

Metals in superficial sediments of a cascade multisystem reservoir: contamination and potential ecological risk

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Abstract Cascade multisystem reservoirs are extremely complex ecosystems that require studies to improve understanding of their dynamics and functioning, including the effects of contamination with metals. In this work, superficial sediments were collected during two sampling campaigns (in the dry and rainy seasons) at 19 sites along a cascade multisystem reservoir in São Paulo, Brazil, formed by five reservoirs. The sediments were evaluated considering the following parameters: pseudo-total metals (Cu, Cd, Cr, Ni, Pb, Zn, Mn, Fe, and Al); bioavailable metal (Cu); organic matter; total phosphorus; total nitrogen; and grain size. In the last reservoir of this system, the enrichment factors indicated enrichment of Cu, Pb, Zn, and Mn. Despite this increased metals content, the pollution load index indicated an absence of pollution ($PLI < 1$), and the ecological risk was low ($RI < 150$). According to sediment quality guideline criteria, toxicity was unlikely to occur. Principal component analysis (PCA) and one-way ANOVA indicated heterogeneity among the reservoirs ($P < 0.01$) and between the sampling periods. The PCA results confirmed higher levels of nutrients in the upstream reservoirs, suggesting that nutrients were precipitated in the first reservoirs of the

system. On the other hand, metal levels were higher in the downstream reservoirs. The main source of metal contamination in the region was the use of copper sulfate as an algicide. This included contamination by Pb and Zn, due to impurities in the copper sulfate employed. High Mn levels were associated with wastewater discharges and erosion. In addition to helping to improve understanding of the dynamics of metals in cascade multisystem reservoirs, this work could serve as a useful tool for the management of reservoirs with contaminated sediments.

Keywords Sediments · Cascade reservoir · Metal · Copper

Introduction

Reservoirs are artificial ecosystems used for multiple purposes including public supply, power generation, and recreation (Straškraba and Tundisi, 2000). The importance of reservoirs in providing ecosystem services has been increasingly recognized (Moggridge et al. 2014), together with the need to maintain their functioning and integrity. Nonetheless, it remains a challenge to safeguard or improve the water quality of these aquatic ecosystems, especially in urban landscapes. This is particularly true in developing countries, where the collection and treatment of sewage is often inadequate (Selborne 2001; Pompêo and Moschini-Carlos 2012), and there is poor planning and control of land use and occupation, which directly affects water quality.

Studies of these ecosystems and understanding of their dynamics are extremely important and need to be expanded, particularly in developing countries where the construction of reservoirs and urbanization of hydrological basins are increasing (Nogueira et al. 2008). Unplanned urbanization

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of the basin and shores of a reservoir leads to degradation of the quality of the water bodies in the region. In particular, studies are required of cascade reservoirs (interconnected reservoirs constructed along the same river) and cascade multisystem reservoirs (interconnected reservoirs that have origins in different rivers). These systems are extremely complex, due to the combination of their morphological, physicochemical, and biological characteristics, together with anthropogenic hydraulic management and water uses (Straškraba and Tundisi 2000).

In cascade reservoirs, the downstream reservoirs are affected by the characteristics of the reservoirs further upstream (Petesse and Petrere 2012; Petesse et al. 2014), in terms of both biotic (Nogueira et al. 2008; Perbiche-Neves and Nogueira 2013; Santos et al. 2016) and abiotic components (Enner et al. 2016; Liu et al. 2013; Pompêo et al. 2003). Among the abiotic components, many studies have focused on the distribution of nutrients along the cascade (Roberto et al. 2009; Liu et al. 2015; Pompêo et al. 2003). On the other hand, there have been few studies that have analyzed metal distributions and contamination in a cascade system as a whole (Rodgher et al. 2005; Smith et al. 2014). Most research has evaluated metals in only one reservoir of the cascade (Kummu and Varis 2007; Wang et al. 2012; Cardoso-Silva et al. 2016a, b; Beghelli et al. 2016). However, in order to understand the processes in one reservoir of a cascade or multiple reservoir system, it is important to study all the reservoirs in the system (Pompêo et al. 2003).

According to cascade reservoir theory (Straškraba et al. 1993; Barbosa et al. 1999; Tundisi and Matsumura-Tundisi 2008; Straškraba and Tundisi 2013), cascading reservoirs that are similarly impacted along their basins are expected to show nutrient levels that decrease from the initial reservoirs of the system to the final ones, in an upstream–downstream direction (Barbosa et al. 1999). Smith et al. (2014) found this decreasing pattern for both nutrients and metals in a cascade system formed by six reservoirs in the Tietê River watershed (São Paulo Brazil). For cascade multisystem reservoirs, since the reservoir system may contain reservoirs derived from different rivers, the upstream–downstream concept may not be the most suitable, since there is no continuity of the river, but there is continuity of water flow between the reservoirs.

In the Cantareira system, a cascade multisystem reservoir that is the largest producer of water for public supply in the metropolitan region of São Paulo, a decreasing trend for nutrients was observed upstream–downstream (Pompêo et al. 2003). In the case of metals, however, there is no information about the system as a whole, although all the basins of the reservoirs of the Cantareira system are impacted by anthropic uses such as urban settlements and agricultural activities and are therefore susceptible to metal contamination. The first papers focusing on metal contamination in the

region were published by Cardoso-Silva et al. (2016a, b) and Beghelli et al. (2016). These investigations mainly focused on the last reservoir of the system (the Paiva Castro) and found signs of copper contamination.

The present study had two main objectives. The first was to know whether metals show a decreasing trend from the initial reservoirs to the final reservoirs, as assumed according to cascade reservoir theory. To this end, the spatial heterogeneity of metals in sediments was evaluated in the Cantareira cascade multisystem reservoir, in strategic areas representative of the main reservoir compartments (riverine, transitional, and lacustrine) (Kimmel et al. 1990), as well as in the water inlet and outlet regions. The second objective was to assess the extent of contamination and the ecological risk by applying several criteria such as enrichment factor (EF), pollution load index (PLI), ecological risk index (RI), and sediment quality guidelines (SQGs) in order to identify areas requiring efforts to control contamination levels and the implementation of future ecotoxicological testing. This research therefore contributes to improving understanding of the dynamics of metals in cascade multisystem reservoirs, which to date has been insufficiently studied.

Materials and methods

Study area

The Cantareira system began operating in May 1973 and is the main source of drinking water for the metropolitan region of São Paulo (Brazil) (MRSP). It has a flow of $33 \text{ m}^3 \text{ s}^{-1}$ (Whately and Cunha 2007), an extent of 48 km (SABESP 2016), and supplies water for 9 million people. It is composed of five reservoirs: Jaguari, Jacaré, Atibainha, Cachoeira, and Paiva Castro, connected using artificial underground tunnels, canals, and pumps (Whately and Cunha 2007).

The reservoirs were developed in two main stages. In the first stage, the Paiva Castro, Atibainha, and Cachoeira reservoirs were built and commenced operation in 1974, contributing a flow of $11 \text{ m}^3 \text{ s}^{-1}$. The second stage was completed in 1981, with the Jaguari and Jacaré reservoirs being included in the system, increasing the flow to $33 \text{ m}^3 \text{ s}^{-1}$ (Whately and Cunha 2007).

Despite its importance for the MRSP, the Cantareira system is suffering from high population growth along its forming watersheds, with significant impacts caused by anthropic activities associated with agriculture (38.70%) and silviculture (42.70%) (Vieira and Vieira 2016). In 2003, anthropic uses corresponded to 69.4% of the watersheds (Whately and Cunha 2007); in 2016, this area had increased to 81.80% (Vieira and Vieira 2016). In all the watersheds that form the system, over half the area has been altered by human activities. The Jaguari watershed, which provides

the greatest amount of water to the system, has experienced major changes. A significant proportion of its area (72.40%) is now occupied by anthropic activities, 2.40% is urbanized, and only 17.70% consists of remaining natural vegetation. The Cachoeira watershed is the most altered of all, with almost 80% of its area occupied by pastures, agriculture, forestry, and exposed soil, despite being the only watershed with areas around the reservoir owned by SABESP, the company responsible for public water supply in the region. The Jacareí watershed has the smallest area occupied by anthropic uses (52.20%), although it also has the highest urbanized area (10.00%) (Whately and Cunha 2007).

Sampling

Superficial sediments were collected (in triplicate) in different regions of each reservoir of the Cantareira system, in the dry (May/June 2013) and rainy (November/December 2013) seasons. Seasonal differences in metal concentrations can occur due to the influence of climatic conditions on metal cycling (Mohiuddin et al. Mohiuddin et al. 2011;

Duman and Kar 2012; Bastami et al. 2014; Pedro et al. 2016; Smith et al. 2014). The sampling sites were located in the three theoretical reservoir zones (riverine, transitional, and lacustrine) (Kimmel et al. 1990), as well as in water inlet and outlet channels (Fig. 1).

A Lenz-type grab (400 cm²) was deployed three times at each site. The fraction from 0 to 4 cm depth was collected in each deployment. A portion was removed for the determination of metals, and another portion was removed for analyses of organic matter (LOI), particle size, total nitrogen (TN), and total phosphorus (TP). The sediments were transferred to previously cleaned vials and kept in the dark at low temperature. For each sampling period, 57 samples were obtained for metal analysis and another 57 samples were obtained for the LOI, TP, TN, and grain size analyses.

Laboratory analyses

On the same day as sampling, the sediments were dried in a forced aeration oven at 50 °C until constant weight. They were later crushed using a glass mortar and pestle. The grain

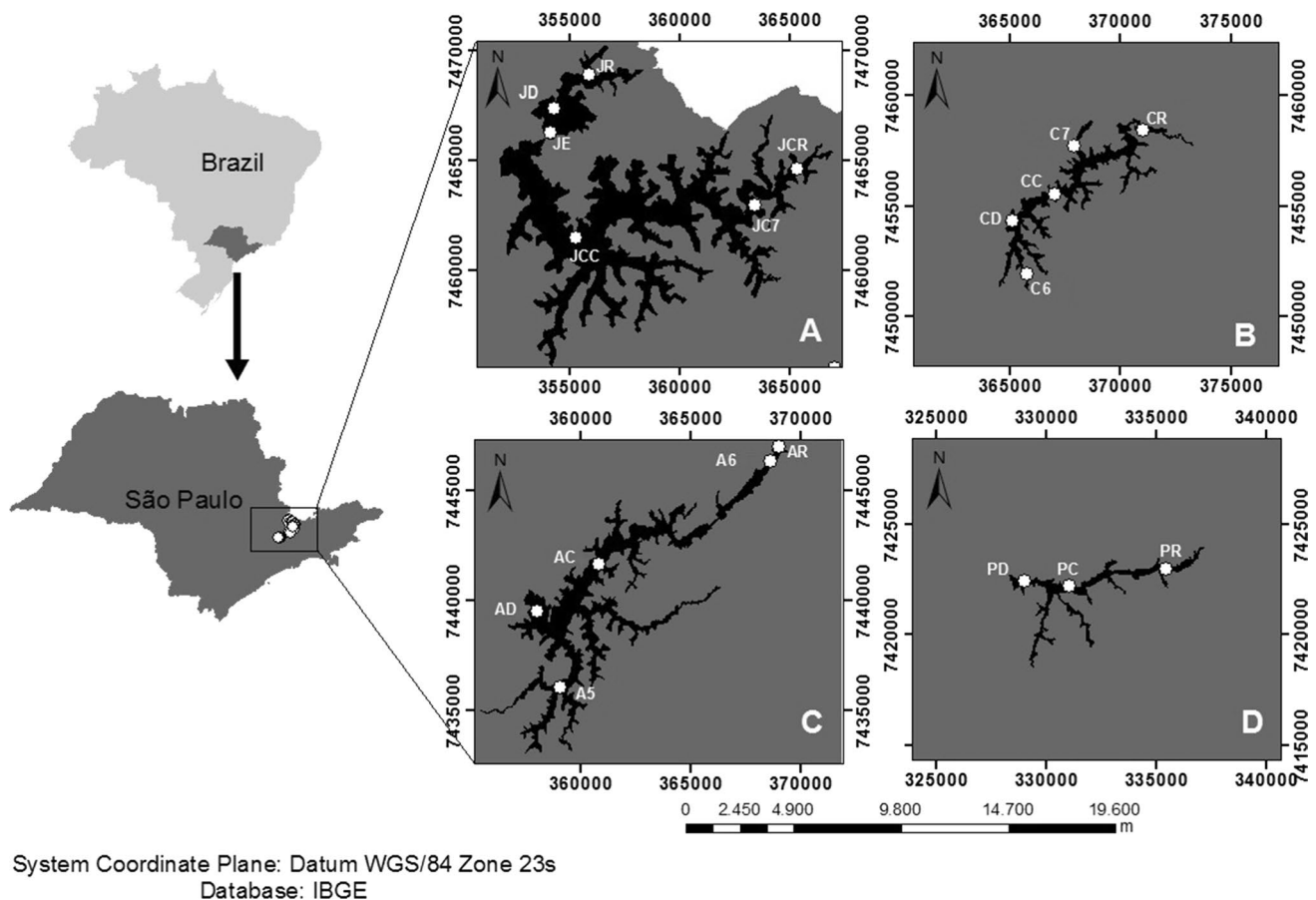


Fig. 1 Locations of the Cantareira system reservoirs (São Paulo, Brazil) and the sampling sites. A: Jaguarí (J) and Jacareí (JC); B: Cachoeira (C); C: Atibainha (A); G: Paiva Castro (P). R–river, C–center, D–dam, 5–channel 5, 6–channel 6, 7–channel 7

size of the sediment was determined by the laser diffraction method, using a Mastersizer 2000 analyzer (Malvern Instruments, UK), at the Geosciences Institute of the University of São Paulo (IG-USP). Organic matter (OM) was determined by the loss on ignition (LOI) method, which involves combustion of the organic matter in an oven at 550 °C (Meguro 2000). Another portion of the sediment was used for analyses of total nitrogen (total Kjeldahl nitrogen (TKN); APHA 2002) and total phosphorus (Andersen 1976), as described previously (Pompêo and Moschini-Carlos 2003).

A third sediment portion was used to determine the pseudo-total and bioavailable metals. Samples for the determination of pseudo-total metals were prepared according to the US EPA SW-846 Method 3050B (US EPA 1996). This method is a very strong acid digestion capable of dissolving almost all elements that could become environmentally available. The elements present in silicate structures are not usually dissolved by this procedure; however, the dissolution of these elements is not of environmental interest, since they are not mobile in the environment (Silvério et al. 2005). After being processed, the samples were stored at 4 °C prior to analysis in duplicate. Zinc, copper, chromium, nickel, cadmium, lead, manganese, aluminum, and iron were analyzed by atomic absorption spectrometry (AAS), using a Thermo Scientific Series S instrument.

Analyses were also performed of the *weakly bound metals* adsorbed onto *sediment particles*, considering those metals that presented concentrations above background also indicating that toxicity was likely or uncertain to occur according to empirical sediment quality guidelines. This metal fraction corresponds more closely to potentially bioavailable contaminants (US EPA 2005; Mozeto et al. 2014; Cardoso-Silva 2016a). The bioavailable metals were analyzed following the recommendations of Snape et al. (2004) and Santos et al. (2005), with extraction of the metals using the addition of 20 mL of 1 M HCl to 1 g of dry sediment. The samples were agitated for 3.5 h on a shaker, filtered through 125 mm Whatman No. 41 quantitative filter papers, and then diluted to 25 mL with ultrapure water. The samples were stored at 4 °C prior to analysis (in duplicate) by AAS.

Analytical grade reagents (obtained from Merck and Sigma-Aldrich) were used in both sets of analyses. All glassware and equipment used for the storage and processing of samples for metals analyses 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 using recovery assays performed using sample solutions fortified with the metals. Additions were made of SpecSol® G16 V standard solutions containing 100 mg/L of the metals in 2% HNO₃. Values between 75 and 125% were considered as the acceptance criteria. The recoveries of the metals ranged from 90 to 117%.

Data analysis

Metal contamination

To assess the level of metal contamination in the sediment, the data were compared to background values (Cardoso-Silva et al., 2016b) (Table 1) and use was also made of enrichment factors (EFs) and pollution load index (PLI) values. The background values used were determined using the US EPA Method 3050B pseudo-total digestion (US EPA 1996) and corresponded to the average concentrations of the elements in the three bottommost samples of cores collected along the Paiva Castro reservoir (Cardoso-Silva et al. 2016b). This procedure was performed because no background values have been established for the other Cantareira system reservoirs or their watersheds. The EFs were calculated as follows:

$$EF = \frac{\frac{Me}{El}}{\frac{Mer}{Elr}} \quad (1)$$

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. Among the conservative elements analyzed (Al and Fe), Al was

Table 1 Interim sediment quality guideline (ISQG, also known as the threshold effect level, TEL) and probable effect level (PEL) values (CCME 1999); effects range low (ERL) and effects range median

	Cd	Cr	Cu	Ni	Pb	Zn	Mn
ISQG (TEL)	0.60	37.30	35.70	18.00	35.00	123.00	–
PEL	3.50	90.00	197.00	36.00	91.30	315.00	–
ERL	1.20	81.00	34.00	20.90	46.70	150.00	–
ERM	9.60	370.00	270.00	51.60	218.00	410.00	–
BG	0.22*	26.50	24.30	32.60	26.70	69.50	261.50

*Background according to Nascimento and Mozeto (2008)

(ERM) values (Long et al. 1995); and background values (BG) (Cardoso-Silva et al. 2016b). The values are expressed in mg/kg of dry sediment

used for this purpose, because it showed the highest correlation with the analyzed metals (Cu $r = 0.49$; Ni $r = 0.48$; Mn $r = -0.63$ in dry season and Cu $r = 0.47$; Cr $r = 0.48$; Ni $r = 0.45$; Pb $r = 0.65$; Mn $r = -0.47$ in rainy season $P < 0.05$).

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

$$PLI = \left(C_f^1 x C_f^2 x C_f^n \right)^{1/n} \tag{2}$$

where C_f is the ratio between the concentration of the metal of interest and the corresponding background value. Table 2 shows the classifications of the indexes and their corresponding interpretations.

Ecological risk

The ecological risk associated with the Paiva Castro sediment was assessed using the following criteria: ecological risk index (Håkanson 1980) and two empirical sediment quality guidelines (SQG), 1) threshold effect level (TEL) a value also known as interim sediment quality guideline (ISQG), and probable effect level (PEL) (CCME 1999) and 2) the effects range low (ERL) and effects range median (ERM) values (Long et al. 1995).

The ecological risk index (RI) was calculated as follows (Håkanson 1980):

$$Ei = Tix Ci/C_0 \tag{3}$$

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

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

The Canadian SQG protocol is also widely used to assess the quality of sediments (Hübner et al. 2009) as well as the SQG established by Long et al. (1995). In these models, there is a range of values for each contaminant, whereby above a certain concentration (PEL/ERM), a toxic effect is

likely to occur, while effects are unlikely at concentrations below the ISQG and the ERL. At values between the ISQG/ERL and the PEL/ERM, effects can possibly occur (CCME 1999; Long et al. 1995) (Table 1).

Statistical analysis

The relations among the different reservoirs, sampling periods, and metal concentration values were explored using a centered and standardized matrix containing concentration values for each sample. Principal component analysis (PCA) was used for data ordination (Legendre and Legendre 1998). The segregation among sample scores was determined using one-way analysis of variance together with a multiple comparisons test (ANOVA; LSD test) at a significance level of $P < 0.05$. These comparisons were used to determine the contribution of differences in metal concentration to the distinction between reservoirs and sampling periods. The calculations were performed using the PAST (Hammer et al., 2001) and Statistica v. 7.0 software packages.

Results and discussion

General physicochemical properties of the sediments

The grain size and organic matter analyses indicated the existence of favorable conditions for immobilization of the metals in the sediments. For all reservoirs, periods, and sampling points, there was a predominance of the fraction below 63 μm (silt and clay), with mean values higher than 94.00% (Table 3). For both periods, the highest levels of sand were found in the riverine zone of the Paiva Castro reservoir (PR), as expected in such areas, with values of 16.36 and 26.65% in the dry and rainy periods, respectively. The concentrations of organic matter indicated that most of the sediments of all the reservoirs could be considered organic, according to the criterion of Esteves (2011), since the levels exceeded 10% (Table 3), hence favoring the binding of metals. The only exceptions were for PR in both periods (values of 9.21 and 7.06%), where the sediments were considered inorganic.

The lowest total phosphorus and total nitrogen concentrations were found in the sediment of the Paiva Castro reservoir, the last of the cascade system. The highest values for

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

EF values	Enrichment	PLI values	Contamination	RI values	Ecological risk intensity
< 2	Absent/very low	PLI > 1	Present	< 150	Low
2 ≤ EF < 5	Moderate	PLI < 1	Absent	150 ≤ RI < 300	Moderate
5 ≤ EF < 20	Considerable			300 ≤ RI < 600	Considerable
20 ≤ EF < 40	High			> 600	Very high
> 40	Very high				

Table 3 Descriptive statistics for parameters of the superficial sediments in the Cantareira system

	Dry season				Rainy season			
	Sil/Cl	TN	TP	LOI	Sil/Cl	TN	TP	LOI
	%	g/kg	mg/kg	%	%	mg/kg	mg/kg	%
Mean	96.12	285.00	429.08	15.53	94.65	273.00	312.87	14.55
SD	4.49	70.00	60.65	2.89	7.60	71.00	54.31	3.06
CV	4.68	24.53	14.13	18.64	8.03	260.10	17.36	21.03
Min	83.64	162.00	313.41	9.21	73.35	121.00	217.46	7.06
Sample	PC-R	PC-R	PC-R	PC-R	CA-C7	PC-R	PC-R	AT-C6
Max	100.00	410.00	548.12	19.38	100.00	408.00	403.61	18.08
Sample	PC-D	AT-C	JC-R	AT-C	JG-D	AT-D	JC-C7	PC-R

SD standard deviation, *CV* coefficient of variation (%), *Sil/Cl* silt/clay ratio, *TN* total nitrogen, *TP* total phosphorus, *LOI* organic matter (loss on ignition)

TP were found upstream in the Jacaréí reservoir, with the highest mean levels during the dry season (Table 3). According to the Canadian sediment quality guidelines, the Paiva Castro sediments would not be considered heavily polluted and no effects on sediment-dwelling organisms would be expected, since the TN and TP values did not exceed 4800 and 2000 mg/kg, respectively (Persaud et al. 1993).

Metals contamination: evaluation using background, EF, and PLI approaches

The mean concentrations and standard deviations for the metals are shown in Fig. 2, with the exception of Cd, for which levels were below the detection limit. The mean concentrations of most of the metals were close to the background values. Exceptions were for Cu, Cr, Pb, Zn, and Mn in the Jacaréí, Cachoeira, Atibainha, and Paiva Castro reservoir sediments, in one or both sampling periods.

The levels of copper exceeded the background (24.27 mg/kg) in the Atibainha reservoir in both periods; in the Cachoeira reservoir in the first period (dry season); and at all sampling points in the Paiva Castro reservoir, with the exception of the PR site in the rainy period. Although above-background concentrations were found for the Cachoeira and Atibainha reservoirs, the enrichment factors indicated minimal enrichment and a geogenic origin of the metal. For the Paiva Castro reservoir, the mean copper concentrations were 44.51 mg/kg (PR fluvial region, dry season); 49.72 and 42.95 mg/kg (PC central reservoir region, dry and rainy periods, respectively); and 48.78 and 67.29 mg/kg (PD dam region, dry and rainy periods, respectively). The high levels in the dam area could be explained by the fact that the limnical zone experiences higher rates of sedimentation, leading to greater metal accumulation (Mariani and Pompêo 2008; Pompêo et al. 2013; Cardoso-Silva et al. 2016a).

Although the highest levels of copper were found in the limnical region, the degree of enrichment was only moderate. Contamination was more critical in the PR region, which

was classified as being considerably enriched in copper in the first period (dry season). Compared to other regions of the Cantareira system, the sediment from this area was less favorable for metal binding, since it had the highest fine sand content, as well as the lowest level of organic matter. Therefore, the aquatic community could suffer greater exposure to potential contaminants.

The highest copper levels were due to applications of copper sulfate in order to control algal blooms. The use of copper sulfate as an algicide is a controversial palliative practice. Although it is effective in immediately reducing an algal bloom, its application can cause sudden mortality of cyanobacteria cells and the simultaneous release of large amounts of cyanotoxins (Pantelić et al. 2013). Several studies have revealed problems associated with the use of this algicide (Oliveira-Filho et al. 2004; Fan et al. 2013; Pantelić et al. 2013), including direct and indirect toxic effects in organisms other than the algal community. Despite such problems, this practice is common in Brazil, where several reservoirs are impacted by high levels of copper, including the Billings and Guarapiranga reservoirs located in the metropolitan region of São Paulo. In these reservoirs, copper sulfate applications have resulted in concentrations of copper up to 143-fold (Mariani and Pompêo 2008) and 46-fold (Pompêo et al. 2013) background, respectively.

In a paleolimnological study of the Paiva Castro reservoir, Cardoso-Silva et al. (2016b) found a positive linear correlation between increased copper levels and increases of the population and agricultural activities in the watersheds of the Cantareira system in recent years. These findings revealed the need to adopt measures to reduce nutrient loads in water bodies, with effective investments in sewage collection and treatment, as well as to control development in the basin area.

For Cr, Pb, and Zn, although values above background were obtained for some of the sediments, the enrichment factors were indicative of geogenic origins or minimal enrichment for these elements, with the exception of

Pb and Zn for point PR in the dry season. Since almost 39.00% of the anthropic uses in the region are mainly related to agriculture, these metals could originate from agricultural practices such as the application of fertilizers. According to Alloway and Ayres (1997), contamination by Cr, Pb, and Zn can be associated with impurities in fertilizers.

It is possible that other metals whose concentrations were above background were associated with the application of copper sulfate, since the commercial product used as an algicide has a purity of around 95.68%, and could therefore contain other metals. The highest levels of Cu, Mn, Zn, and Pb were found for point PR during the dry season (Fig. 3), when lower water levels could lead to increased nutrient concentrations (Duman and Kar 2012) and higher trophic levels, resulting in greater application of algaecides. Furthermore, Pearson correlation analysis showed that the concentration of Pb was significantly ($P < 0.05$) correlated with that of copper ($r = 0.73$ and $r = 0.57$ for the dry and rainy periods, respectively), suggesting the same source of these metals.

The highest mean Mn concentrations were obtained for the Atibainha and Paiva Castro reservoirs. According to the EF values, the enrichment could be considered moderate for locations A6, PR, and PC. Enrichment was only classified as considerable for point PR in the dry season (Fig. 3). High levels of Mn may be associated with processes of erosion (Wang et al., 2012), especially in the fluvial regions of reservoirs, as observed for point PR. Mn is also commonly found in municipal wastewater (Vymazal and Svehla 2013; Zahra et al. 2014), and in the case of the Paiva Castro reservoir, the high levels could be attributed to discharges from a sewage treatment plant located in the nearby city of Mairiporã, as discussed by Cardoso-Silva et al. (2016b). Another possible source of Mn contamination was the agricultural use of pesticides in the watershed (Alloway and Ayres 1997).

Application of the PLI (Fig. 4), which evaluates the degree of contamination considering the sum of all metals of interest, showed no significant contamination in the region, while the EF values indicated minimal enrichment and the existence of geogenic origins for most of the metals analyzed (Fig. 3). Nonetheless, although the current level of contamination was not considered significant, the concentrations of metals in the region merit attention. Pearson correlation analysis revealed significant correlations ($P < 0.05$) between the PLI and Cu ($r = 0.79$) and Pb ($r = 0.56$) in the dry period, and between the PLI and Pb ($r = 0.50$) and Mn ($r = 0.67$) in the rainy period. The EFs also indicated contamination by Cu, Pb, Mn, and Zn. The findings highlighted the need to control the sources of these contaminants.

Risk assessment of metals

Ecological risk

Although some criteria (background level, PLI, and EF) revealed the presence of contamination in sediment from at least one point of the Paiva Castro reservoir, the RI values indicated that the risk in the region was low (Fig. 5). However, even with low risk, the possibility of damage to the biota should not be ruled out. The Pearson correlation analysis suggested that this risk was higher for Cu and Pb, as these elements showed significant correlations ($P < 0.05$) with RI. For the dry period, the coefficients (r) for correlations between RI and the concentrations of Cu and Pb were 0.85 and 0.96, respectively, while for the rainy period, the values were 0.73 and 0.97, respectively.

The risk is likely to increase, especially if the sources of these contaminants persist or intensify. The situation is of particular concern in the case of Cu, because evidence has been found for bioaccumulation of this metal in the macroinvertebrate benthic community in the Paiva Castro reservoir (Beghelli et al. 2016). Monitoring data obtained for the Paiva Castro reservoir in 2014 were indicative of poor sediment quality in the dam area, according to ecotoxicological tests employing *Hyalella azteca* (acute test with mortality $< 50\%$) (CETESB 2015). Although other pollutants may also have exerted toxic effects, the observed toxicity could be associated with the metal content.

Ecotoxicological testing should also focus on Pb and Zn, with analysis of bioaccumulation in the fluvial area, because the sediments in this area were found to be inorganic and showed the lowest levels of silt and clay, which are important for binding with metals. Although Pb is a stable element, it is extremely toxic to humans and animals (Sayadi et al. 2010), and even at low concentrations can present a greater threat to aquatic life, compared to other metals (Bastami et al. 2014). Ecotoxicological tests for copper should also be performed for several regions of the Paiva Castro reservoir.

Sediment quality guidelines

Sediment quality guideline models provide useful indicators of toxicity and are recommended for areas where metal concentrations are not very high (Chapman et al. 1999; Hübner et al. 2009), as in the present case. The SQGs indicated that toxicity was unlikely to occur for the pseudo-total metals in the Cantareira system, with the exceptions of Ni for the Cachoeira reservoir during the dry season and Cu for the Paiva Castro reservoir (Fig. 2). Although the Ni values for the Cachoeira reservoir exceeded the ERL and ISQG, they were below the background value. In such situations, the SQG should be replaced by the background value, unless a

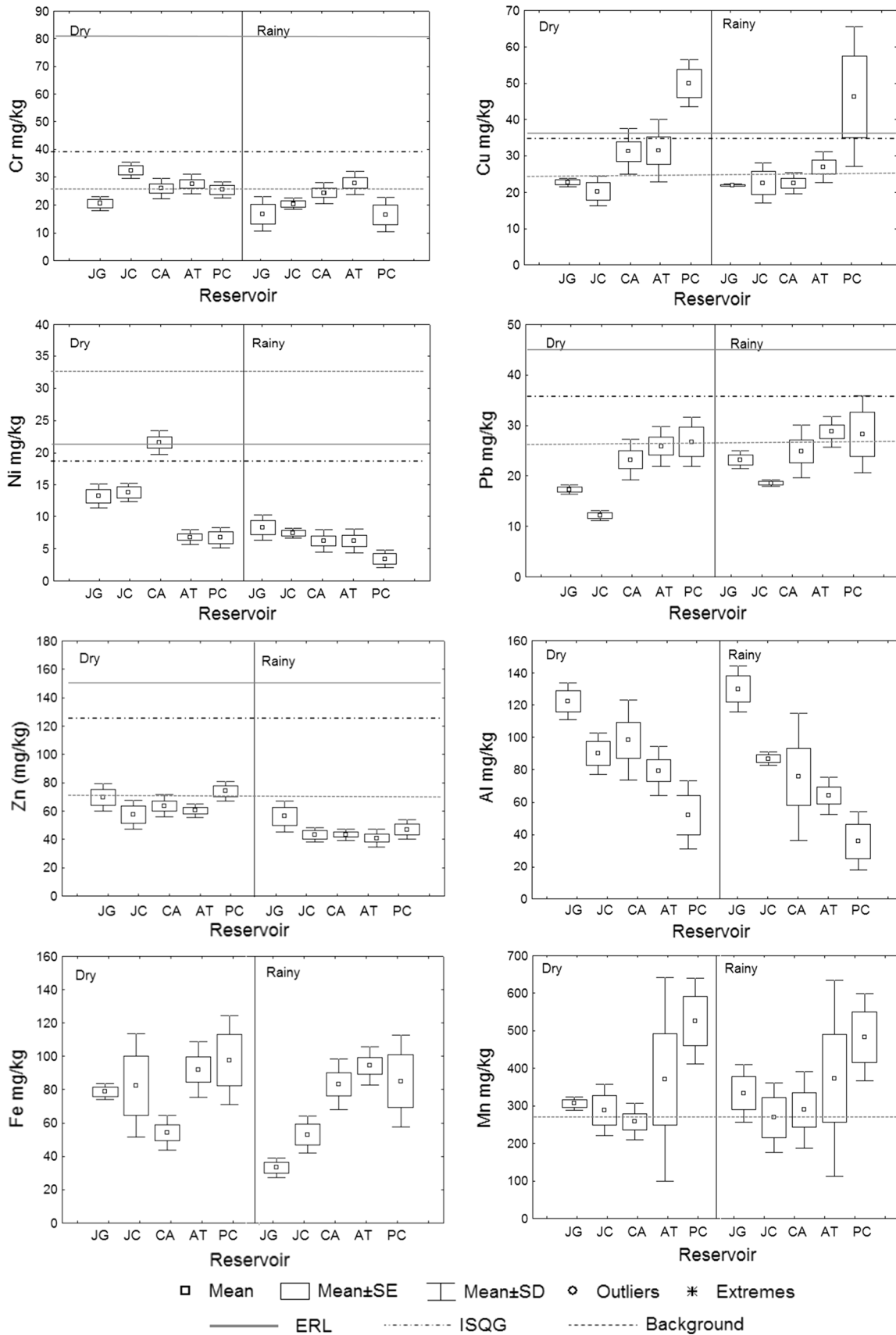


Fig. 2 Box plots of pseudo-total metals (Cu, Cr, Ni, Pb, Zn, Mn, Al, and Fe) in the sediments of the Cantareira system reservoirs: Jaguari (JG), Jacareí (Jc), Cachoeira (CA), Atibainha (AT), and Paiva Castro (PC). The background concentration values (Cardoso-Silva et al. 2016b) are indicated by the dashed lines. Dry season: May/June 2013; rainy season: November/December 2013

more suitable alternative is available (Chapman et al. 1999). Therefore, toxicity due to Ni was unlikely to occur in the Cachoeira reservoir.

Since Cu was the metal that showed the highest enrichment along the Cantareira system reservoirs (Figs. 2 and 3), with concentrations above the ERL and ISQG/TEL, a bioavailable metal analysis was performed for Cu, considering the 19 sampling points and both seasons, in order to investigate the toxicity potential (Fig. 5). This indicated that toxicity was unlikely to occur, according to the same SQGs (ERL, ERM, ISQG/TEL, and PEL). Although not essential, toxicity tests are recommended to complement the application of the SQGs, as suggested by Pompêo et al. (2013).

Principal component analysis: heterogeneity among reservoirs and seasons

Spatial heterogeneity among the reservoirs and temporal heterogeneity between the seasons were evaluated using PCA. Based on the eigenvalues, three principal components (PCs) explained 59.59% of the total variance (Fig. 6). ANOVA applied to the scores of PCs 1–3 showed that there were significant differences among the reservoirs, which were mainly explained by PC1 ($df = 37$; $F = 14.44$; $P < 0.01$). PC1 showed positive loadings for TP (0.84), Al (0.71), Ni (0.73), and LOI (0.59), with influence of the sampling points in the upstream reservoirs of the Cantareira system (Jaguari, Jacareí, and Cachoeira) in the first period (dry season) (Fig. 6; Table 4). In contrast, Cu (-0.50) and Pb (-0.56) showed negative loadings in PC1, with influence of the sampling points located in the downstream reservoirs of the Cantareira system (especially the Paiva Castro reservoir), in both periods (Fig. 6; Table 4). These features explained the Fisher's test results, which identified the Jaguari, Jacareí, and Cachoeira reservoirs as being significantly different from the Atibainha and Paiva Castro reservoirs, and the latter two as being significantly different from all the other cascade reservoirs.

A predominance of phosphorus and organic matter in upstream reservoirs is expected in cascade systems (Barbosa et al. 1999). Although the Cantareira system is not a typical cascade system, but rather a cascade multisystem reservoir, as defined by Straškraba and Tundisi (2000), it behaves as a typical system with respect to the distributions of organic matter and total phosphorus (Pompêo et al. 2003). This is due to the precipitation of nutrients and organic matter along

the reservoirs. On the other hand, the marked gradients observed for Cu and Pb did not follow the expected decay pattern. The anthropic activities in the drainage basin could have altered the typical patterns of an operational cascade system. For example, Nogueira et al. (2008) observed higher nutrient levels in a reservoir located in the middle of a cascade system, due to the effects of land use and occupation.

Al showed the upstream–downstream gradient (Fig. 2) expected in cascade reservoir systems. In the case of Ni, although there were significant differences among the reservoirs, these were probably related to different geological weathering in the sub-watersheds, since there was no sign of contamination for this element.

The second PC showed highly positive factor loadings for TN (0.65) and Fe (0.64) (Table 4; Fig. 6). TN showed a relation with the samples from the Atibainha reservoir, which could have been due to agricultural practices and effluent discharges in the sub-basin. Fe, on the other hand, is considered a conservative element that is usually associated with the geochemical matrix of the sediment (Landajo et al. 2004), so the observed variations were probably due to geological differences between the sub-watersheds, or chemical process that could lead to the release of iron to the water column.

The variability between seasons was explained by the first and third PCs. These patterns were evidenced by the ANOVA applied to the scores for the dry and rainy periods in PCs 1 ($df = 37$; $F = 10.57$; $P < 0.01$) and 3 ($df = 37$; $F = 33.18$; $P < 0.01$). On axis 1, the high TP values during the dry season, together with Ni (12.81 ± 6.30 mg/kg during the dry season), contributed to the scores distributed on the right-hand side of the diagram (Table 3, Fig. 6). The third PC was mainly influenced by Zn (Table 4), which showed higher concentrations in the dry season, especially for the Paiva Castro reservoir (Fig. 3). For the third PC, application of the Fisher's multiple comparison test identified the Jaguari, Cachoeira, and Atibainha reservoirs as being significantly different from the Paiva Castro reservoir. The seasonal differences observed for the variables analyzed in the superficial sediments could be a consequence of land drainage to the reservoirs, together with sewage discharges, as also observed by Landajo et al. (2004) for an estuary in Spain.

Conclusions and recommendations

From multiple lines of evidence used in this work, which included multivariate and univariate statistical analyses, SQGs, background values, and pollution and ecological risk indexes, it is clear that metal levels along the Cantareira reservoir system presented spatial and temporal heterogeneity attributable to natural and geogenic factors, as well

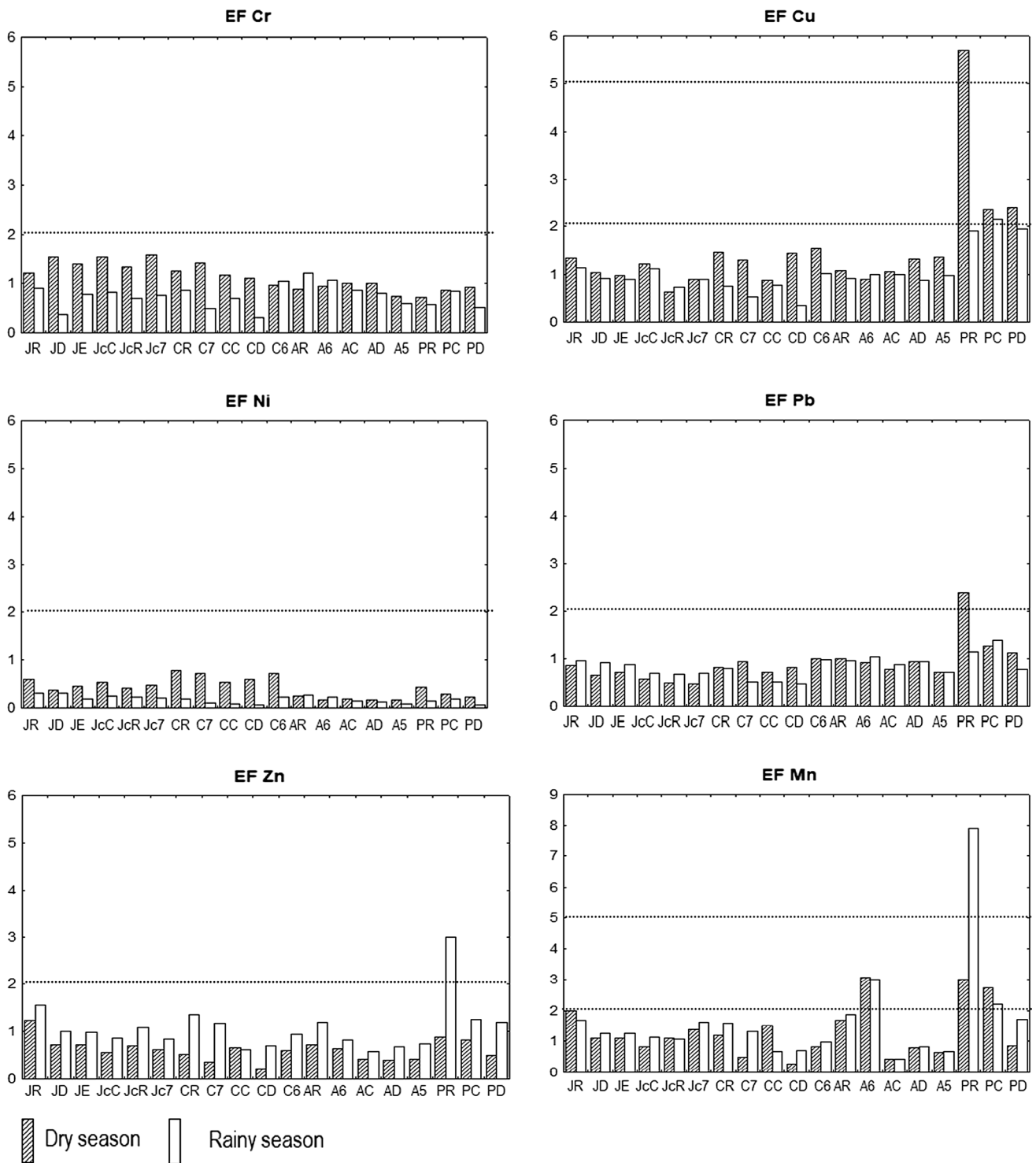


Fig. 3 Enrichment factors (EF) for metals in sediments of the Cantareira system reservoirs: Jaguari (J), Jacareí (Jc), Cachoeira (C), Atibaína (A), and Paiva Castro (P). R–river, C–center, D–dam, 5–channel 5, 3–channel 3, 7–channel 7, 6–channel 6. Dry season: May/June

2013; rainy season: November/December 2013. Values below 2 indicate geogenic origin or minimal enrichment; values between 2 and 5 indicate moderate enrichment; values above 5 indicate considerable enrichment

as to anthropogenic contamination. The anthropogenic contamination was concentrated in the reservoir located farthest downstream and was mainly associated with the palliative

Fig. 4 Pollution load index (PLI) values for sediments of the Cantareira system reservoirs. Dry season: May/June 2013; rainy season: November/December 2013

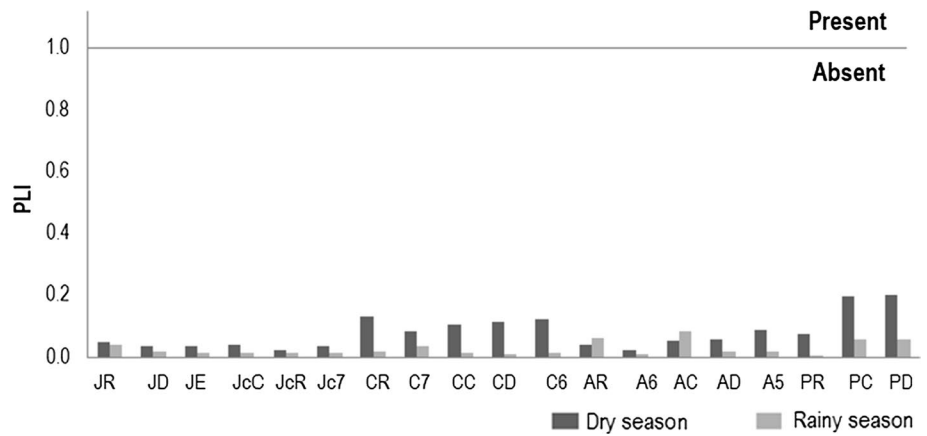


Fig. 5 Ecological risk index (RI) and bioavailable Cu (mg/kg) values for sediments of the Cantareira system reservoirs. ISQG values below 35.70 indicate that toxicity is unlikely to occur. Dry season: May/June 2013 (S1); rainy season: November/December 2013 (S2)

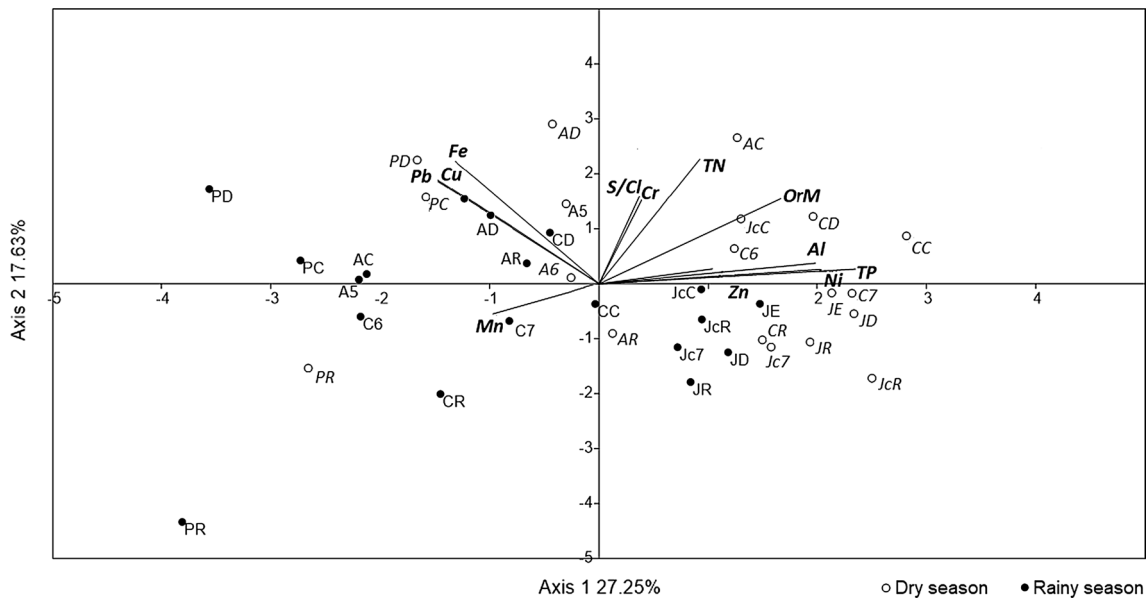
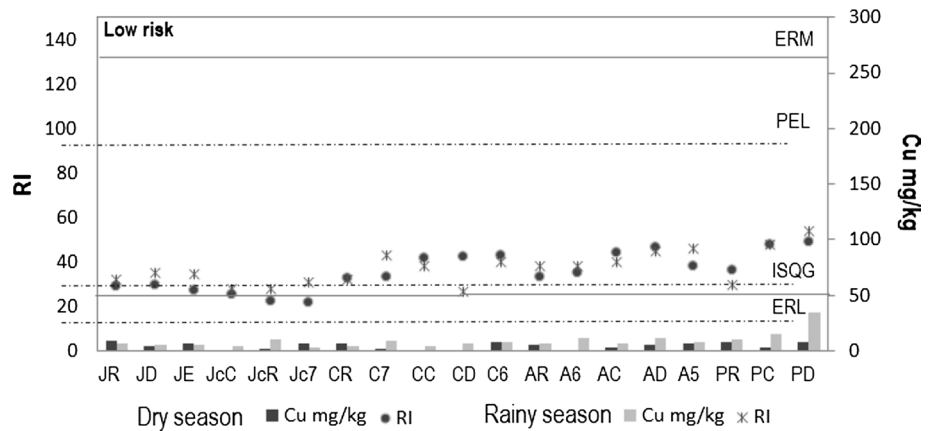


Fig. 6 Principal component analysis for the metals, organic matter (LOI), grain size (silt and clay ratio, S/Cl), total phosphorus (TP), and total nitrogen (TN) in superficial sediments of the Cantareira system reservoirs: Jaguari (J), Jacaré (Jc), Cachoeira (C), Atibainha (A), and

Paiva Castro (P). R–river, C–center, D–dam, 5–channel 5, 7–channel 7, 6–channel 6. Samples collected in May and June 2013 (dry season), and in November and December 2013 (rainy season)

Table 4 PCA loadings for the variables in the first three principal components

	PC1	PC2	PC3
Cu	-0.50	0.53	0.39
Cr	0.14	0.46	0.31
Ni	0.73	0.08	0.28
Pb	- 0.56	0.58	-0.23
Zn	0.37	0.08	0.78
Mn	-0.35	-0.16	0.44
Al	0.71	0.11	-0.43
Fe	-0.47	0.64	0.15
S/Cl	0.13	0.47	0.11
LOI	0.59	0.45	-0.30
TN	0.33	0.65	-0.35
TP	0.84	0.08	0.40

Values higher than 0.50 are highlighted in bold type

and controversial applications of copper sulfate used to control algal blooms.

Despite the observed contamination, the levels of metals were not sufficient to cause metal bioavailability, although previous studies have shown copper bioaccumulation in the benthic macroinvertebrate community in the Paiva Castro reservoir. To complement risk analysis, ecotoxicological tests should be carried out in the Paiva Castro fluvial area, especially for Cu and Pb, since the sediment in this area is less favorable to metal binding. In addition to improving understanding of the dynamics of metals in cascade multi-system reservoirs, this work draws attention to the outcome of poor water resources management and could assist in decision-making processes and in the management of reservoirs with contaminated sediments.

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