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Metals and limnological variables in an urban reservoir: compartmentalization and identification of potential impacted areas

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Abstract Reservoirs in urban areas are used for different purposes and are liable to different types of pressures that can cause the loss of chemical and biological quality, hence diminishing their ecological, economic, and cultural benefits. Here, a study of surface water heterogeneity was undertaken at the Guarapiranga urban reservoir (São Paulo, Brazil) in order to improve understanding of the structure and functioning of these ecosystems. Sampling was performed during the dry and rainy seasons at 33 sites. Limnological variables and total contents of the metals cadmium, nickel, lead, and zinc were analyzed. The risks associated with the metals were evaluated based on the toxicity unit approach. A principal component analysis enabled differentiation of the reservoir into six different areas. Some of the most powerful discriminatory variables (nutrients and metals) showed the existence of anthropogenic impacts on the system. The most strongly affected compartments were located in the following: (1) upstream area, under the influence of the Parelheiros stream, with the highest total phosphorus levels (318 mg L^{-1}) and (2) dam area, with high values for total nitrogen, suspended organic matter, total solids, and pH. The results for the dam compartment were a consequence of substantial urbanization and a longer residence time. Despite high levels of cadmium during the rainy season, no significant potential risk for zooplankton was observed. The data indicated the need to control unauthorized land occupation and to implement adequate sanitation in the Guarapiranga watershed. This research provides information that should assist water resource agencies in the sustainable management of urban reservoirs.

Keywords Spatial heterogeneity · Water quality · Urban impact · Cadmium contamination

Introduction

A majority of the human population is now concentrated in urban areas, with the proportion likely to increase to 70% by 2050 (ONU 2012a). Latin America currently has one of the world's highest urbanization rates (80%), with a value of 90% expected by 2020 (ONU 2012b).

The expansion of urban areas and the associated populations requires a greater supply of water of appropriate quality for economic and social development (Liu et al. 2015). This demand has resulted in the construction of reservoirs to ensure availability (Lehner et al. 2011; Liu et al. 2015). Approximately 850,000

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reservoirs close to urban areas are in operation or will soon be built worldwide (Nilsson et al. 2005; Zarfl et al. 2015). However, population growth and unplanned urbanization can threaten economic and social sustainability, especially due to the degradation of natural resources (Chen et al. 2014; Zhou et al. 2015).

Water bodies located in urban areas, as in the case of reservoirs, are used for a variety of purposes, including water supply, power generation, and recreation and landscaping (Moggridge et al. 2014). In these regions, they can be liable to various pressures leading to loss of chemical and biological quality, which can restrict their potential uses (such as in the case of integrated use of reservoirs in urban areas) and cause water quality problems. These impacts include the inputs (from point and diffuse sources) of complex mixtures of pollutants (pesticides, nutrients, emerging pollutants, metals, and acid compounds) due to runoff from urban paved surfaces such as roads and industrial areas, discharges of treated and untreated sewage, and aerial deposition of materials emitted from industrial or transportation sources (Hall and Ellis 1985; Ellis and Mitchell 2006; de Morais and Guandique 2015). A well-documented phenomenon is the eutrophication of water resources due to nutrient enrichment, which can lead to alterations in reservoir structure and function, with negative consequences in terms of both the ecosystem and the economy (Smith et al. 1999; Moschini-Carlos et al. 2009; Azevedo et al. 2015a; Azevedo et al. 2015b).

Although there is increasing interest in the study of urbanization impacts and the effects of urbanized landscapes on water bodies, there are still challenges involved in monitoring, maintaining, and improving the quality of these ecosystems. In the case of Brazil, a country with an emerging economy and rapid economic and industrial growth, there are many examples of such challenges, including in the Metropolitan Region of São Paulo (RMSP), the country's most important economic and industrial center. The metropolitan region has experienced rapid growth over the past 50 years and now includes the city of São Paulo and a further 39 municipalities, with a total population of 21,000,000 inhabitants and an area of 8000 km^2, making it the largest metropolitan area in South America. The main land uses are urban and industrial (Braga et al. 2006; Drucrot et al. 2005; Formiga-Johnsson and Kemper 2005; SEADE 2015). The RMSP is supplied by 23 reservoirs (Tundisi and Matsumura 2008), some of which (such as the Guarapiranga and Billings reservoirs) are located in the metropolitan region itself. The water quality in these reservoirs is degraded due to inputs of untreated sewage containing high levels of organic and inorganic pollutants, resulting in eutrophication and loss of biological quality (Braga et al. 2006; CETESB 2013; Fontana et al. 2014).

The Guarapiranga reservoir is the second largest source of water for the RMSP, providing water to 3.7 million people (Whately and Cunha 2006). The reservoir basin has a high rate of urbanization, with anthropic uses corresponding to 42% of the area (Whately and Cunha 2006). Approximately 10% of the population lives in squatter slum settlements (Santoro et al. 2008). The water of this reservoir has, since the 1960s, shown a historic loss of chemical and biological quality, due to increased loads of organic material and nutrients (ANA 2005; CETESB 2014). The presence in sediment of metals (such as cadmium and copper) at concentrations above background has been confirmed in various reports and studies (CETESB 2014; Pompêo et al. 2013).

Conservation of the biological and chemical quality of reservoirs is essential in order to ensure the continuing economic and cultural benefits of these systems (Turner and Daily 2008; Molozzi et al. 2012). As pointed out by Pinto-Coelho et al. (2010), the detection of spatial patterns is a fundamental step in establishing the real causes of declines in the ecological health of tropical reservoirs. Therefore, the objective of this study was to identify possible spatial and temporal patterns in the Guarapiranga reservoir, based on the water quality (considering nutrients and metals) determined at various sampling points distributed throughout the water body. Since metals are among the contaminants that have been detected in this reservoir, the potential risk to biota was also evaluated. This work aims to provide water resource managers with information helpful for managing reservoirs in a more sustainable way.

Materials and methods

Study area

The Guarapiranga subwatershed covers a total area of 630 km^2 and is located in the Alto Tietê watershed in the municipalities of São Paulo, Embu, Embu-Guaçu, and Itapecerica da Serra, as well as small portions of the territories of Cotia, São Lourenço da Serra, and Juquitiba (SABESP 2016). The Guarapiranga reservoir, the second most important source of water supplied to the RMSP, is considered polymictic (Maier 1985) and has a maximum volume of 194×10^6 m^3, an area of 34 km^2 (Melchor et al. 1975), a mean water residence time of between 110 and 143 days (Beyruth 1996), a flow of 14 m^3 s^{-1} (SABESP 2016), equivalent to 1.2 billion liters of water per day, and a maximum depth of 13 m (Maier and Takino 1985).

The main tributaries of the reservoir, in terms of water volume, are in the downstream direction, with the Embu-Mirim and Embu rivers on the left bank and the Parelheiros stream on the right bank (Melchor et al. 1975) (Fig. 1). The Guarapiranga river basin exhibits dendritic drainage, with crystalline and sedimentary soils (Ab Saber 1957). The region has a mean annual temperature of 17.5 °C and a mean annual rainfall of 1400 mm. According to the Köppen classification, the climate is humid subtropical (class C, type C + b) (Melchor et al. 1975).

Sampling, laboratory procedures, and data analysis

Two sampling campaigns were performed, one in the dry season (September 2006) and one in the rainy season (April 2007), at 33 locations along the Guarapiranga reservoir (Fig. 2). Surface water samples were collected in polyethylene bottles and stored in thermal bags until analyzed in the laboratory. The following parameters were measured in situ in the surface water: pH, electrical conductivity, and water temperature (YSI 63 multiparameter probe); dissolved oxygen (Hanna HI 9142 probe); and turbidity (Secchi disk depth). In the laboratory, measurements were made of total suspended solids by a gravimetric method (Wetzel and Likens 1991), total suspended particulate matter and the corresponding organic and inorganic fractions (Wetzel and Likens 1991), chlorophyll a and pheophytin (Lorenzen 1967), and total nitrogen and total phosphorus (Valderrama 1981). All reagents were of analytical grade (Synth) and were used as received without further purification.

After collection, the samples used for analyses of metals (cadmium, nickel, zinc, and lead) were acidified to pH 2 with HNO_3 and then stored in polyethylene bottles at 4 °C until analyzed. Samples were digested (in replicate) in 10-mL test tubes, with addition of 0.5 mL of analytical grade HNO_3 (Merck), at a temperature of 105 °C until the volume was reduced to about 2 mL. The samples were then filtered through 125-mm Whatman 41 filters and stored at 4 °C prior to analysis using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Spectro spectrometer) (APHA 1998).

The data were analyzed using basic descriptive statistics and principal component analysis (PCA) based on a correlation matrix (Legendre and Legendre 1998). In the PCA, the centroid was calculated as the mean values of the scores of axes 1 and 2 corresponding to each group, observed using cluster analysis employing Euclidian distances and Ward's method, as described by Cardoso-Silva et al. (2016). Data analysis was performed using the PAST software package (Hammer et al. 2001).

The risks associated with the total metal concentrations were evaluated using the toxicity unit (TUs) approach, described by Sprague (1971). The TUs were calculated for each metal at each sampling point, according to Eq. 1:

$$TUi = Ci/LC_{50i} \tag{1}$$

where Ci is the concentration of the metal i measured in the environment (mg/L) at the sampling point, and LC_{50i} is the concentration (mg/L) of the metal lethal to 50% of a population of the Cladoceran *Daphnia magna*. Assuming that the toxicity of the mixture of metals was additive for each point, the total TU value was calculated based on the sum of the individual TU values for each metal (Eq. 2).

$$\mathrm{TU}_{total} = \Sigma \mathrm{TU}i + \ldots + \mathrm{TU}n \tag{2}$$

The existence of toxicological risk was assumed when $TU \geq 1$, while $TU < 1$ indicated an absence of risk. The Cladoceran *D. magna* was selected as a representative zooplankton organism because its community was dominant in the study area. The LC_{50} values were obtained from the database available at: www.systemecology.eu.

Results

The existence of horizontal spatial heterogeneity in the surface water of the Guarapiranga reservoir was evident in both sampling periods, with the formation of a gradient along the reservoir. The use of PCA enabled the identification of six different compartments, some of which varied in terms of extent and location.

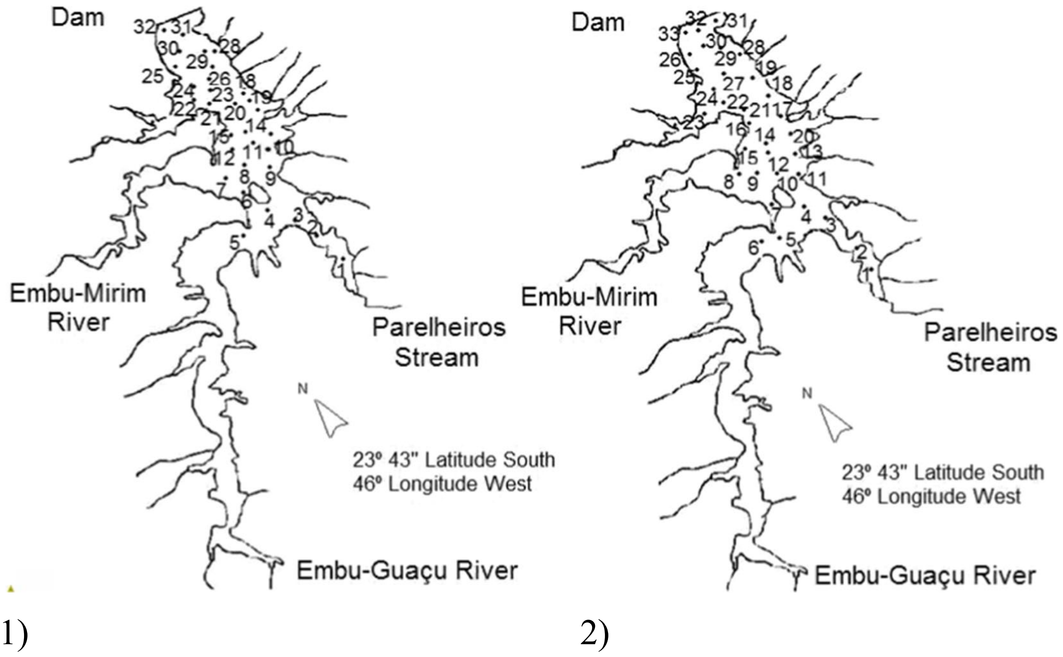

Fig. 1 Sampling sites at 33 locations in the Guarapiranga reservoir. 1 Dry season (September 2006). 2 Rainy season (April 2007). Sampling stations were georeferenced according to the UTM coordinates system (datum SAD69 and central meridian 45°)

Compartments I and II

In order to improve interpretation of the PCA results, some of the sampling points were removed. In both campaigns, points 1 and 2 showed the highest solids, total nitrogen, total phosphorus, and electrical conductivity values, and the lowest Secchi disk values (Table 1), differentiating these points from the rest of the sampling network. The data suggested that these areas formed a separate compartment in the reservoir, which was denoted compartment I (Fig. 2).

Other points removed from the PCA were point 5 (first campaign) and points 5 and 6 (second campaign). These locations showed the highest SIM and total zinc (dry season) values, together with the lowest values for electrical conductivity, solids, TSM, and total

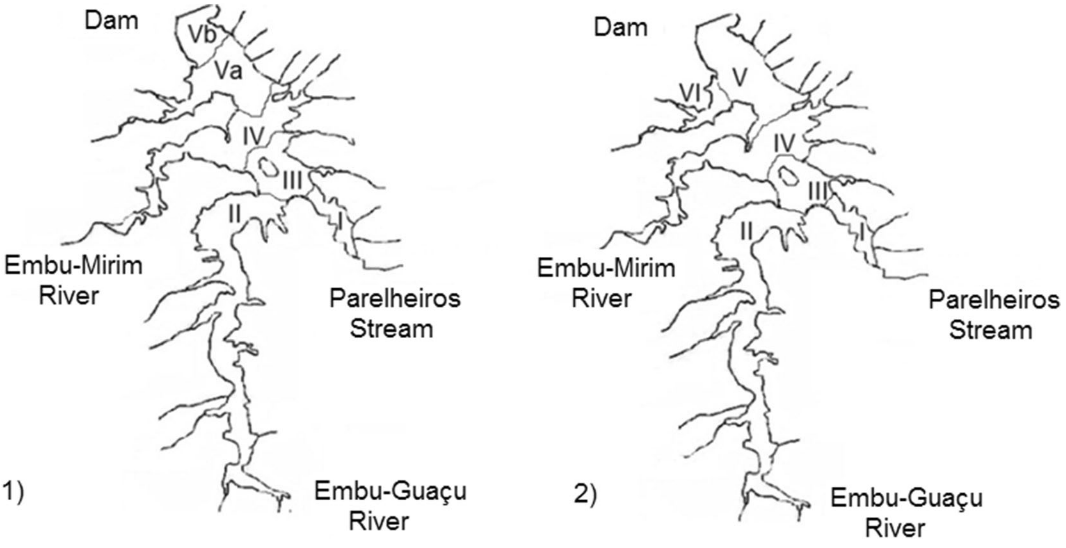

Fig. 2 Compartments of the Guarapiranga reservoir identified using PCA based on limnological parameters measured in the surface water. Sampling campaigns performed in 1 the dry season (September 2006) and 2 the rainy season (April 2007)

Table 1 Means and standard deviations (X ± SD) for the following variables: depth (Z, m); Secchi disk depth (SD, m); temperature (T, °C); pH; electrical conductivity (EC, µS cm^{-1}); total solids (TS, mg L^{-1}); suspended particulate matter: total (TSM, mg L^{-1}), organic (SOM, %), and inorganic (SIM, %); total phosphorus (TP, µg L^{-1}); total nitrogen (TN, µg L^{-1}); chlorophyll a (Chl, µg L^{-1}); pheophytin (Phe, µg L^{-1}); total Zn (mg L^{-1}); total Cd (mg L^{-1}); and total Ni (mg L^{-1}). The designation of compartments (C) was based on the PCA results. For compartments I, II, and VI, only the raw values are presented (P sampling point)

Campaign 1

	CI	CII	CIII	CIV	CVa	CVb
	X	P5	X ± SD	X ± SD	X ± SD	X ± SD
Z	1.8	5.0	4.1 ± 1.2	5.8 ± 2.3	8.8 ± 0.6	6.4 ± 2.1
SD	0.6	1.2	11 ± 0.2	1.3 ± 0.1	1.4 ± 0.1	1.9 ± 2.7
T	17.9	18.5	18.6 ± 0.3	19.1 ± 0.3	19.3 ± 0.3	16.5 ± 6.3
pH	7.2	7.6	7.5 ± 0.04	7.7 ± 0.2	8.0 ± 0.3	6.9 ± 2.4
EC	227.2	99.7	1286 ± 3.2	128.4 ± 2.3	127.8 ± 0.9	111.2 ± 44.1
TS	143.3	68.0	84.4 ± 1.0	82.5 ± 2.5	88.5 ± 16	75.2 ± 29.1
TSM	14.1	3.3	5.0 ± 0.6	4.0 ± 1.32	4.6 ± 0.6	5.3 ± 4.7
SOM	53.0	45.0	59.4 ± 4.7	91.2 ± 11.1	97.7 ± 3	76.0 ± 31.5
SIM	47.1	55.0	40.6 ± 4.7	8.8 ± 11.1	2.3 ± 3	17.9 ± 28.7
TN	794.1	399.0	406.9 ± 26.4	393.6 ± 101.4	368.6 ± 136.5	373.8 ± 174.9
TP	116.7	12.7	24.7 ± 4.2	21.5 ± 6.0	26.4 ± 3.8	22.6 ± 7.8
Chl	2.9	0.9	*	11.2 ± 8.3	25.7 ± 11.8	36.4 ± 300.8
Phe	23.0	5.3	28.4 ± 7.3	36.3 ± 15	19.9 ± 9.6	26.9 ± 15.0
Zn	*	0.3	*	0.02 ± 0.03	0.02 ± 0.03	0.1 ± 0.1
Cd	*	*	*	*	*	0.001 ± 0.001

Campaign 2

	CI	CII	CIII	CIV	CV	CVI
	X	X	X ± SD	X ± SD	X ± SD	P23
Z	3.8	6.7	6.5 ± 2.2	6.9 ± 2.4	8.3 ± 2.8	9.3
SD	0.9	1.6	1.3 ± 0.2	1.4 ± 0.1	1.4 ± 0.1	1.4
DO	5.0	5.8	5.0 ± 0.3	5.7 ± 0.5	6.6 ± 0.8	6.2
T	22.9	24.1	24.0 ± 0.2	24.4 ± 0.1	24.9 ± 0.2	25.1
pH	6.6	6.4	6.5 ± 0.1	6.4 ± 0.1	6.6 ± 0.2	6.3
EC	143.4	80.3	106.2 ± 3.1	109.1 ± 2.0	110.8 ± 2.1	112.4
TS	83.8	63.8	78.8 ± 7.0	79.7 ± 4.1	75.3 ± 9.2	88.0
TSM	8.7	2.4	4.5 ± 0.8	6.1 ± 2.8	6.0 ± 3.3	9.2
SOM	78.3	64.6	70.4 ± 8.4	91.0 ± 5.8	95.4 ± 4.9	100.0
SIM	21.7	35.4	29.6 ± 8.4	9.0 ± 5.8	4.6 ± 4.9	5.0
TN	834.2	349.3	438.0 ± 158.3	582.5 ± 80.9	649.2 ± 82.5	609.3
TP	194.7	14.2	23.7 ± 3.8	27.0 ± 2.7	28.2 ± 2.2	35.4
Chl	54.3	6.2	15.7 ± 3.7	11.2 ± 7.6	8.8 ± 11.8	16.0
Phe	13.5	6.0	12.9 ± 6.1	15.7 ± 7.5	22.1 ± 10.2	13.6
Cd	*	0.04	0.04 ± 0.05	0.03 ± 0.01	0.01 ± 0.03	0.1
Zn	0.004	0.03	0.002 ± 0.001	0.004 ± 0.001	0.005 ± 0.001	0.01
Ni	0.001	0.01	*	0.002 ± 0.001	0.002 ± 0.002	0.01

*Values below the method detection limit phosphorus (Table 1). These points were located in a more remote region of the central reservoir body (Figs. 1 and 2), under the influence of the Embu river, and suggested the formation of another compartment in the reservoir, denoted compartment II.

Compartments III, IV, V, and VI

The data analysis presented below suggests that the extents of the observed compartments varied according to the season (dry or rainy).

Sampling campaign 1

The results of the PCA showed that most of the data variability (50.02%) could be explained by the first two axes (Fig. 3). The most influential variables were chlorophyll a (0.85) and pH (0.79) in axis 1, and nitrogen (0.72) and pheophytin (− 0.54) in axis 2.

The SIM variable influenced the points located in the upstream area of the reservoir, suggesting the formation of a third compartment (Figs. 2 and 3). The pheophytin variable was responsible for the arrangement of the points located after the eucalyptus island (in the upstream-downstream direction) in an area under the influence of the Embu Mirim river, which was designated compartment IV.

Another observed compartment (Va) showed positioning influenced mainly by the parameters chlorophyll a, pH, and Secchi disk depth (Fig. 2). Points located in the dam area showed the influence of the variables Cd, Zn, total solids, and total nitrogen, indicating the existence of a compartment Vb (Fig. 3).

Sampling campaign 2

In the PCA results for the second sampling campaign, axis 1 explained 26.82% of the variability and together with axis 2 explained 42.26% of the variability (Fig. 4). Inclusion of the third axis resulted in explanation of most of the data variability (56.91%). The most influential variables in axis 1 were SIM (− 0.85) and total nitrogen (0.69), while cadmium (0.59) and pH (− 0.59) were most important in axis 2.

The results for the second sampling campaign showed a compartmentalization pattern in the reservoir that was similar to that for the first campaign, in terms of compartments III and IV (Fig. 2). The variables Zn, total solids, and chlorophyll a influenced the identification of compartment IV. The existence of compartment V was indicated by grouping of the variables Cd, phosphorus, electrical conductivity, depth, and pheophytin (Fig. 4). Point 23, located on the left bank of the reservoir in a dendritic area under the influence of the Guaravituva and Itupu streams, remained isolated in the scores plot, suggesting the existence of a sixth compartment.

Although the existence of compartments in the Guarapiranga reservoir was evident in both sampling periods, there were differences in the variables that influenced the arrangements. For example, in the first sampling period, chlorophyll a influenced the arrangement of the points located further downstream, while in the second period the effect of chlorophyll a was further upstream (Table 1, Figs. 3 and 4).

The metal analyses showed that the Pb concentrations remained below the method detection limit (0.12 mg L^{-1}), throughout the reservoir and in both sampling periods. Ni was only detected at some points in the second period, with the highest values in compartment V (0.001 ± 0.002 mg L^{-1}). In the first period, the concentrations of Cd were below the method detection limit (0.0001 mg L^{-1}) at most sampling points. However, in the second period, higher mean concentrations were measured in the compartments located near the dam (Table 1).

Toxicological risk

Calculation of the toxicological risk, following the TU approach (Sprague, 1971), revealed no risk to zooplankton at any of the sampling points, with values ranging from 0 to 0.125 for the first sampling campaign and from 0.014 to 0.27 for the second campaign. In the first sampling campaign, the highest value was obtained in compartment II, with Zn being responsible for the total toxicity, while in the second campaign, the highest value was obtained in compartment III, with Cd providing the main contribution to the toxicity. However, the TU values obtained were low, and any toxicological risk could be discounted, according to the criterion of the TU method.

Discussion

Based on the water quality at the different sampling points, the reservoir could be differentiated into six

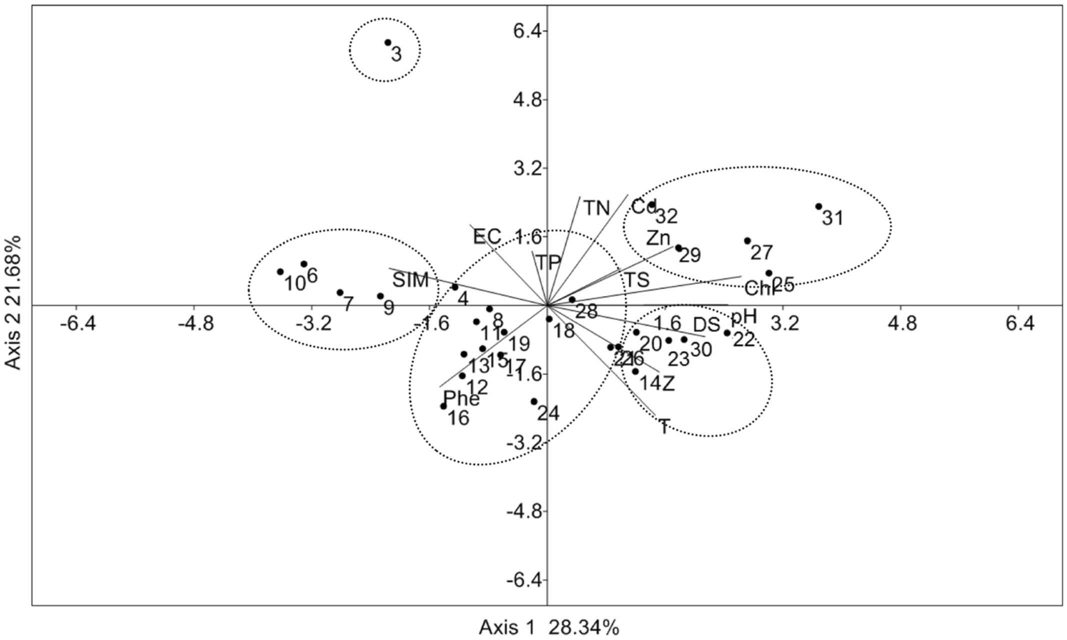

Fig. 3 PCA of variables measured in the Guarapiranga reservoir surface water. Points 1, 2, and 5 were removed. The scores were related to the variables depth (Z), temperature (T), pH, electrical conductivity (EC), Secchi disk depth (SD), total solids (TS), suspended inorganic particulate material (SIM), chlorophyll a (Chl), pheophytin (Phe), total nitrogen (TN), total phosphorus (TP), Zn, and Cd. Sampling performed in September 2006

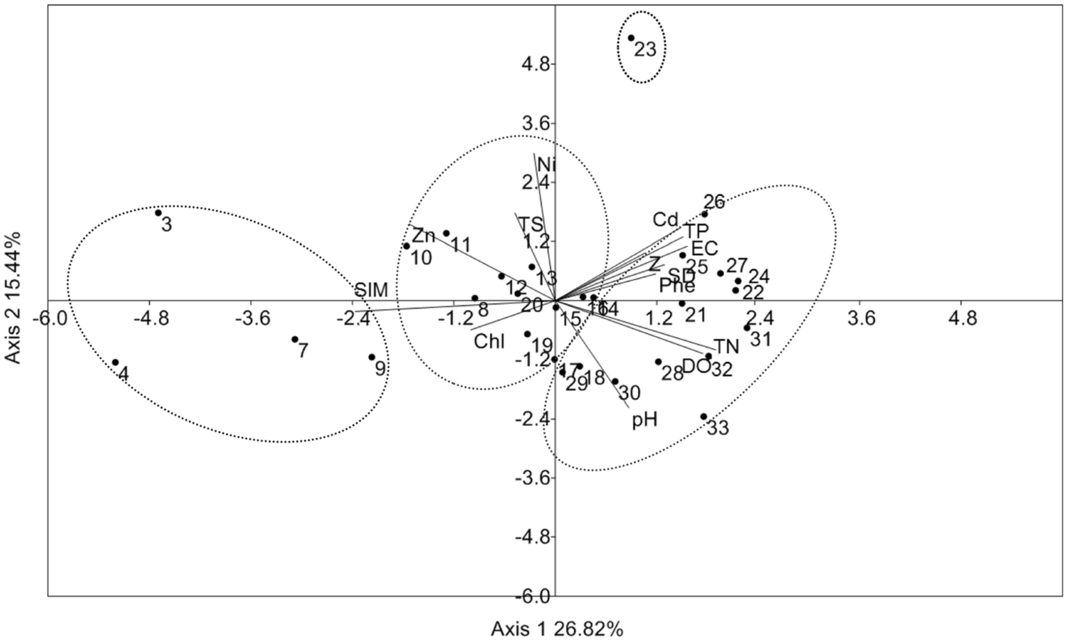

Fig. 4 PCA of variables measured in the Guarapiranga reservoir surface water. Points 1, 2, 5, and 6 were removed. The scores were related to the variables depth (Z), temperature (T), pH, electrical conductivity (EC), Secchi disk depth (SD), total solids (TS), suspended inorganic particulate material (SIM), chlorophyll a (Chl), pheophytin (Phe), total nitrogen (TN), total phosphorus (TP), Zn, and Cd. Sampling performed in April 2007

different areas, showing the existence of spatial heterogeneity. The zoning was seasonally dependent, with some of the most powerful discriminatory variables (nutrients and metals) revealing anthropogenic impacts on the system. However, considering the metal concentrations in the water and the TU values, there was no significant potential risk to zooplankton.

Compartments I and II

The formation of compartment I, located near the Parelheiros stream, was associated with characteristics typical of riverine areas of reservoirs, as well as anthropogenic impacts. The former included increased amounts of particulate matter that restricted light penetration in the water body, hence limiting primary productivity (Henry 2004). This area presented the most critical water quality conditions, even though previous research has suggested improvement of the quality of the water entering the reservoir, due to the presence of the Parelheiros wetland (Andrade 2005).

The Parelheiros region receives a high amount of sewage and occasionally the water pumped from Billings reservoir, between 2.0 and 4.0 $m^3 s^{-1}$ (Pires et al. 2015), also an important but impacted reservoir with high levels of nutrients. Therefore, the poor water quality that enters the Parelheiros area is responsible for the characteristics of this compartment, such as high EC and nutrient concentrations (Nishimura et al. 2014). According to the local environmental agency, CETESB, who monitors the reservoir in the Parelheiros and in the dam areas, since 2006, high levels of phosphorus have been recorded in Parelheiros region exceeding the Brazilian Standards limit value (Resolution 357–CONAMA 2005) (CETESB 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2017). The environmental local agency classified the area as eutrophic between 2006 and 2010 and as supereutrophic between 2011 and 2016, according to the Trophic State Index of Carlson (1977) adapted to tropical ecosystems, as proposed by Lamparelli (2004) (CETESB 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2017). The high levels of nutrients in the area have been observed by several other authors as Nishimura et al. (2014), Pires et al. (2015), Machado et al. (2016), and López-Doval et al. (2017). The critical water quality in Parelheiros area was also evidenced by biological indexes applied by CETESB (2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2017), such as the zooplankton community index (ZCI) and the aquatic life index (ALI). The ZCI was classified as bad and the ALI presented values oscillating between the regular and bad state. These findings suggest that the public policies adopted in Guarapiranga basin have not been effective once the water quality is getting worst and indicate the need to control unauthorized occupation and to invest in sewage collection and treatment in areas currently not served. The formation of compartment II was associated with the fact that the region has a distinct residence time (Occhipinti 1973; Beyruth 1996), since it is located in a dendritic area that is relatively isolated from the influence of the central flow. Dendritic regions in reservoirs generally increase the heterogeneity of the system (Henry et al. 1998; Nogueira 2001), with characteristics different to those of the other regions of the water body, as observed in the present case.

Compartments III and IV

Compartment III showed characteristics typical of intermediate areas of reservoirs, with increasing light penetration, decreasing concentration of suspended solids, and progressive decrease of SIM, relative to the upstream region (Fig. 2). In addition to these characteristics, these reservoir zones typically exhibit longer mean residence times and higher sedimentation rates (Kimmel et al. 1990), making them more favorable for primary productivity, associated with higher contents of chlorophyll a and nutrients (Pagiori et al. 2005). In the present case, however, this was only observed for chlorophyll a in the second sampling period. This pattern of higher productivity in the intermediate zone occurs because less turbulence leads to a smaller amount of suspended material, so light availability is no longer a limiting factor in productivity (Kimmel et al. 1990).

Compartment IV consisted of a region with a water residence time distinct from the other reservoir areas (Occhipinti 1973; Beyruth 1996). This compartment was mainly characterized by the presence of the highest pheophytin levels, which could be correlated with the senescence of phytoplankton derived from the waters of the Embu-Mirim river. Critical water quality conditions were found by Santos et al. (2015) in a sampling performed in compartment IV, in 2010 during dry season in a 48-h period (sampling every 3 h). The authors observed in superficial water, high levels of total nitrogen 1912.4 ± 198.8 $\mu g\ L^{-1}$, and total phosphorus 42.5 ± 8.7 $\mu g\ L^{-1}$ as well as high levels of chlorophyll a 32.4 ± 5.1 $\mu g\ L^{-1}$. These data suggested an increase in anthropic impacts in anthropic impacts as observed in Parelheiros area, once in this research mean values for phosphorus, nitrogen and chlorophyll a where lower than these.

Compartments V and VI

In the first sampling period, compartment V could be divided into two subcompartments, with the results indicating the influence of temporary factors. Compartments Va and Vb (first period) and V (second period) were in the downstream region of the reservoir (Fig. 2), with the longest mean residence time (Occhipinti 1973; Beyruth 1996). In compartment Vb, located closer to the dam in the area generally considered as the lentic zone of the reservoir, it was expected to observe low levels of nutrients and TSM, but the opposite was found. This probably reflected the presence of a large urban settlement in the region, together with the accumulation of these species due to a longer water residence time.

In compartment Vb, the highest average values for pH could be explained by increased CO_2 consumption during the photosynthesis process. This was corroborated by high values for chlorophyll a, as well as a statistically significant correlation between pH and chlorophyll a. An increase in pH is usually associated with algal blooms, and consequently with high concentrations of chlorophyll a (Buzelli and Cunha-Santino 2013; Tracann et al. 2014).

In the second sampling campaign, the characteristics of compartment V were similar to those of compartments Va and Vb, although the values of some of the variables that influenced these groupings varied between sampling periods. These differences were probably due to seasonal factors. The higher nutrient levels found during the rainy season (second sampling period) were expected, since at this time there is an increase in the supply of nutrients from the drainage basin to the reservoir (Akinyemi and Nwankwo 2007; Smith et al. 2014). The solids concentrations (TSM and SOM) were generally higher in the second period, possibly for the same reason given for the nutrients.

In the case of chlorophyll a, the observed differences in the distribution patterns between the two sampling periods could be attributed to two main factors: (1) the residence time and (2) the application of algicides to control algal blooms. In the Guarapiranga reservoir, the residence time of the water tends to increase from upstream to downstream. The mean values range from 11 to 83 days in the dam area, and from 0 to 27 days in the central reservoir region (Occhinpinti 1973; Beyruth 1996). Therefore, greater nutrient accumulation can occur in the dam area, favoring primary productivity, as indicated by the higher chlorophyll a concentrations downstream which exceeded the Brazilian Standards limit value (Resolution 357–CONAMA 2005). During the rainy season, despite a greater input of nutrients, higher flow rates lead to a shorter water residence time, so that nutrients are continuously transferred to the downstream system (Leite et al. 2004). This hindered observation of a clear pattern of higher chlorophyll concentrations upstream, opposite to the pattern observed by Olds et al. (2011) in Harlan County Reservoir (Nebraska).

The application of algicide to control phytoplankton in the reservoir could also have influenced the spatial distribution pattern of chlorophyll a. The application of algicides (copper sulfate and hydrogen peroxide) was higher in 2006 than in the previous year, with values between 12 and 62 t (CETESB 2007). Applications tend to be higher during the dry season (Szajubok 2000), which could explain the lower chlorophyll a concentrations observed upstream during the first sampling period.

The use of copper sulfate was responsible for the observed high concentrations of this metal. According to data published by CETESB (2007, 2008), the dissolved copper concentrations measured in 2006 and 2007 were above the limit of 0.009 mg L^{-1} established in current legislation (CONAMA regulation 357/05). Although, at least in the short term, copper does not cause severe harm to humans (Gárcia-Villada et al. 2004), this metal can disrupt the balance of the ecosystem. Treatment with copper sulfate leads to the release of large quantities of nutrients, kills algae, reduces competition, and promotes the formation of anoxic sediments, with the subsequent resuspension of nutrients favoring opportunistic species (Beyruth 2000).

The use of copper sulfate as an algicide is a controversial palliative practice. This practice has resulted in concentrations of copper in sediments up to 46-fold (Pompêo et al. 2013) background, and up more than tenfold the PEL (probable effect level—137 mg kg^{-1}) value for copper, which suggest toxicity is likely to occur in sediments (Leal et al. 2017). Leal et al. (2017) evaluated copper concentrations along Guarapiranga sediments and through a geostatistical approach estimated the sediment copper stock in the reservoir. The stock was estimated in a value of 1158.85 $t_{(copper)}$, corresponding to 11 years of copper sulfate application. Extrapolation to a period of 43 years of constant copper application gave a value of 4530.05 t of copper applied to the Guarapiranga reservoir. The authors concluded that the Guarapiranga water management policy is mainly structured considering short-term financial costs, without adopting middle-term or long-term strategies as the sewage treatment.

For metals, the highest concentrations found in surface water in the dam area could be explained by the tendency of this material to accumulate here due to the longer residence time. This finding was in agreement with Pompêo et al. (2013), who reported high levels of Cr, Ni, Cu, and Cd in superficial sediments from the Guarapiranga dam area.

The concentrations of total cadmium measured in the second sampling period also exceeded the current limit established in CONAMA regulation 357/05, but were within the limit of 0.005 mg L^{-1} established by the World Health Organization. However, attention to cadmium concentrations is required since the metal is toxic towards humans and aquatic organisms (Barbier et al. 2005; Garcia-Santos et al. 2005). Cadmium is widely recognized as one of the most toxic pollutants in the environment, due to its neurotoxic effects and its capacity to cause injury in various organs and tissues, following acute or chronic exposure (Méndez-Armenta and Ríos 2007). In fact, in the present work, the elements Cd and Zn showed the highest TU values. The presence of cadmium in the reservoir could be attributed to the existence of industrial activities in the northern and northwest reservoir regions, with possible sources of contamination including pigments and plastics manufacturing facilities (Pompêo et al. 2013).

The highest metal concentrations were observed during the rainy season, probably associated with the drainage of water from the basin to the reservoir (Gaur et al. 2005; Mastoi et al. 2008). For the metals, no ecotoxicological risk was indicated using the TU criteria. Since the risk level was calculated based on the total concentrations of the dissolved metals (as a worst case scenario), rather than dissolved metal concentrations, as recommended (EU 2011; Schmidt et al. 2010), there was no evidence of any risk posed by these metals to *D. magna* or, by extrapolation, to other zooplankton organisms.

As observed in compartment I, critical conditions for the water quality in compartment V persist and high nutrients and chlorophyll a concentrations, exceeding the Brazilian Standards limit value (Resolution 357–CONAMA 2005), have been recorded (CETESB 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2017; Machado et al. 2016; López-Doval et al. 2017). However, for cadmium, besides Pompêo et al. (2013), no other study pointed the high levels for this element.

Conclusions and final considerations

The six compartments observed along the Guarapiranga reservoir were the result of the operational regime and the dendritic structure of the water body, as well as the human impacts affecting the system. Anthropogenic effects were evident in the compartment in the Parelheiros region, associated with high levels of nutrients, and in the compartment near the dam, where high levels of nutrients and metals were recorded. Remedial measures are required in order to reduce nutrient inputs into this ecosystem, by means of the control of urban settlements in the region, implementation of appropriate basic sanitation, and effective sewage collection and treatment. Only by taking protective and restorative measures will it be possible to maintain the sustainability of this important watershed.

This research provides decision makers with information to assist in the management of urban ecosystems. Given the increasing number of water bodies potentially affected by urbanization processes, we believe that the findings of this work should be useful in other geographical contexts.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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