and Cunha-Santino, 2013; David et al., 2016) and the use of fertilisers in agricultural areas (Buzelli and Cunha-Santino, 2013).

The Salto Grande reservoir has been considered eutrophic since the 1950 s (Wengrat et al., 2019), with notable increases of C_{org} and TP observed after this period (12.0–18.0 cm, 1954–1986). The highest C_{org} concentrations occurred in the mid-1980 s (approx. 1986), while TN concentrations started to decrease in the 1950 s (14.0–18.0 cm, 1954–1978) (Fig. 3). The opposite trends for TN and TP could be explained by the mineralisation of OM under anoxic conditions, with consequent losses of N to the water column due to denitrification. Denitrification is the main mechanism leading to the loss of N from top sediments and is a common feature in the hypolimnion of eutrophic water bodies (Hou et al., 2014). Although P is also usually released under anoxic conditions (Mortimer, 1941; Fonseca et al., 2011), other mechanisms could affect P retention. For example, the presence of redox-insensitive P-binding systems, such as $Al(OH)_3$, and the partial resistance of oxidised Fe minerals may prevent P release, even in the case of an anoxic hypolimnion (Hüpfer and Lewandowski, 2008). Further research is recommended to better understand the processes of P retention and release in this reservoir. From the late 1970 s to 2007 (14.0–8.0 cm), increases in TN and C_{org} were reported by the local environmental agency (CETESB, 2015), indicating eutrophication.

Considering Ontario sediment quality guidelines and current local legislation (CONAMA n° 454/2012), the reservoir sediments could be considered polluted most of the time, with mean values > 4.8 mg N/g for the Rio Grande reservoir and > 2.0 mg P/g for the Barra Bonita, Salto Grande, and Rio Grande reservoirs (Table 3). Anthropogenic origins of P were also suggested by the Redfield molar ratio (C:N:P = 108:16:1) and mean C:P molar ratios of 36.41:1 (Barra Bonita) and 57.30:1 (Rio Grande). The distributions of C/P in the sediment cores are provided in the supplementary material (Table SM 3).

3.3.2. Mesotrophic reservoirs

Increases in TN and C_{org} concentrations were observed in the Broa sediment, especially from the 1990 s (14.0 cm, 1992), and in the Itupararanga sediment, from 2000 (6.0 cm, 2003). A general increase in TN was detected in the Atibainha sediment from the 1990 s (8.0 cm, 1993) (Fig. 3).

In the case of the Broa reservoir, the nutrient increase was mainly caused by nonpoint sources of pollution. Applying empirical models, Anjinho et al. (2021) found that 81% of TN and 76% of TP in the reservoir were derived from nonpoint sources. The increase in recreational activities, including the use of feed in sport fishing, the rise in deforestation, and the replacement of native vegetation by farms, mainly in the 1980 s, with agricultural activities, such as sugarcane cultivation, cattle ranching, and small-scale orchards (Tundisi and Matsumura-Tundisi, 2016, Soares-Silva et al., 2020), resulted in intensification of the eutrophication process. Population growth and the consequent increased discharge of effluents into the tributaries feeding the reservoir also contributed to the increased concentration of nutrients and C_{org}. According to the Brazilian Institute of Geography and Statistics (IBGE), municipalities in the Broa reservoir watershed showed population growth rates of 52% (Brotas) and 62% (Itirapina) between 1975 and 2017 (IBGE (Brazilian Institute of Geography and Statistics), 2021a). Sewage collection and treatment in the region remains inadequate, with around 14% of effluents discharged without any treatment (IBGE (Brazilian Institute of Geography and Statistics), 2021b). The reservoir sediment could be considered polluted most of the time, with mean N values higher than the limit established in current local legislation (4.8 mg N/g).

For the Itupararanga reservoir, a period of almost 40 years was evaluated (12.0–0.0 cm, 1978–2015). As reported by Wengrat et al. (2019), this reservoir has been considered mesotrophic since the 1970 s. Decreases of C_{org}, TN, and TP were observed from the late 1970 s until 1987 (14.0 cm), 1995 (8.0 cm), and 2003 (6.0 cm), respectively, while increases were observed after 2000. Nutrient sources, especially in the sediment from the dam area, included agricultural activities and inputs of eutrophic water from tributaries (Frascareli et al., 2015). The discharge of untreated effluents in the watershed remains a problem to be resolved. In 2016, calculation of the ICTEM (an indicator of urban sewage collection and treatment) classified five of the seven municipalities in the hydrographic basin as being in poor or very bad condition (FABH, 2021).

In the Igaratá and Atibainha reservoirs, the reduction of TN in the uppermost core sediments could be attributed to denitrification. Anoxic conditions could also explain the continuous decreases in TP concentrations in the Atibainha reservoir after the 1990 s (Fonseca et al., 2011), with releases of P from the sediment (Fig. 3). Conversely, the concentrations of photosynthetic pigments (lutein and fucoxanthin) in the sediment increased during the same period (manuscript in preparation), suggesting an increase in the trophic state of the reservoir.

3.4. Metals

Most of the metals analysed showed no significant changes over time in the reservoirs, suggesting that the water bodies had not been significantly impacted by these contaminants (Fig. 4–5). The metal content was similar to background values (Table 4), although the concentrations of Cu, Mn, and Ni increased over time in some reservoirs.

The Ni concentration in the uppermost layers of the sediment from the Barra Bonita reservoir showed an increase after 2011 (Fig. 4). Despite the Ni increase, the EF indicated minimal enrichment. The PLI revealed the absence of significant contamination over time, and the RI indicated a low potential risk to the biota (Tables 5 and 6). Although the SQG suggested that adverse effects on biota were unlikely to occur, the Ni background was higher than the ISQG value. In such situations, the SQG should be replaced by the background value (Chapman et al., 1999). Previous reports did not indicate any Ni contamination in the Barra Bonita reservoir dam area (Silva et al., 2002; Silvério et al., 2005; Rodgher et al., 2005; Bevilacqua et al., 2009). However, according to the local environmental agency, Ni levels in the central portion of the reservoir have been increasing since 2005 (CETESB, 2016), with values above the PEL. These high Ni concentrations could originate from sources in the extremely industrialised and urbanised Piracicaba basin, located upstream of the Barra Bonita reservoir (Rodgher et al., 2005; Silvério et al., 2005). Some activities in the Piracicaba watershed that could contribute to Ni inputs are the burning of fossil fuels (Nriagu and Pacyna, 1988), electroplating and paint industries, and the inappropriate disposal of batteries containing Ni in landfills (Azevedo and Chasin, 2003).

At the Salto Grande and Itupararanga reservoirs, reductions in Pb levels were observed in the early 1990 s (Fig. 4) due to the decreased use of tetraethyl lead in gasoline, as also observed in other areas (Pienitz et al., 2006; Chalmers et al., 2007; Michelutti et al., 2009; Cardoso-Silva et al., 2016a). At the Broa and Salto Grande reservoirs, increases of Mn in the sediment (Fig. 4) could be attributed to inputs of municipal wastewater since these reservoirs are known to be impacted by human wastes derived from nonpoint sources (Tundisi et al., 2003; Periotto and Tundisi, 2013; Fonseca and Matias, 2014). Manganese is commonly found in municipal wastewater, although the concentrations usually do not pose any environmental risks (Vymazal and Svehla, 2013). There could also be a contribution from erosion since the watersheds of these reservoirs are influenced by the presence of intense agricultural activities that extend along the margins of the reservoirs (Frascareli et al., 2018).

Despite these increases, the Broa, Barra Bonita, and Salto Grande reservoirs did not exhibit substantial enrichment, contamination, or ecological risk (Tables 5 and 6). Furthermore, the SQGs suggested that adverse effects on biota were unlikely to occur (Fig. 4). However, signs of contamination were evident in the Rio Grande reservoir (Fig. 5). All

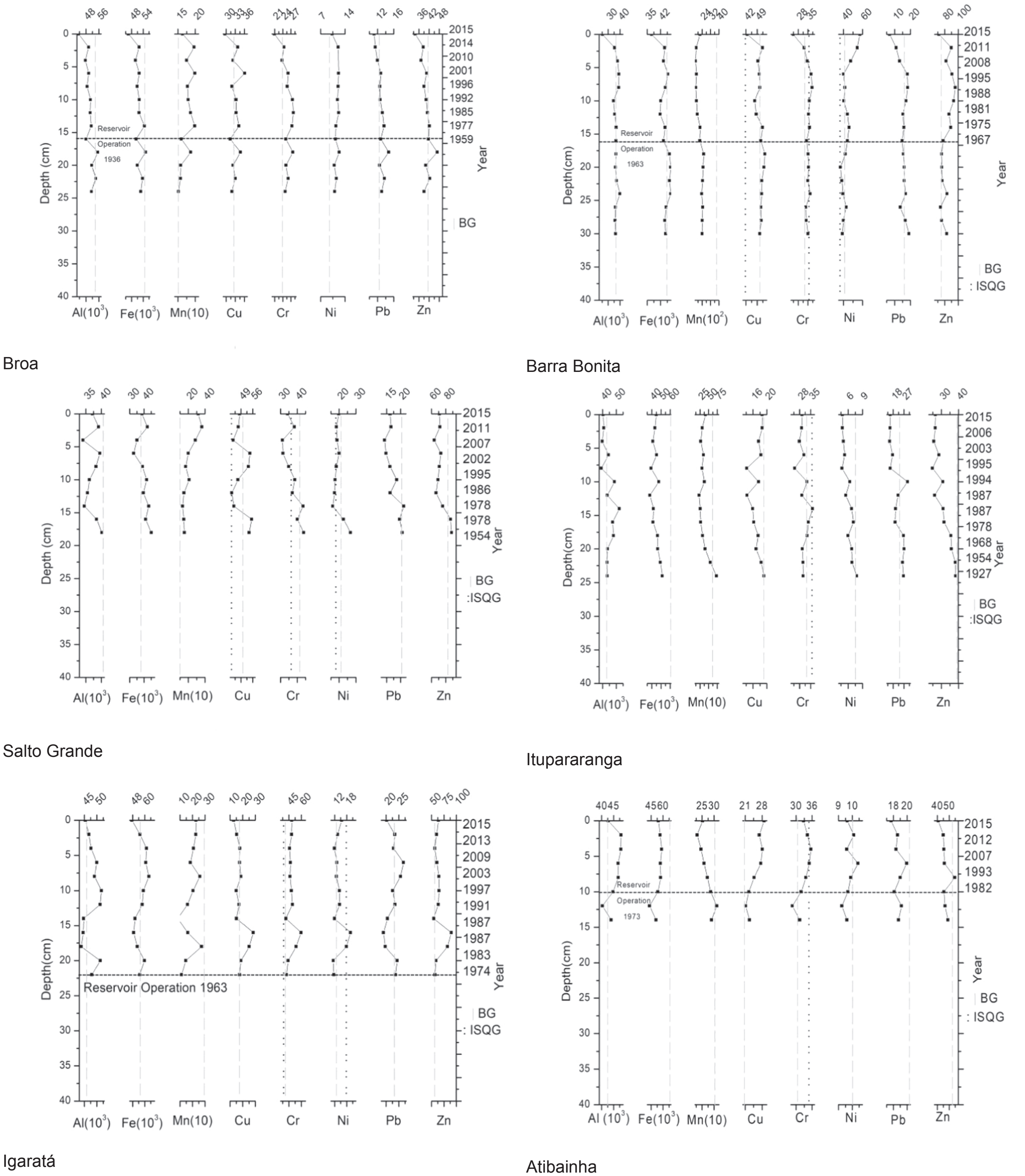

Fig. 4. Concentrations (mg/kg) of Al, Fe, Mn, Cu, Cr, Ni, Pb and Zn in sediment cores collected from six São Paulo State reservoirs. ISQG: interim sediment quality guideline; BG: background. The ISQG are: Cu (35.7 mg/kg), Cr (37.3 mg/kg), Ni (18 mg/kg), Pb (35 mg/kg), Zn (123 mg/kg).

indices indicated contamination in this region (Figs. 6a and 6b; Tables 5 and 6). In the case of Mn enrichment, the EF values were moderate at the start of reservoir operation (2.9), followed by stabilisation in the mid-1960 s (2.1), and a subsequent increase from the 1980 s (2.4), resulting in considerable enrichment in the three most recent core slices (for the year 2015), with values of 8.3, 8.4, and 8.6 (Fig. 6a). These high Mn contents could be explained by the input of effluents (Vymazal and Svehla, 2013), as well as erosive processes, since there was a significant correlation between Mn and SR ($r = 0.73$, $p < 0.0001$). For Cu, the enrichment factors were very high, with a value of 35.2 for the depth of 22 cm (in 1945) and the highest value of 267.6 in 1984 (Fig. 6a).

The PLI values for the Rio Grande reservoir suggested that

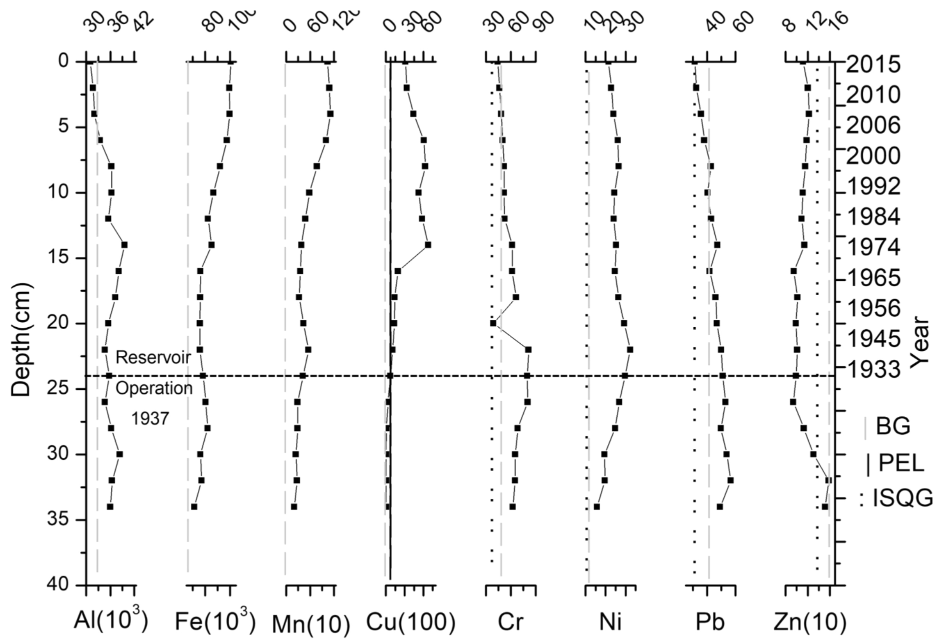

Fig. 5. Concentrations of Al, Fe, Mn, Cu, Cr, Ni, Pb and Zn in sediment cores collected from the Rio Grande reservoir. ISQG: interim sediment quality guideline; PEL: probable effect level; BG: background. The ISQG are: Cu (35.7 mg/kg), Cr (37.3 mg/kg), Ni (18 mg/kg), Pb (35 mg/kg), Zn (123 mg/kg).

Table 4
Background values for metals (mg/kg dw) in the dam areas of the reservoirs.

Metal	Broa	Barra Bonita	Salto Grande	Itupararanga	Igaratá	Atibainha	Rio Grande
As	-	-	-	3.0 ± 0.9	-	-	14.05 ± 2.71
Cr	24.6 ± 2.2	34.1 ± 0.9	42.5 ± 2.1	32.7 ± 1.7	43.5 ± 3.2	32.3 ± 2.6	58.0 ± 8.9
Cu	32.2 ± 3.3	51.1 ± 0.5	51.3 ± 5.7	19.2 ± 0.9	16.3 ± 2.2	23.1 ± 1.8	-
Ni	11.5 ± 2.0	40.6 ± 2.0	21.9 ± 5.4	8.7 ± 0.6	12.2 ± 0.5	10.6 ± 0.3	14.9 ± 2.7
Pb	12.9 ± 1.1	16.4 ± 2.8	20.5 ± 0.8	25.8 ± 2.1	23.8 ± 3.0	21.1 ± 0.5	43.2 ± 6.9
Zn	41.1 ± 4.2	77.6 ± 4.8	83.6 ± 6.8	40.8 ± 4.4	58.8 ± 4.1	50.6 ± 5.0	141.0 ± 32.1
Mn	116.5± 20.2	2422 ±26.9	143.1 ± 1.5	583.9 ±131.6	332 ±154.5	289.8 ±19.8	176.8 ± 31.1
Al*	53.8 ± 5.8	36.1 ± 0.2	43.1 ± 2.0	43.5 ± 2.1	46.6 ± 2.2	44.7 ± 3.4	34.1 ± 2.9
Fe*	55.0 ± 4.5	44.6 ± 0.54	37.7 ± 2.9	61.0 ± 11.0	51.2 ± 8.5	71.8 ± 10.3	67.6 ± 8.2

*g/kg dw

Table 5
Mean enrichment factors (EFs) for sediments from seven reservoirs in São Paulo State, Brazil. Moderate and very high EF values are highlighted in bold type.

Metal	Broa	Barra Bonita	Salto Grande	Itupararanga	Igaratá	Atibainha	Rio Grande
As	-	-	-	1.82 ± 0.98	-	-	1.09 ± 0.19
Cr	1.09±0.06	1.01 ± 0.04	0.95 ± 0.04	0.93 ± 0.04	1.07± 0.26	0.95± 0.06	1.28 ± 0.23
Cu	1.07±0.06	0.99 ± 0.07	1.05 ± 0.15	0.90 ± 0.11	1.04± 0.13	0.90±0.26	**42.99±42.52**
Ni	0.97±0.40	1.09 ± 0.27	0.98 ± 0.16	0.69 ± 0.10	1.06± 0.24	0.87± 0.15	1.84 ± 0.23
Pb	1.05±0.05	0.92 ± 0.15	0.92 ± 0.07	0.03 ± 0.01	0.96± 0.09	0.93± 0.08	1.22 ± 0.16
Zn	1.04±0.04	1.07 ± 0.11	0.96 ± 0.10	0.78 ± 0.14	1.03 ±0.20	0.97± 0.16	1.03 ± 0.18
Mn	1.47±0.03	0.90 ± 0.16	1.63 ± 0.66	0.67 ± 0.25	0.62± 0.29	0.46± 0.74	**3.66 ± 2.53**

contamination began before the reservoir entered operation, from a depth of 26 cm (3.0), with the highest value of 86.3 in 2006 (Fig. 6b). The RI (Fig. 6b) increased significantly over time, reaching the highest value of 484.9 in 1984. Although the risk remained very high, the three uppermost layers (2015) showed lower values of 249.1, 269.3, and 350.9. Cu was the main element responsible for the high RI, with a significant correlation between RI and Cu ($r = 0.99$; $p < 0.001$). In the case of PLI, significant correlations were observed for Mn ($r = 0.74$) and Cu ($r = 0.92$).

Cu content, up to 270-fold higher than the regional reference value established by Nascimento and Mozeto (2008) for the Alto Tietê watershed (15 mg/kg dw), was due to applications of copper sulphate to control algal blooms. Although Cu is effective in reducing algal blooms, this algaecide has toxic effects on aquatic organisms (Jančula and MarŠálek, 2011). Alternatives to its use are needed, since Cu, together with As and Hg, are among the elements most toxic to aquatic communities (Luoma and Rainbow, 2008). Although the metals in the Rio Grande sediment are not bioavailable, since they are mainly complexed with sulphides and OM (Mariani and Pompêo, 2008), this does not preclude adverse effects on aquatic biota. For example, in the Paiva Castro reservoir, Cu concentrations up to four-fold higher than background levels were suggested to have bioaccumulative effects on benthic macroinvertebrates (Beghelli et al., 2016), which could also occur in the Rio Grande reservoir.

Cu contamination was so significant in the Rio Grande reservoir that it was not possible to establish background conditions. In periods when

Table 6
Descriptive statistics for the pollution load index (PLI) and ecological risk index (RI) values for the sediments of seven reservoirs in São Paulo State, Brazil.

		Broa	Barra Bonita	Salto Grande	Itupararanga	Igaratá	Atibainha	Rio Grande
PLI	Min	0.1	0.0002	0.2	0.01	0.03	0.01	0.03
	Max	0.6	0.001	0.6	0.2	0.4	0.02	86.0
	Mean	0.3	0.001	0.4	0.1	0.2	0.02	25.6
	SD	0.1	0.003	0.1	0.05	0.1	0.003	28.9
	CV	53.7	54.8	39.2	0.8	75.7	17.6	112.8
RI	Min	6.3	17.5	12.9	6.8	10.0	2.2	12.7
	Max	10.5	19.4	17.4	10.5	14.2	14.3	484.9
	Mean	9.4	18.2	14.5	8.8	11.7	10.4	191.6
	SD	0.9	0.5	1.4	1.2	0.9	5.0	175.1
	CV	10.1	2.98	9.3	13.6	8.1	47.7	91.7

SD: standard deviation; CV: coefficient of variation (%); Min: Minimum; Max: maximum.

copper sulphate was not applied, the levels of Cu reached 300 mg/kg dw. This was 20-fold higher than that found for the Alto Tietê basin (Nascimento and Mozeto 2008), which could have been due to industrial activities or the vertical migration of Cu to deeper layers (Smol, 2008; Liu et al., 2018). An industrial source is a remote possibility because industrialisation in the Rio Grande watershed in the first half of the 20th century was low and restricted to the Santos-Jundiaí railway. Although not common, vertical migration to deeper layers is a possibility. For example, Liu et al. (2018) attributed lateral and vertical mobility of the metal Tl to complex processes such as mechanical disturbance/mixing and vertical migration by means of colloidal (or microparticle) transport with alumino-phyllosilicates and Fe/Mn (hydr)oxides. Some of these factors could apply to the Rio Grande reservoir. Although Cu is a low mobility metal with high affinity for OM, the presence of insufficient binding sites for Cu could lead to migration to deeper layers. However, further research is needed, including sequential metal extractions, to improve the understanding of Cu dynamics in sediments of the Rio Grande reservoir.

Despite Cu migration, the highest Cu concentrations occurred in 1984 (6183.0 mg/kg dw) and 1992 (5518.3 mg/kg dw). During the same timeframe (1981–2017), high levels of total Cu in surface water in the dam area were found by the local environmental agency (CETESB). High concentrations in the 1980 s and 1990 s were related to the large quantities of sewage discharged into the watershed, resulting in severe problems with contamination by potentially toxic cyanobacteria (Capobianco and Whately, 2002), leading to increased applications of copper sulphate in the Rio Grande reservoir.

The concentrations of dissolved Cu in surface water were mostly below the threshold value of 0.02 mg/L established in current legislation (CONAMA 357/2005), with only eight samples presenting values higher than the threshold. Monitoring of dissolved Cu in this reservoir began in 2006 (bimonthly samplings from 2006 to 2010 and from 2015 to 2017, and quarterly samplings from 2011 to 2014). The low levels of dissolved Cu, compared to Cu in the sediment, indicated that the metal was present in the form of complexed species, mainly due to the presence of high levels of OM and sulphides (Mariani and Pompêo, 2008).

3.5. Spatial heterogeneity among the reservoirs

Spatial heterogeneity among the reservoirs was evaluated using PCA. Based on the eigenvalues, two principal components (PCs) explained 59.42% of the total variance (Fig. 7). PC1 showed positive loadings for Zn (0.95), Cu (0.73), Pb (0.70), and Ni (0.67), with the influence of the samples from the Rio Grande reservoir (Fig. 7). In contrast, PC2 showed negative loadings for Mn (-0.76), Ni (-0.68), and TP (-0.53), with the influence of the samples from the Barra Bonita reservoir. Therefore, there was separation of the reservoirs according to the characteristics of the impacts. The Rio Grande reservoir exhibited the highest values for metals (especially Cu), followed by the Barra Bonita reservoir (for Pb, Mn, and Ni).

In general, the Rio Grande reservoir, the only one located in the Metropolitan Region of São Paulo (MRSP), one of the most densely populated regions in the world (21.9 million inhabitants), presented the highest concentration of metals. This reservoir has been subjected to eutrophication processes for decades. The transposition of the waters of the Tietê River in the early 1940 s, followed by the establishment of residential areas in the 1960 s, led to continuous degradation of the reservoir. The applications of copper sulphate after 1985 (Beyruth and Pereira, 2018), a controversial measure, intensified the degradation of the reservoir. In the case of the Guarapiranga reservoir, which has surface sediment copper levels similar to those of the Rio Grande reservoir (manuscript in preparation), the sum spent on copper sulphate applications over 43 years was 28% higher than the cost of installing full sewage treatment in the drainage basin (Leal et al., 2018). Several actions have been taken to improve water quality in the watershed. During the 1970 s and 1980 s, various policies were elaborated to control and regulate unplanned urbanisation in the spring areas (Santoro et al., 2008). In 1982, the Rio Grande was isolated from the Billings reservoir by construction of a dam to control algal blooms. Despite these actions, inadequate investment in basic sanitation persisted during the following years, resulting in increased nutrient inputs.

In the Barra Bonita reservoir, contamination by TP and Ni was due to both the discharge of urban effluents and the presence of an adjacent petrochemical installation (Silva et al., 2002; Silvério et al., 2005; Rodgher et al., 2005; Bevilacqua et al., 2009). The Barra Bonita reservoir is in the vicinity of the São Paulo metropolitan region, and for years, there have been records of intensification of the eutrophication process. The reservoir receives water from both the Tiête and Piracicaba rivers, which flow through the city of São Paulo and agricultural areas of Piracicaba, respectively, consequently transporting high loads of OM and nutrients, in addition to metals and other potential contaminants, to the Barra Bonita region.

A second PCA was performed with exclusion of the Rio Grande reservoir samples to investigate the distribution of the variables for the other reservoirs. Two principal components (PCs) explained 61.52% of the total variance (Fig. 8). PC1 showed positive loadings for Ni (0.92), Cu (0.86), Mn (0.84), and TP (0.83), associated with samples from the Salto Grande and Barra Bonita reservoirs (Fig. 8). PC1 reflected the impacts of anthropogenic activities, such as Ni contamination in the Barra Bonita reservoir and the high phosphorus levels in the Salto Grande and Barra Bonita reservoirs, which have both been affected by eutrophication (Zanata and Espíndola, 2002; Dornfeld et al., 2006; Buzelli and Cunha-Santino, 2013).

Despite presenting lower levels of nutrients and metals, compared to the Barra Bonita and Rio Grande reservoirs, the Salto Grande reservoir also has records of persistent fish mortality, low levels of oxygen, and increasing eutrophication. Intense agricultural activity, mainly the cultivation of sugar cane, is an important factor contributing to increased concentrations of nutrients in the reservoir, since part of the inputs used in this monoculture may be discharged into the watershed (Martins et al., 2011). Its main water source, the Atibaia River, receives contributions from several small tributaries draining urban centres

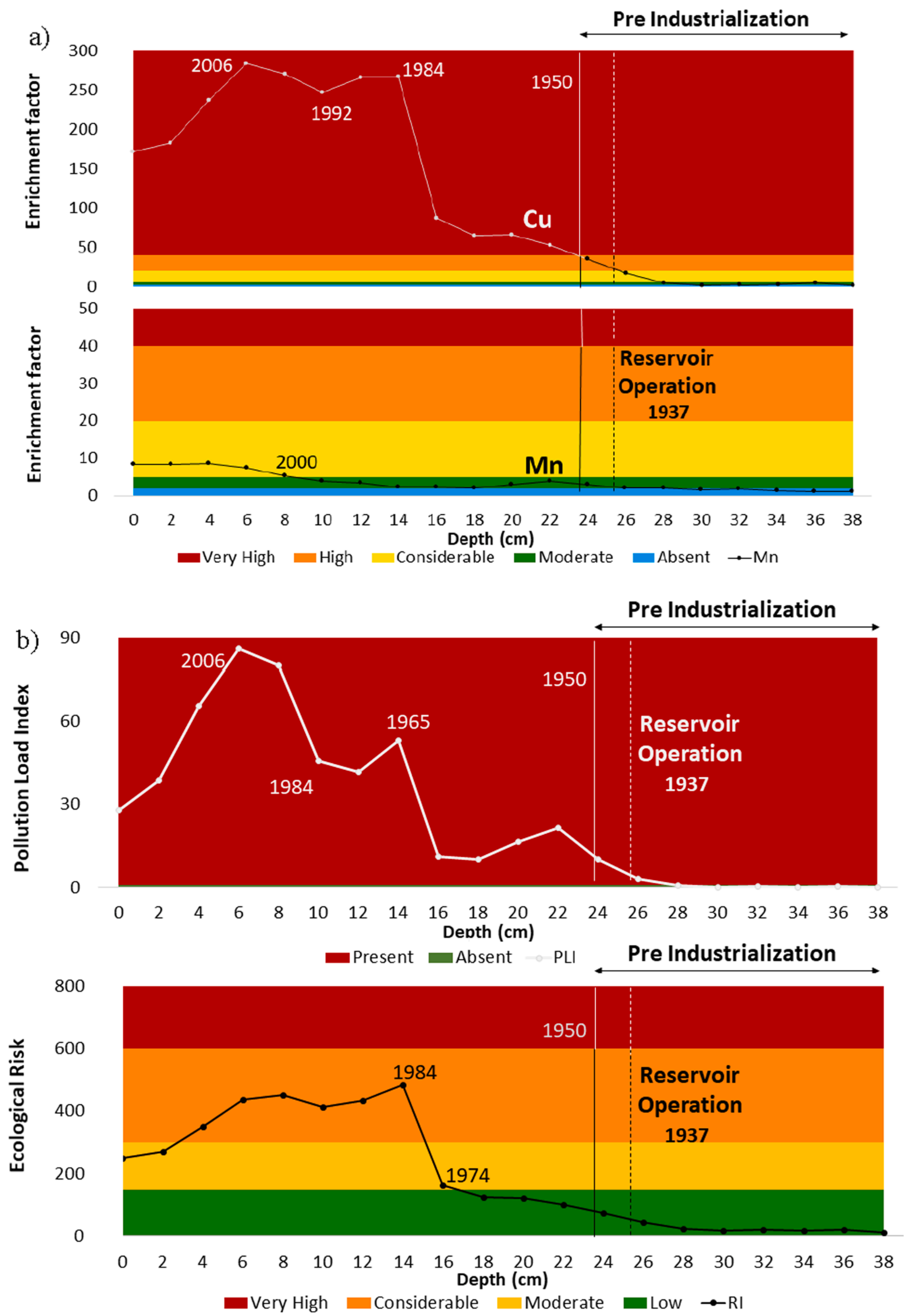

Fig. 6. Enrichment factors for Cu and Mn (a) and pollution load index (PLI) and ecological risk index (RI) (b) in the Rio Grande reservoir. Warmer colors indicate more intense impacts, while colder colors indicate lower impacts.

(Rietzler et al., 2018). The higher levels of Mn in the Barra Bonita reservoir can be explained by the natural characteristics of the drainage basin. However, in the Salto Grande reservoir, Mn has increased since the 1990 s, probably associated with increased erosion processes and eutrophication, as discussed previously.

PC2 showed positive loadings for Cr (0.89) and Pb (0.77), together with negative loadings for C_{org} (-0.71) and TN (-0.61). The Igaratá reservoir samples were influenced by Cr and Pb, while C and TN were important for the Broa reservoir samples. Therefore, PC2 could be characterised as a natural environment component, indicated by the presence of geogenic Cr and Pb in the Igaratá reservoir, while the higher C_{org} and TN content in the Broa reservoir reflected the contribution of eutrophication processes (Tundisi and Matsumura-Tundisi, 2013; Soares-Silva et al., 2020). The PCA loads are provided in the supplementary material (Table SM 4).

4. Conclusions and final considerations

All seven reservoirs displayed anthropogenic impacts of various magnitudes, which tended to increase in recent years. Increases in SRs in

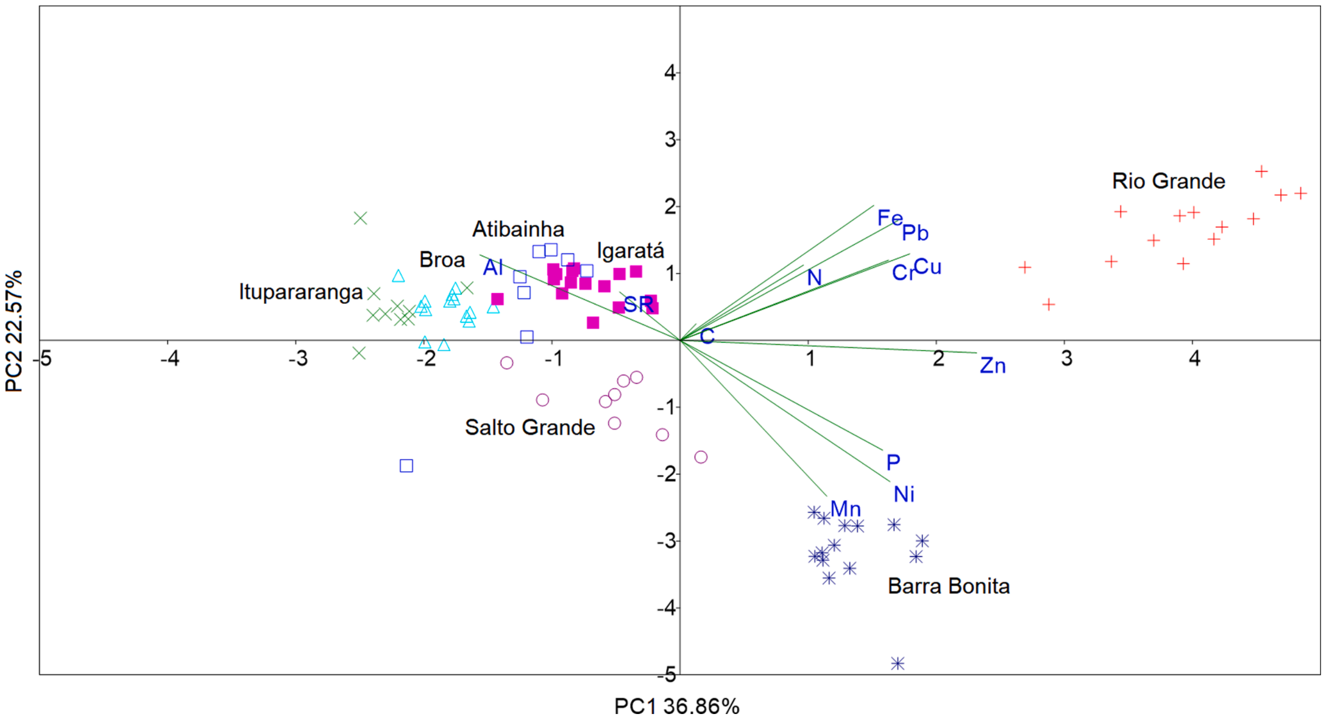

Fig. 7. Principal component analysis using the data for metals, carbon (C), total phosphorus (TP), total nitrogen (TN), and sedimentation rate (SR), for sediment cores collected from seven reservoirs in São Paulo State, Brazil.

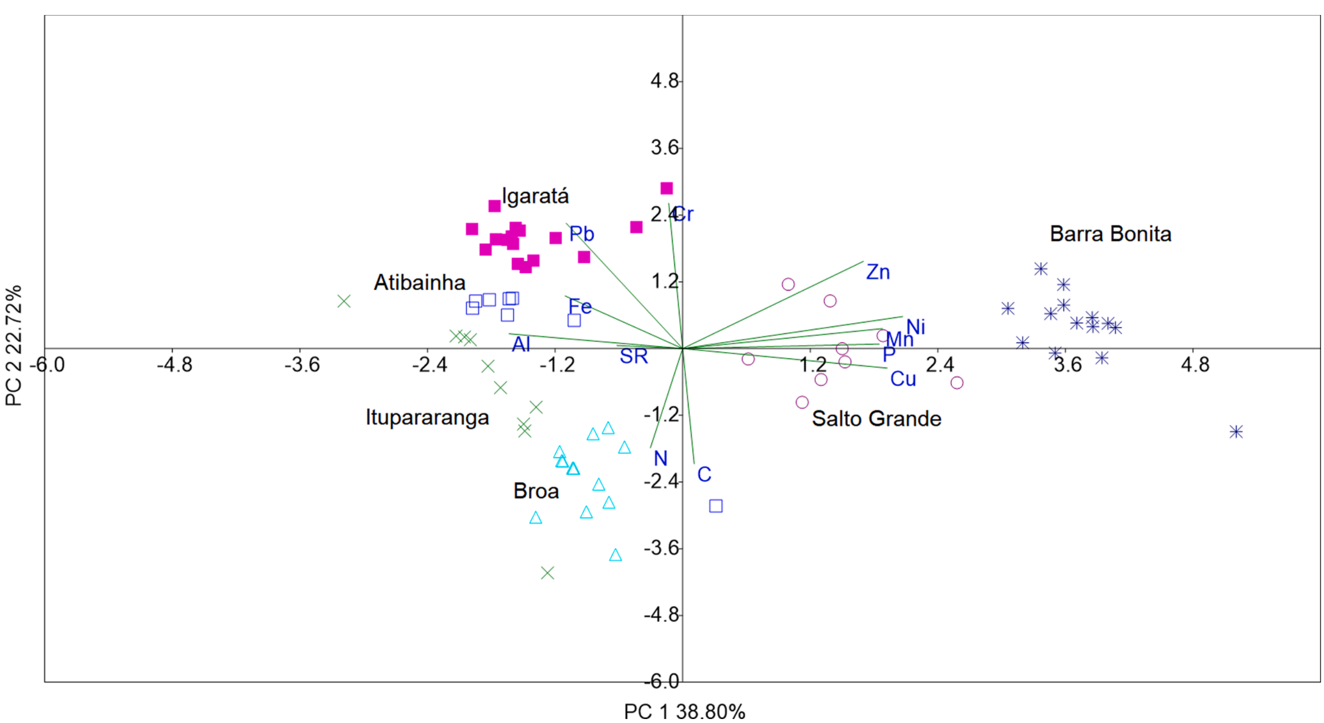

Fig. 8. Principal component analysis using the data for metals, carbon (C), total phosphorus (TP), total nitrogen (TN), and sedimentation rate (SR), for sediment cores collected from six reservoirs in São Paulo State, Brazil (the data for the Rio Grande reservoir were excluded).

these reservoirs were mainly attributed to eutrophication and changes in land use and occupation. Signs of eutrophication were especially evident in the Broa, Barra Bonita, Salto Grande, and Rio Grande reservoirs, where the sediments were polluted by TP and TN, with low C:P molar ratios.

Analyses of the metals enabled the establishment of background values, while the EF, PLI, RI, and SQG (ISQG/PEL) values were indicative of no significant impacts for most of the reservoirs. Increases were observed for Ni, Mn, and Cu, together with decreases of Pb. An increase of Ni in the Barra Bonita reservoir was related to the presence of sources in the highly industrialised and urbanised Piracicaba basin, located upstream of the reservoir. Increases of Mn in the Broa, Salto Grande, and

Rio Grande reservoirs were correlated with increases of SR, possibly due to erosive processes. Decreases in Pb were observed in the Itupararanga and Salto Grande reservoirs, coinciding with the period when the use of Pb as a petroleum additive was restricted.

The Rio Grande was the most heavily impacted reservoir, especially by metals linked directly (Mn) and indirectly (Cu) to effluent discharges and consequent eutrophication. In the case of Cu, the contamination originated from the application of algaecides containing copper sulphate. The Cu concentration exhibited an increase of up to 49-fold since the initiation of reservoir operation in 1933. This was a period prior to industrialisation in the region and the application of copper sulphate algaecides. The increase of Cu in bottom sediments could be explained by industrial sources, although this is a remote possibility, or to vertical migration by means of complex mechanisms, such as colloidal (or microparticle) transport with alumino-phyllosilicates. However, further research is needed to improve the understanding of Cu dynamics in sediments of the Rio Grande reservoir. In addition, in paleoenvironmental reconstruction studies, caution is needed in the interpretation of data concerning the levels of metals in cases of excessive metal inputs.

The PCA results suggested that the Rio Grande reservoir presented the greatest risks related to anthropogenic impacts, followed by the other reservoirs, in the following order: Barra Bonita > Salto Grande > Broa > Itupararanga = Atibainha = Igaratá. The data highlighted the lack of urban planning and public policies to preserve or enhance the quality of water in some of these reservoirs. This work makes an important contribution to the field of paleolimnology since environmental reconstruction applied to reservoirs has not been actively explored. Given the increasing number of water bodies affected by urbanisation processes, the findings of this research can also be applied in other geographical contexts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catena.2021.105432.

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