LETTER TO THE EDITOR

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Factors that control the spatial and temporal distributions of phosphorus, nitrogen, and carbon in the sediments of a tropical reservoir

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Abstract

The impacts of anthropic activities have had profound effects on the nitrogen (N) and phosphorus (P) cycles in many aquatic ecosystems. We investigated the spatial and temporal distributions of carbon (C), N, and P in the sediments of a tropical Paiva Castro Reservoir (São Paulo, Brazil), as well as their release and retention in the system. In 2010, surface sediments were collected at nine sites in the reservoir, and a core was obtained in the limnetic zone, in 2010. The core was dated using the ^{210}Pb technique. The organic C content was estimated from organic matter concentration, which was measured by the loss-on-ignition method, and the concentrations of P and N were determined by spectrophotometry. Marked spatial heterogeneity in the Paiva Castro sediments associated with both natural variations in the water body and variations induced by human impacts was observed. Heterogeneity was evidenced by a decrease in the allochthonous contribution of organic matter (C/N) in the upstream-downstream direction and increases of N and P, mainly associated with water flows in the different compartments of the reservoir. In the core, C and N concentrations display significant positive correlations with increases in population and agricultural activities in the drainage basin through time. The C/P molar ratios in surface sediments are indicative of human impacts in the region, as C:P ratios in the sediment are low (7.8:1) compared to the Redfield ratio (C:P = 108:1). Predominance of oxic conditions at the sediment surface and particles sizes < 63 μm provided favorable conditions for P retention in the sediments, which helps prevent eutrophication. Approaches used in this research should be extended to other locations, especially in mesotrophic and oligotrophic reservoirs, to provide information on historical impacts in such aquatic ecosystems.

Keywords Anthropic impacts · Eutrophication · Nitrogen · Paleolimnology · Phosphorus · Reservoir · Sediment core

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Introduction

Nitrogen (N) and phosphorus (P) are important elements in aquatic ecosystems, supporting the growth of algae and aquatic macrophytes (Hayakawa et al. 2015). Changes in the biogeochemical cycles of these elements, caused mainly by human activities, have enhanced nutrient delivery to water bodies and led to increases in productivity. Such cultural eutrophication is now a global environmental problem (Wetzel 2001; Smith and Schindler 2009). This process is responsible for many ecological changes and socioeconomic costs, such as loss of biodiversity (Hautier et al. 2009), development of potentially toxic algae blooms (Moschini-Carlos et al. 2009; Cunha et al. 2017), and increased costs of water treatment (Smith and Schindler 2009).

Although there is a large body of research on this issue, uncertainties remain (Smith and Schindler 2009) and further studies that can contribute to a better understanding of the dynamics of the N, P, and C biogeochemistry in aquatic environments and the process that control trophic states of water bodies. Such studies should include sediment analysis, since bottom sediments act as a nutrient sink, but also as a potential source of nitrogen and phosphorus for the water column, under certain conditions (Wetzel 2001; Liu et al. 2009). For example, anoxic conditions in the hypolimnion can intensify denitrification and promote the release of nitrogen from sediments (Hou et al. 2014), as well as cause the release of phosphorus (Fonseca et al. 2011), thereby contributing to eutrophication.

Phosphorus is the principal limiting nutrient for the growth of algae in most water bodies (Oluyedun et al. 1991). Dissolved oxygen concentration at the sediment surface is important for retention of P in sediments, but other factors like temperature, redox conditions, pH, and the concentrations of other inorganic species such as sulfide and iron in the sediment and the water column can influence P release (Ribeiro et al. 2008). An increase in temperature generally reduces phosphorus adsorption by mineral particles in the sediments (Perkins and Underwood 2001), whereas low pH values prevent the release of phosphorus to the water column (Wetzel 2001). Under oxic conditions, dissolved phosphate is combined with iron and aluminum oxides in the sediment (Fonseca et al. 2011; Dittrich et al. 2013; Hayakawa et al. 2015). In contrast, under anoxic and reducing conditions, the phosphate is then released to the water column (Perkins and Underwood 2001; Wetzel 2001; Esteves 2011; Dadi et al. 2017). The presence of sulfate can increase the effects of anaerobic conditions, a consequence of the double reaction of ferric iron with sulfate and sulfide to form ferrous iron and iron sulfide (Perkins and Underwood 2001). Under such anaerobic conditions, increases in pH associated with sulfate reduction of ferric iron and polyphosphate breakdown lead to the release of phosphorus from the sediment (Perkins and Underwood 2001).

Despite the potential of sediment analysis, to lead to a better understanding of biogeochemical cycles and trophic state conditions, caution is required in interpreting the data. As mentioned above, under anoxic conditions, phosphorus is released to the water column. Under eutrophic conditions, phosphorus release from the sediments will often be intense even if external loading is low, because of the intense internal loading, as observed in Paranoá Reservoir, Brazil, by Angelini et al. (2008). In such situation, phosphorus in sediments will not necessarily reflect the precisely trophic state in the water column. Therefore, it is important to concomitantly analyze other macronutrients such as nitrogen and carbon. For example, important information about the trophic state of the environment can be obtained from measures of C/N and N/P molar ratios in the sediments. And use of the C/N molar ratio as an indicator of organic matter sources is a common approach in geochemical studies (Ruttenberg and Gofii 1997) and can distinguish between autochthonous or allochthonous sources of organic matter (Liu et al. 2010). Shifts in the N/P ratios, which are indicative of the limiting nutrient (Koerselman and Meuleman 1996), can affect the phytoplankton community composition, especially in relation to the cyanobacteria (Eillers et al. 2004).

Caution in data interpretation is prudent when using sediment profiles to infer the trophic state history of a water body. In addition to elements such as nitrogen and carbon, many studies have also employed biological indicators such as diatoms or photosynthetic pigments (Boyle 2001; Smol 2008). Such bioindicators often provide a better understanding of past trophic state, especially in eutrophic environments. The use of biological variables as proxies for trophic state conditions requires accurate identification of taxonomic groups present, or the use of sophisticated techniques such as high-performance liquid chromatography (HPLC) to identify pigments. In comparison, geochemical analyses cost less and can be applied if the environment is not eutrophic (Boyle 2001). Chemistry of surface sediment samples and sediment cores can provide important information about both current and past environmental change, respectively (Boyle 2001; Rippey and Anderson 2008; Zan et al. 2012; Hou et al. 2014).

We measured carbon, nitrogen, and phosphorus concentrations in surface sediments and a core from tropical Paiva Castro Reservoir, a system that fluctuates between mesotrophy (CETESB 2002–2009) and oligotrophy (CETESB 2002–2009; Pires et al. 2015). The spatial and temporal distributions of these elements were investigated, along with analysis of sediment release and retention of nutrients in this system. We expected that analyses of C, N, and P, along with analysis of variables responsible for nutrient retention and release, would shed light on natural and anthropogenic changes in the reservoir over the recent past. We also expected that the data would enable us to identify areas most susceptible to nutrient contamination and provide insights into the recent effects of human activities on the reservoir.

Material and methods

Study area

The Cantareira system is the largest source of drinking water for the metropolitan region of São Paulo. It is formed by five reservoirs that are connected by 48 km of artificial underground tunnels, canals, and pumps (Whately and Cunha 2007; SABESP 2018). This artificial cascade system was developed in two main stages. The first involved construction of the Paiva Castro, Atibainha, and Cachoeira Reservoirs, which

began operation in 1974, with a flow of 11 m^3 s^{-1}. The second stage was completed in 1981, with inclusion of the Jaguari and Jacareí Reservoirs, when the flow increased to 33 m^3 s^{-1} (Whately and Cunha 2007).

The Paiva Castro Reservoir, the last in this artificial cascade system, is located in the Alto Tietê hydrographic basin and was formed by damming of the Juquery River. Effluents from the Mairiporã city sewage treatment station are released into the Paiva Castro upstream area. The reservoir lies at an altitude of 745 m and has a drainage area of 314 km^2 and a mean flow of 4.4 m^3 s^{-1} (SABESP 2018). Rapid population growth (Whately and Cunha 2007) has led to increased nutrient inputs into this reservoir (Giatti 2000; Silva 2002). Regular applications have been made of algicides such as copper sulfate and hydrogen peroxide which have been used to control algae blooms resulting from these excessive nutrient inputs.

Sampling

Two samplings were carried out at the Paiva Castro Reservoir. In March 2010, a gravity corer (Ambühl and Bührer sampler—Ambühl and Bührer 1975) was deployed twice in the deepest part of the reservoir near the dam (C) (Fig. 1). Each 32-cm core was sliced at 2-cm intervals down to 26-cm depth, and at 1-cm intervals thereafter. Samples were stored in sealed plastic bags and kept in thermally insulated bags, until analysis in the laboratory. One core was used for determination of iron, manganese, phosphorus, and nitrogen, and for ^{210}Pb dating. The other core was used for determination of organic matter content and particle size. The core slices were numbered in ascending order.

The second sampling was completed on 13 July 2010 and involved collection of surface sediment samples for measurements of biogeochemical variables. Nine sites were sampled, with seven along the main axis of the reservoir and two (sites 5 and 6) in a lateral arm from where water is extracted for the public water supply (Fig. 1).

At each sampling site, reservoir depth was first determined, followed by two deployments of an Ambühl and Bührer sampler (Ambühl and Bührer 1975). The first collected sample was used for in situ determination of the redox potential (E_H) (electrode: Digimed Model DMP-CP1; base: Gehaka Model PG1400), pH, and temperature (T) in the uppermost centimeter of the sediment, and dissolved oxygen (DO)— 5 cm above sediment line (YSI 556 MPS multi-parameter probe). The topmost 3 cm of the sediment column was then used for N and P analyses. The second sample collected, the first 3 cm of the sediment column was removed for grain size and organic matter analyses. The sediment samples were transferred to sealed plastic bags, which were stored in thermally insulated bags prior to analysis in the laboratory. In all sampling and stations, depth was determined throwing a measuring tape with a weight at its end.

Laboratory analyses

Sedimentation rate and ^{210}Pb dating

A portion of each sample from the cores was dried at 45 °C to constant weight to assess percent dry weight. Dry material was then ground with a glass mortar until homogenized and was then used for the elemental analysis. Samples for measurements of ^{210}Pb and ^{137}Cs activities were sealed and stored for at least 20 days to enable ^{214}Pb and ^{214}Bi to reach secular equilibrium with in situ ^{226}Ra. Samples were counted for 50,000 s with a high-efficiency, low-background detector (EG&G Ortec Model GMX 25190P) and the spectra were analyzed using Maestro 2 software. The CIC (Constant

Fig. 1 Paiva Castro Reservoir and sediment sampling sites (1–9, surface sediment; C, core sites). The sampling sites were georeferenced using a Garmin Model 72 GPS, according to the UTM coordinate system, datum SAD69, and central meridian 45°00 (based on Frascareli et al. 2018)
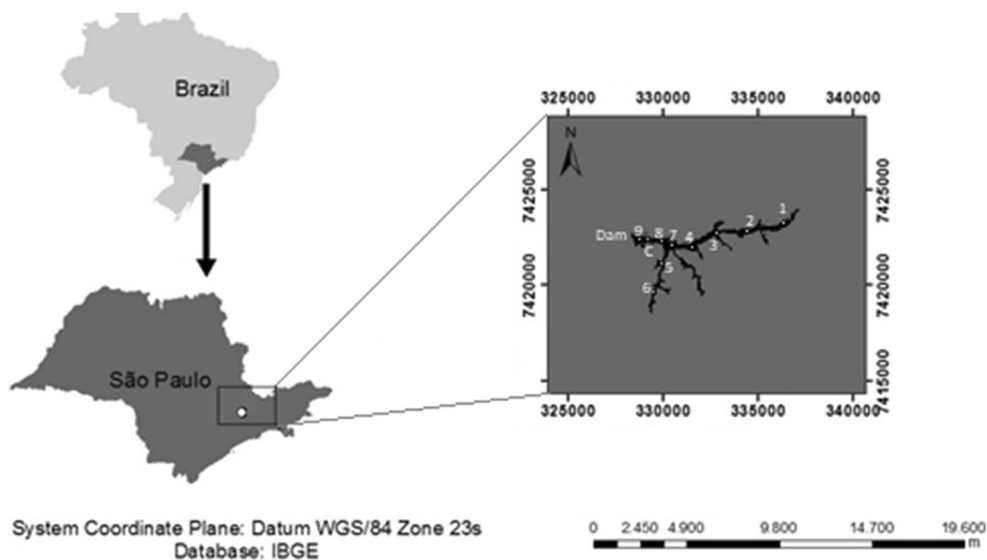
Initial Concentration) model was used for the calculating dates and sedimentation rate calculations (Robbins and Edgington 1975).

Geochronology and sedimentation rate and results were presented in Cardoso-Silva et al. (2016a). Vertical profiles of ^{137}Cs and ln (^{210}Pbxs) (unsupported) can be observed in Fig. 2a, b. The ^{210}Pb total shows an exponential decay throughout the core, which is due to its radioactive decay, stabilizing around the value of ^{210}Pb supported. Two different curves of ^{210}Pb were observed: (1) from 0- to 16-cm depth and (2) from 16- to 32-cm depth. As the core displayed two different curves, this system presented two periods with different sedimentation rates. For sedimentation rate assessment, the natural logarithm (ln) of the ^{210}Pbxs data was estimated for both phases. Then, regression lines for the vertical profiles of ^{210}Pbxs curves where calculated, for the distinct periods. Having the values of a, the corresponding sedimentation rates were evaluated. The analyzed core displayed an average sedimentation rate of 0.91 cm/year ($\pm$ 0.19) from 0- to 16-cm depth, and 0.26 cm/year ($\pm$ 0.19), from 16- to 32-cm depth. Based on sedimentation rates, the years of deposition for each

sedimentary layer were estimated (Fig. 2c). Samples were analyzed every 2 cm. Some samples presented values below the limit of detection, and for this reason, they are not represented in the graphic analysis (Fig. 2a, b).

Nutrients, organic carbon, grain size, sulfate, and metals

Total phosphorus was determined according to the calcination method described by Andersen (1976); after calcination, a solution of HCl 1 M was added and the sediments were heated in water bath for 1 h. The phosphorus was then determined spectrophotometrically (spectrophotometer—Micronal B572) with the molybdenum blue method described by Strickland and Parsons (1960). Total nitrogen was determined by digestion in concentrated sulfuric acid, followed by distillation with boric acid (APHA 2005). Grain size analysis employed the Atterberg system and the beaker method, proposed by Piper (1947) and modified by Meguro (2000). Organic matter (OM) was determined gravimetrically by weight loss on ignition (Meguro 2000) at a temperature of
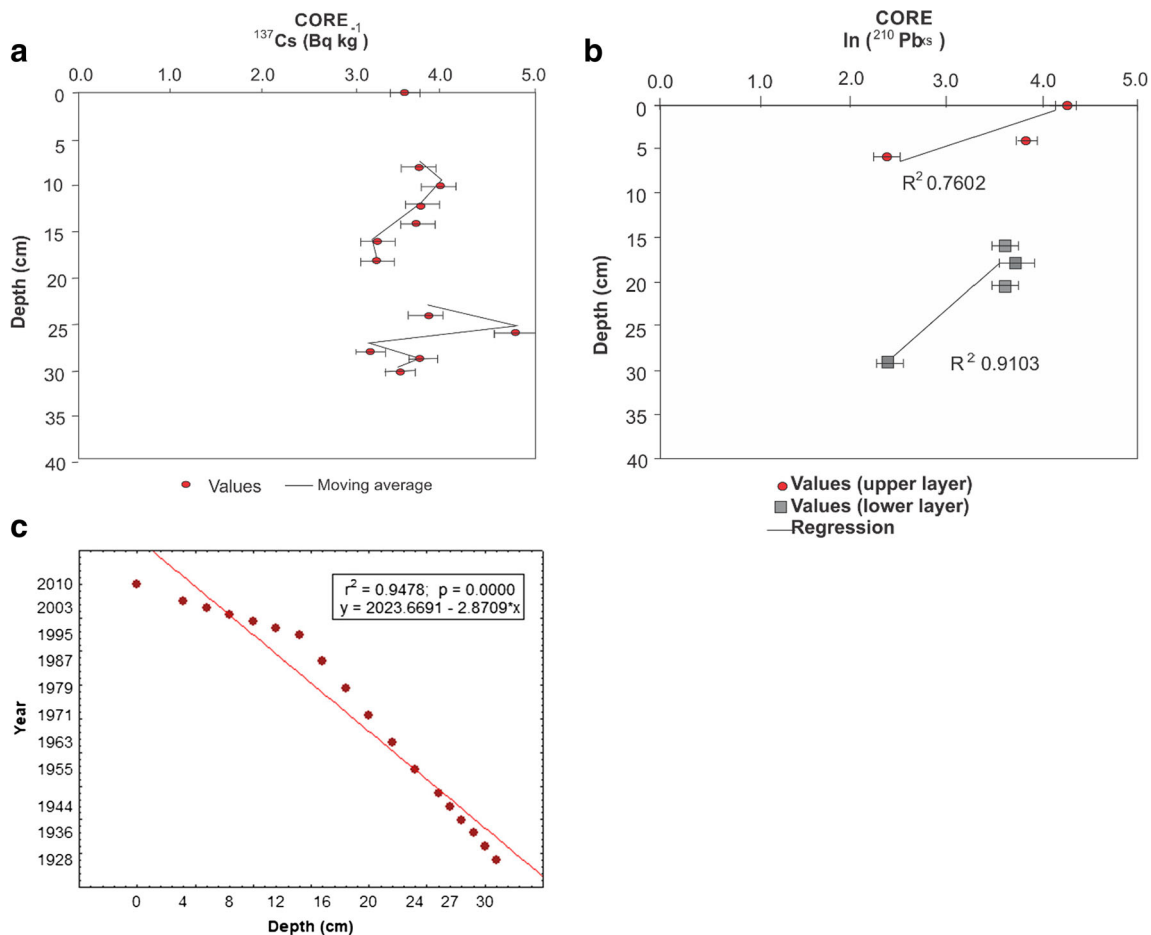
Fig. 2 Vertical profiles of ^{137}Cs (**a**) and ln (^{210}Pbxs) (unsupported) (**b**) in core sediments (adapted from Cardoso-Silva et al. 2016a) and depth and age data by CIC model (**c**)

500 °C. Organic carbon was estimated from OM, assuming that OM is 58% carbon by weight (Meguro 2000).

Manganese and iron were also measured in the core, using US EPA method 3050B EPA SW-846 series (US EPA 1996). This method evaluates the concentration of pseudo total metals through the sediment digestion with HNO_3, HCl, and H_2O_2 additions under heating at 90 °C. Manganese and iron were investigated to determine past redox conditions at the sediment/water interface. According to Mackereth (1966), the ratios of these elements can be used to determine whether there was oxygen in the hypolimnion. Under oxic conditions, Fe and Mn are highly insoluble. Under anoxic and reducing conditions, however, the solubilities of both elements increase, and they are mobilized to the water column (Ladwig et al. 2017). Manganese is more soluble than iron, and mobilities of these elements are closely associated with the reducing potential of the environment (Mackereth 1966; Boyle 2001; Smol 2008).

Sulfide and Mn in superficial sediments were determined according to the analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM), following the recommendations of Allen et al. (1991). Samples were stored at 4 °C before analysis (using three replicates) of the metals by atomic absorption spectrometry (AAS). Sulfide was determined spectrophotometrically with Hach test kits (sulfide 1, cat. no. 1816-32 3; sulfide, cat. no. 1817-33), as described by Cardoso-Silva et al. (2016b). The concentrations of AVS and Mn were expressed as milligram/kilogram of dry sediment. All metals analyzed were obtained by an atomic absorption spectrophotometer—flame mode—Thermo model S.

Data analysis

Data were analyzed using basic descriptive and multivariate statistical analyses, performed using the PAST program (Hammer et al. 2001). Nutrient accumulation rates in the core were calculated as described by Cochran et al. (1998):

$$F_x = R_x \rho_x C_x$$

where F_x is the nutrient accumulation rates for the xth depth interval (mg cm^{-1} year^{-1}); R_x is the ^{210}Pb-derived sedimentation rate for the xth interval (cm year^{-1}); ρ_x is the dry bulk density of the xth interval (g cm^{-3}); and C_x is the nutrient concentration for the xth interval (mg g^{-1}). The use of nutrient accumulation rates core is more appropriate than simply reporting the concentrations of nutrients or other contaminants, because such concentrations are determined by the accumulation of the nutrient/contaminant of interest, relative to accumulation of other sediment components.

The C/N, C/P, N/P, Fe/P, and Fe/Mn molar ratios were calculated to obtain information concerning the origin of the organic matter, redox conditions, and the potential for release

of phosphorus from the sediment over time. Principal component analysis (PCA) was applied to the surface sediment data in order to elucidate the spatial distribution patterns and geochemistry of the nutrients. Cumulative mass water flow mass was obtained by digital processing, using ArcGIS software. Firstly, the reservoir was delimited from a Landsat image 7, an image was then generated with the combination of different bands to produce a classification according to the reflectance color emitted by the reservoir. For each color of reflectance, a code was established that ranged from 1 to 255, the higher the cumulative mass water flow the greater the numerical value. The applied geoprocessing model was based on methodology developed for the determination of the land use classification by reflectance and false color ArcGis 10.3 software as described in Ortega et al. (2016).

To illustrate increasing or decreasing trends along the main axis of the reservoir, some of the graphical representations exclude sites 5 and 6, which are located in a dendritic side arm of the reservoir. These sites, however, are included in the PCA results and in the tables.

Results and discussion

General characteristics of the sediments

Sediments of the Paiva Castro Reservoir display uniform coloration, with no clear temporal or spatial differences. Both surficial and deeper sediments are largely inorganic, with OM contents < 12% (Esteves 2011). Silt and clay particles (< 63 μm) predominated along the reservoir (Fig. 3a), except for the superficial sediments in the higher energy fluvial area (He et al. 2011; Molinaroli et al. 2009). To highlight downstream increase in clay proportion, only the seven sampling points located in the longitudinal axis of the reservoir are shown in Fig. 3a. The core indicates that the sand contents have decreased since the operation of the reservoir began (Fig. 3b). Silt and clay fractions dominate, especially in areas with lower water velocity, as observed in reservoir limnetic regions (He et al. 2011). The reservoir depth presented a gradient of increase in the upstream-downstream direction (Fig. 3a, Table 1).

Spatial heterogeneity of the superficial sediments

Geochemistry of nutrients and carbon

Concentrations of nitrogen, phosphorus, and organic carbon in the superficial sediments of the Paiva Castro Reservoir were spatially heterogeneous, with coefficient of variation values ≥ 49% (Table 1). Nitrogen and phosphorus concentrations tended to increase downstream, i.e., in the direction of the
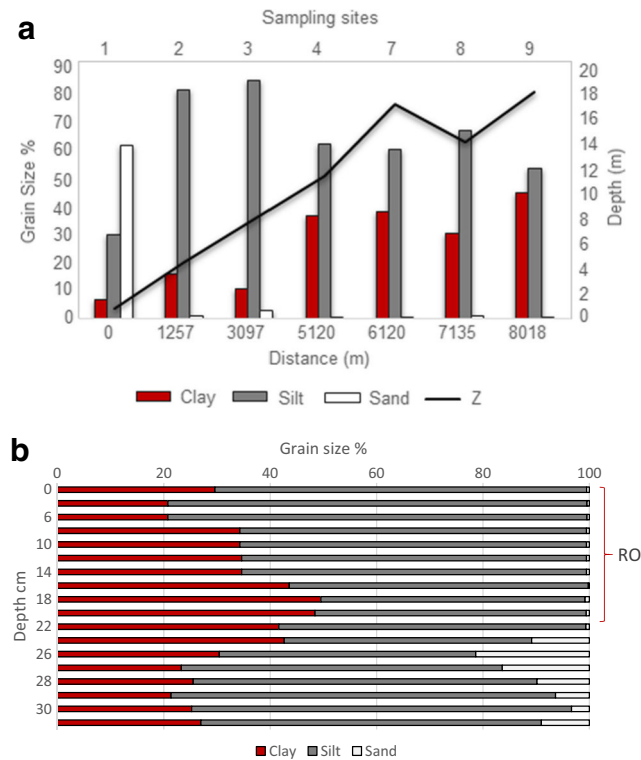
Fig. 3 Reservoir depth (Z) (**a**) and percent of particles of different sizes in the superficial sediments (**a**) and the sediment core (**a**) from the Paiva Castro Reservoir. RO, period of reservoir operation. Distances in ms from site 1. Only data for the sampling sites located in the longitudinal axis of the reservoir are shown. 1 to 9 sampling sites

dam (Fig. 4a, b), while the levels of carbon tended to decrease in the upstream-downstream direction (Fig. 4c).

Two principal components (PCs) explained 77.21% of the total variance (Fig. 5). The main variables influencing PC1 were nitrogen (-0.97) and phosphorus (-0.92), responsible for the arrangement of the sites located downstream, and the carbon content (0.83), which influenced the fluvial and transition area sites and the site where there was extraction of water for the public water supply (sample 6). Higher levels of organic carbon were found in the areas with higher water flow, especially in the fluvial region, under greater influence of the main reservoir-forming river, and in the catchment area for public water supply. This revealed the predominance of allochthonous (Figs. 4d and 5) organic matter, with C/N ratios of 75.74 (sample 1), 27.6 (sample 2), and 110.31 (sample 6 which lies outside the main channel).

The spatial distribution of nutrients in surficial sediments could be explained by higher water flow in the upper part of the reservoir. Greater turbulence in the fluvial and transition regions, together with shallower depths, would create an unstable depositional environment, as observed by Hou et al. (2014) in Dalinouer Lake, China, and by Bartoszek and Tomaszek (2007) in Solina–Myczkowce Reservoirs, in Poland. In the dam area, however, the higher sedimentation

rate (Cardoso-Silva et al. 2016a) favors greater accumulation and retention of nutrients in the sediments (Jia et al. 2017).

The association between phosphorus and the clay and silt particles (Fig. 5) indicates the importance of these sediment fractions in binding the element. Fine-grained sediments have large surface areas that provide binding sites available for P adsorption (Wetzel 2001). Particles < 63 μm predominated along the reservoir (silt, $59.1 \pm 18.0\%$; clay, $27.8 \pm 15.1\%$; Table 1), with the relative proportion of clay particles increasing in the downstream direction (Fig. 4b). Lowest water flows were observed in the limnetic zone at sites 8 and 9 (Table 1), resulting in greater accumulation of fine-grained sediments in this region, following the general pattern observed for reservoirs (Zan et al. 2012; Cardoso-Silva et al. 2016b).

The second PC was mainly influenced by the variables dissolved oxygen (0.87), pH (-0.65), and water flow (0.53), which were responsible for the arrangement of the upstream reservoir sites. Higher water flows could explain the high oxygen concentrations at these sites. Highest DO concentrations were found in the dam area, although the sediments throughout the reservoir displayed oxic characteristics, which was corroborated by the low values for sulfides and E_H (Table 1), as observed by Cardoso-Silva et al. (2016b). Oxic conditions, together with high Mn concentrations in the region and the pH values close to neutrality (pH 6.9 ± 0.5), should favor retention of phosphorus in the sediments (Ribeiro et al. 2008; Wang et al. 2016), but there was no positive correlation between these variables and phosphorus content. Lowest values for phosphorus and nitrogen in the sediment were found in the upstream reservoir area and could be related to high flow and turbulence associated with the shallower depth in the area which promotes an unstable environment for phosphorus and nitrogen sedimentation (Bartoszek and Tomaszek 2007; Smal et al. 2013; Hou et al. 2014).

C/N, C/P, and N/P molar ratios

The C/N molar ratios suggested the predominance of autochthonous organic matter in the sediments and C/N values decline significantly, downstream matter towards the dam (Fig. 4d). Allochthonous organic matter typically has C/N ratios > 20, whereas autochthonous organic material is indicated by ratios between 4 and 10 (Meyers 1994; Hedges and Oades 1997). The phytoplankton community generally shows low molar C/N ratios (5–10), because of its high content of N-rich protein and absence of organic C-rich cellulose (Meyers 1994). The allochthonous material recorded in areas with higher water flow is associated with both the discharge of effluents in the upper reservoir area and the surrounding terrestrial vegetation in the region where there is the extraction of water for public supply. The general pattern expected in reservoirs is a greater allochthonous input in the fluvial area, with a tendency to decrease towards the dam, where there is a predominance of autochthonous

Table 1 Descriptive statistics for sampling depth (m) and for sediments of the Paiva Castro Reservoir: Total nitrogen (N) total phosphorus (P), organic carbon (C), molar ratios (C/N, N/P, and C/P), grain size, sulfate, dissolved oxygen, E_H, pH, and Mn. *SD*, standard deviation; *CV*, coefficient of variation

	Unit	Minimum	Site	Maximum	Site	Mean	SD	CV
N	mg/g	0.61	1	3.4	9	2.2	1.1	49.8
C	mg/g	14.1	5	64.3	6	28.7	15.8	55.2
P	mg/g	0.6	1	11.5	7	6.5	3.1	58.4
C/N	–	5.2	5	110.3	6	29.8	37.6	126.2
C/P	–	3.3	7	162.5	1	38.1	60.2	157.8
N/P	–	0.5	7	2.2	1	0.9	0.5	52.5
Silt	%	30.5	1	85.7	3	59.1	18.0	30.2
Clay	%	7.1	1	46.7	5	27.8	15.1	54.4
Sand	%	0.2	4	62.4	1	12.6	23.3	185.2
Sulfate	mg/kg	9.3	7	22.3	6	16.6	8.4	50.7
DO	mg/L	6.3	8	10.0	3	8.2	1.4	16.7
E_H		17	7	135	1	69.4	34.1	49.1
pH		6.5	4	8.0	1	6.9	0.5	7.1
Mn	mg/kg	107.1	8	690.1	1	241.7	224.8	93.0
Flux	–	4	8 and 5	64	6	17.8	18.1	101.9
Depth	m	0.9	1	18.1	9	10.3	5.8	55.9

production that mainly originates from the phytoplankton community, with C/N values between 5 and 10 (Holligan et al. 1984).

The C/P molar ratios were also higher for the upstream area, with a tendency to decrease towards the dam (Fig. 4e). The mean value was 38.1 ± 60.2, with high spatial variability indicated by the coefficient of variation of 157.8% (Table 1). With respect to the Redfield C:P ratio (108:1), only sites in the fluvial area (sample 1, 154:1) and in the catchment area for public water supply (sample 6, 120:1) presented values greater than or equal to this ratio. This is probably because these sites have the highest sand contents, with proportionally fewer binding sites for phosphorus. The reservoir mean for the Redfield C:P ratio was 7.8:1, with a minimum of 3.3:1 at site 7. Data obtained for the superficial sediments revealed anthropic contamination, likely caused by effluent discharges, because the relative high concentrations of phosphorus compared to the carbon concentration. The N/P ratio also showed an increase towards the dam (Fig. 4f).

Different from the findings of Pompêo et al. (2017), the N/P ratio of 0.5 ± 0.9 (Table 1) suggests that nitrogen is the limiting element. For aquatic ecosystems, N/P > 16 generally indicates that phosphorus is the limiting nutrient, whereas N/P < 14 indicates nitrogen limitation (Elser et al. 2009). Ratios between 14 and 16 indicate that the environment is limited by either nutrient or plant growth is limited by N and P together (Elser et al. 2009).

Temporal changes in the sediment core

Geochemistry of nutrients and carbon

The sediment core showed no significant changes over time in terms of the contents of C, N, and P concentrations, or the relationships between them, as shown by the low coefficients

of variation (Table 2; Fig. 6). Nutrients (N, P) and carbon accumulation rates increased significantly between the years 1979 and 1987, a consequence of the increase in bulk sedimentation rate (Table 2; Fig. 6). According to Cardoso-Silva et al. (2016a), this increase could be attributed to two main events. Firstly, in 1981, two additional downstream reservoirs in the region entered into operation and the flow rate in the system increased from 11 to 33 m³/s, directly affecting the dynamics in the water body. Secondly, between 1975 and 1980, the first major urban expansion in the Juqueri River Basin occurred, following the construction of the Paiva Castro Reservoir (EMPLASA 2006). Urbanization is known to alter the rate of sedimentation in a water body (Moreira et al. 2002; Alighalehbabakhani et al. 2017), which can affect the flow and the contributions of nutrients and organic matter, as we observed.

After the significant increases in the nutrient and carbon concentrations and mass accumulated, there were increases in the phosphorus and carbon contents in the 6–8-cm layer (2003) (Fig. 6). These slight increases in C and P coincided with the period in which there was a significant increase in the copper concentration to around three times the background value, as reported by Cardoso-Silva et al. (2016a), which was attributed to applications of copper sulfate as an algicide in the Cantareira system watershed. This period also coincided with record water scarcity in the region, when the Cantareira system reached 1% of its storage capacity (Whately and Cunha 2007). Dry periods are generally associated with higher phytoplankton productivity (Nogueira et al. 1999; Santos et al. 2014), mainly because nutrients become concentrated in a smaller volume of water and because residence time of the water in the reservoir increases, leading to greater production
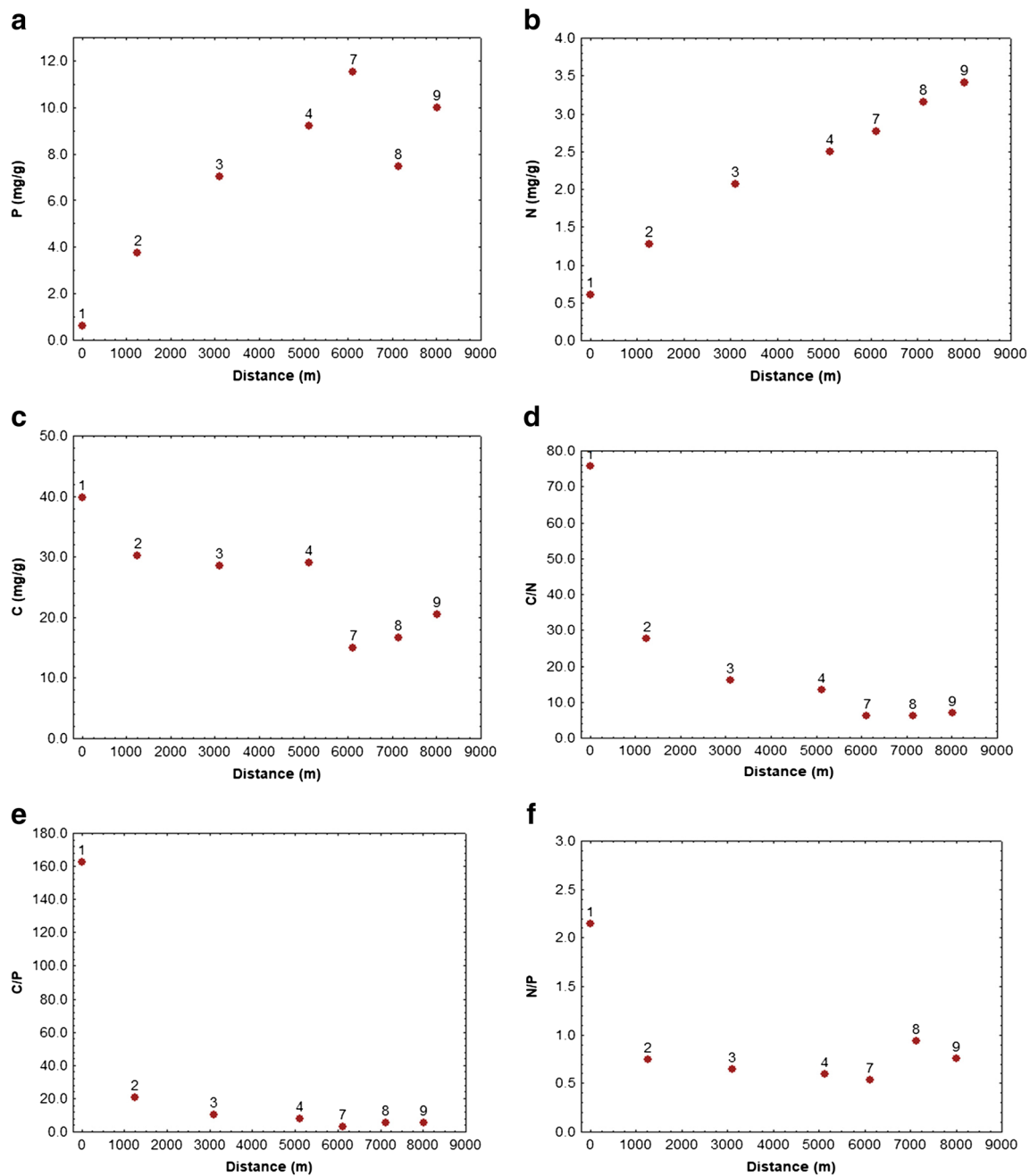
Fig. 4 Surface sediment **a** phosphorus (P), **b** nitrogen (N), and **c** carbon (C) concentrations, and the molar ratios **d** C/N, **e** C/P, and **f** N/P, for the Paiva Castro Reservoir related to distance downstream from site 1. Only the sampling sites located in the longitudinal axis of the reservoir are shown (1 to 9)

of organic matter and higher levels of P and C, as recorded in the sediments. On the other hand, during this same period with increased carbon and phosphorus contents, there was a slight decrease in the N content, which could have been a consequence of an increase in denitrification. Denitrification is the main mechanism leading to the loss of N from top sediments (Hou et al. 2014), and here it may have been associated with decomposition of the greater amounts of organic matter observed for this period. Subsequently, in the topmost layers, the

P and C contents decreased, returning to values close to the mean, indicating that the loss of nitrogen by denitrification was also reduced. Therefore, the dry period recorded in the area leading to a higher productivity in the system is the possible main factor driving changes in accumulation rates and nutrient concentrations in sediments.

From 1989 to 1999, an increase of phosphorus in surface water was observed, caused by urban growth in the Paiva Castro Basin (Giatti 2000). This increase, however, was not

Fig. 5 Principal component analysis applied to the data for the superficial sediments in the limnetic area of the Paiva Castro Reservoir
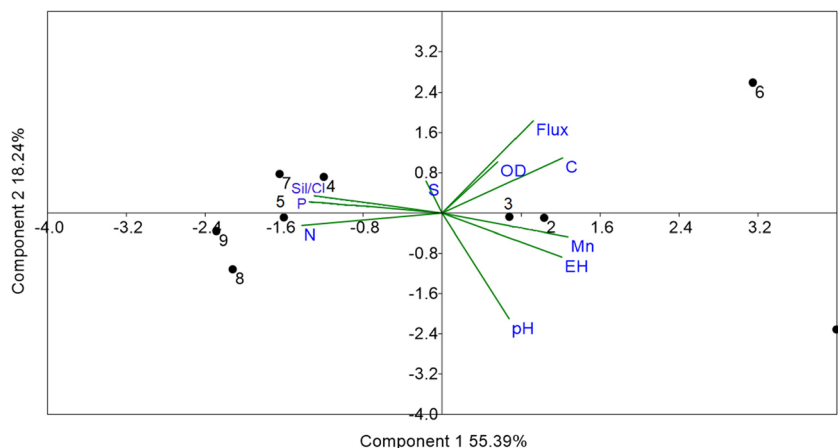
reflected in the sediment. Using the data available from IBGE (Brazilian Institute of Geography and Statistics) for population growth and agricultural activities from 1992 to 2010, no significant Pearson correlations ($p > 0.05$) were observed between phosphorus concentration and population growth ($r = 0.31$), or between phosphorus content and temporary ($r = 0.31$) or permanent ($r = 0.37$) agricultural activities. Nevertheless, this does not imply that these activities did not influence the ecosystem. For the same period, Cardoso-Silva et al. (2016a) observed a significant correlation between the copper content of the sediment and population increase, which was attributed to the application of algicides. The absence of a significant correlation between phosphorus concentrations and population numbers may be explained by the fact that the Paiva Castro reservoir experiences periods of mesotrophy. In eutrophic and mesotrophic environments, the input of P

over time is typically larger than the amount ultimately stored in the sediment (Rydin 2000). According to data from CETESB (Companhia de Tecnologia de Saneamento Ambiental - Environmental Sanitation Technology Company 2005–2015), between 2005 and 2010 conditions in the dam region ranged from mesotrophic to oligotrophic, with a mesotrophic average in 6 out of the 9 years evaluated (Table 3). Although higher levels of phosphorus in sediments can be an indicative of increased nutrient inputs to an ecosystem (Liu et al. 2010; Zan et al. 2012; Hou et al. 2014), the results showed the need for the levels of phosphorus in sediments to be carefully evaluated, taking into account the changing concentrations of phosphorus in the water.
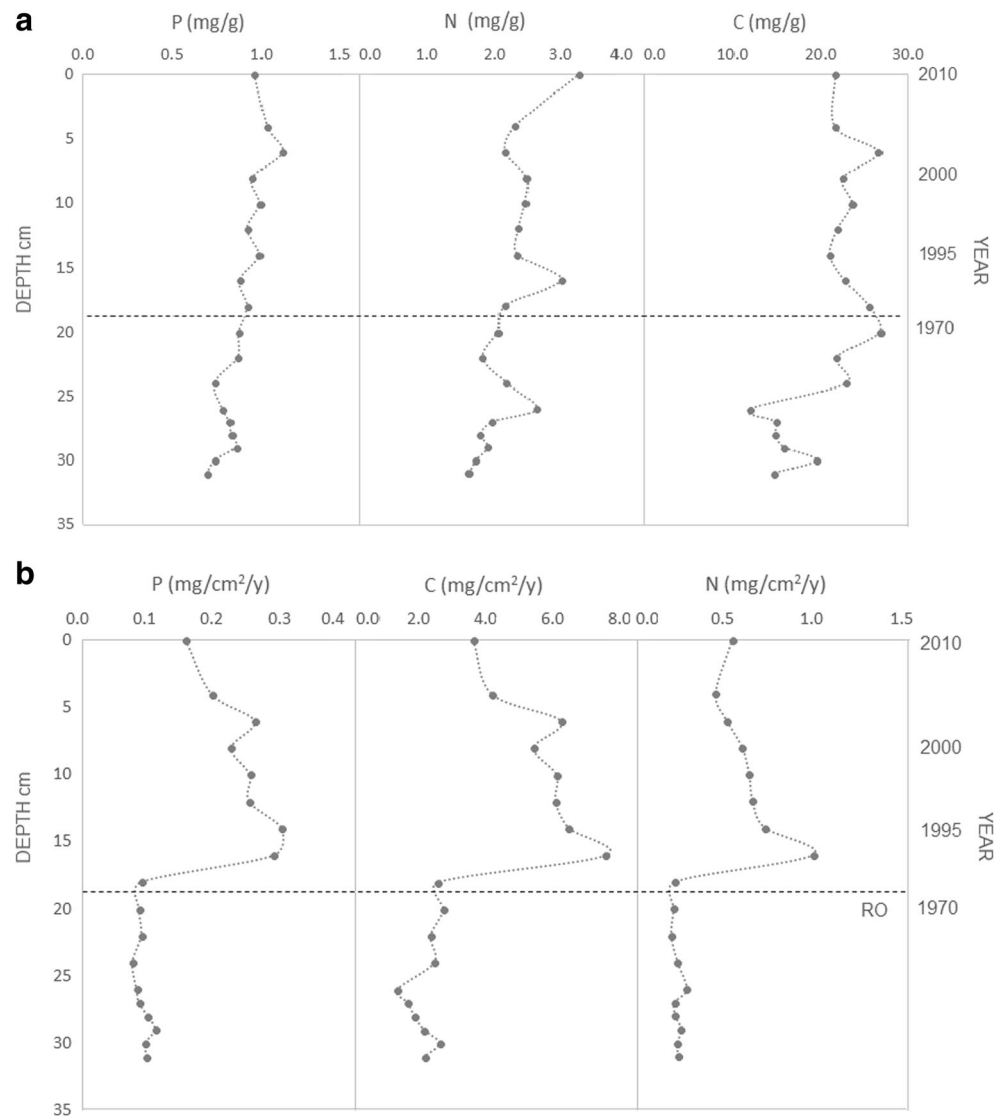
There were significant correlations ($p < 0.05$) of nitrogen with population growth ($r = 0.50$) and temporary agricultural production ($r = 0.55$). For carbon, there was only a significant

Table 2 Descriptive statistics for the concentrations (mg/g) of total nitrogen (N), total phosphorus (P), and organic carbon (C); the molar ratios C/N, N/P, C/P, Fe/P, and Fe/Mn; the dry bulk sediment density (BSD) (g/cm³); and the accumulation rates AR of N, P, and C, in the sediment core collected in the limnetic zone of the Paiva Castro Reservoir. *SD*, standard deviation; *CV*, coefficient of variation; *Min*, minimum value; *Max*, maximum value ($n = 18$)

	Unit	Min	Sample	Max	Sample	Mean	SD	CV
N	mg/g	1.6	31–32 cm	3.3	26–27 cm	2.2	0.4	19.4
C	mg/g	12.0	24–26 cm	26.7	6–8 cm (2003)	20.6	4.4	21.2
P	mg/g	0.7	26–27 cm	1.1	20–22 cm (1971)	0.9	0.1	12.5
Fe	mg/g	40.5	31–32 cm	75.5	20–22 cm (1971)	60.1	9.7	16.0
C/N	–	5.3	26–27 cm	15.2	20–22 cm (1971)	10.9	2.5	23.1
C/P	–	39.8	26–27 cm	80.7	24–26 cm	60.2	11.2	18.5
N/P	–	4.3	6–8 cm (2003)	7.6	0–4 (2010); 16–18 cm (1987)	5.7	1.0	17.9
Fe/P	–	30.4	28–29 cm	48.2	20–22 cm (1971)	38.0	5.7	14.9
Fe/Mn	–	0.1	22–24 cm	0.4	28–29 cm	0.2	0.4	40.0
N AR	mg/cm²/year	1.2	20–22 cm (1971)	7.4	16–18 cm (1987)	3.6	2.0	55.0
C AR	mg/cm²/year	0.2	26–27 cm	1.0	16–18 cm (1987)	0.4	0.2	58.6
P AR	mg/cm²/year	0.1	24–26 cm	0.3	14–16 cm (1995)	0.2	0.1	52.6
BSD	g/cm³	0.2	0–4 cm (2010)	0.5	31–32 cm	0.4	0.1	27.8

Fig. 6 Concentrations (**a**) and accumulation (**b**) rates of P, C, and N in the sediment core from the limnetic zone of the Paiva Castro Reservoir

correlation with permanent agricultural production ($r = 0.73$). Despite the increase in nutrient contents and the significant correlations between nitrogen and carbon and the anthropic activities, the sediments in the region were not considered polluted in terms of the contents of nitrogen (2.2 ± 0.4 mg/g) and phosphorus (0.9 ± 0.1 mg/g) (Table 2), according to the Ontario sediment quality guidelines (SQGs). The Ontario SQGs constitute one of the few sediment quality guides for TN and TP in aquatic environments (Hou et al. 2014) and consider sediments to be contaminated when the concentrations exceed 4.8 mg/g for nitrogen and 2.0 mg/g for phosphorus (Persaud et al. 1993).

The Pearson correlation analysis identified positive correlations of the carbon content with the silt fraction ($r = 0.53$) and the iron content ($r = 0.57$). The variation as a function of the silt fraction was because organic carbon is progressively concentrated in finer-grained sediments (Meyers 1994;

Bergamaschi et al. 1997) that provide more binding sites for the adsorption of organic matter (Froehner and Martins 2008). The grain size variation is shown in Fig. 3. The correlation between the carbon and iron contents could be explained by the organic matter decomposition process, during which iron oxides are consumed (Wetzel 2001) and because organic matter also acts as a metal binding phase (Cardoso-Silva et al. 2016b).

C/N, C/P, and N/P molar ratios

Stratigraphic fluctuations of C/N in sediment cores are interpreted as temporal shifts in the relative contributions of terrestrial and aquatic OM to the sediment (Brenner et al. 2006; Piwińska et al. 2018). The C/N molar ratios (10.2 ± 2.5) indicated a predominance of autochthonous OM over time in the dam region (Table 2; Fig. 7). When all the sediment

Table 3 Mean values for Carlson's (1977) Trophic State Index (TSI) adapted for tropical environments by Lamparelli (2004): (1) at a point monitored by CETESB in the Paiva Castro reservoir dam area (1 TSI); (2) at the dam area (2 TSI); (3) mean values in two seasons in three points at the reservoir (fluvial, central, and dam areas) (3-TSI). Ultraoligotrophic (≤ 47), oligotrophic (47 < IET ≤ 52), mesotrophic (52 < IET ≤ 59), eutrophic (59 < IET ≤ 63), hypereutrophic (63 < IET ≤ 67), supereutrophic (> 67)

	1-TSI CETESB	2-TSI (Pires 2015)	3-TSI (Matta 2016)	
			Dry season	Rainy season
2005	*52*	–	–	–
2006	**53**	–	–	–
2007	**55**	–	–	–
2008	*51.3*	–	–	–
2009	**55.75**	–	–	–
2010	**53**	–	–	–
2011	**53**	*50.2*		
2012	*49*	–	–	–
2013	*51*	–	–	–
2014	*51*	–	–	–
2015	**54**	–	–	–
2016	–	–	*46.6 ± 1.8*	**53.8 ± 0.8**

Entries in italic mean oligotrophic 47 < IET ≤ 52; entries in bold mean mesotrophic 52 < IET ≤ 59

organic matter is derived from the phytoplankton community, the C:N:P ratio should be close to the Redfield ratio (108:16:1) and the C/N ratio will be close to 6.6, as observed in Table 2. This pattern is expected in reservoirs where the allochthonous contribution generally predominates only in the fluvial areas and decreases downstream (Kimmel et al. 1990).
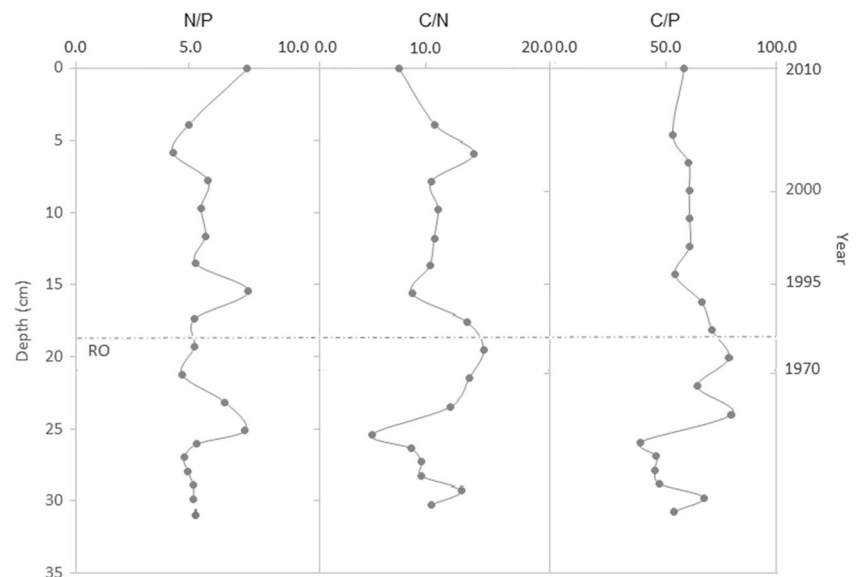
The C/P ratios presented a mean of 60.2 ± 11.2, with a maximum of 80.7 and a minimum of 39.8. Considering the Redfield ratio (108:1), it was found an average of 54:1, therefore a low C/P ratio. This might indicate anthropogenic source of P, or diagenetic changes in the sediment, involving C loss. Current local legislation (CONAMA no. 344/04) and the Ontario SQGs only consider the sediment to be polluted when TP > 2 mg/g, at which an alert is issued. Considering the classification of Zhang et al. (2008) for lacustrine environments, the Paiva Castro sediments are moderately polluted with phosphorus. According to the latter classification, sediments with total phosphorus contents < 0.5 mg/g are not considered polluted by this element, while values between 0.5 and 1.3 mg/g indicate moderate pollution environments and values > 1.3 mg/g indicate highly polluted sediments. The sediment quality guidelines provide useful tools, although there is a need to establish regional reference values for nutrients. A change from the reference condition and the present status is a crucial consideration in any ecological research and assessment program (Bennion et al. 2004). The N/P ratio obtained here (2.9 ± 0.5) suggests that nitrogen has been the limiting element over time (Table 2).

Retention and release of phosphorus over time

Several factors suggested that over time, the phosphorus was largely retained in the sediment, as indicated by the Fe/Mn and Fe/P molar ratios and the correlations between P and the conservative elements Al and Fe. The Fe/Mn molar ratio remained relatively constant during the reservoir operational period, with a low coefficient of variation (22.01%) suggesting that oxic conditions persisted in the environment. Small changes were observed in the Mn content, together with peaks

Fig. 7 Distribution of N/P, C/N, and C/P molar ratios for the sediment core from the limnetic area of the Paiva Castro Reservoir

in Fe levels and minimum values for the Fe/Mn ratio during the period corresponding to filling of the reservoir, suggesting the existence of reducing conditions in the hypolimnion (Fig. 8). The initial phase of operation of a reservoir is usually characterized by increases in productivity, caused by the decomposition of organic matter, which can cause depletion of oxygen and a shift in the redox potential.

The Fe/P molar ratio (38.0 ± 5.7) corroborated the predominance of oxic conditions over time. It was previously reported that freshwater sediments with a total Fe/P molar ratio > 8.5 could retain phosphate in the oxidized surface layer, but that phosphate is released when the ratio is < 8.5 (Jensen et al. 1992). When the sediment surface is oxic, strong adsorption of dissolved phosphate onto solid iron oxyhydroxides limits the efflux of phosphorus by preventing diffusion of phosphate into the water column (Katsev et al. 2006). On the other hand, under anoxic conditions, iron oxyhydroxides reductively dissolve phosphate, which is released into the water column (Katsev et al. 2006). Significant positive correlations between total phosphorus and the contents of Fe ($r = 0.51$) and Al ($r = 0.53$) suggest favorable conditions for phosphorus immobilization by adsorption of inorganic forms of P onto sediment metallic oxides (Fonseca et al. 2011; Dittrich et al. 2013; Hayakawa et al. 2015) favoring the retention of P in the sediment.

Conclusions and final considerations

The spatial heterogeneity observed in the Paiva Castro sediments is associated with both natural variations in the water body and variations induced by human impacts. The marked spatial heterogeneity, seen as a downstream decrease in the allochthonous contribution to the sediments of organic material and increases in nitrogen and phosphorus concentrations, is mainly associated with different water flow velocities and OM sources in the different compartments of the reservoir. Considering temporal variability, although there was not a

significant change over time in C or N concentration, evidenced by the coefficients of variation < 21%, these variables showed significant correlations with the population increase and the agricultural activities in the drainage basin. The sediment C/P molar ratios were indicative of anthropic impacts in the region, because they were low compared to the Redfield ratio. Although there are signs of environmental degradation in the composition of the Paiva Castro Reservoir sediments, predominance of oxic conditions over space and time and particle sizes < 63 μm provided conditions favorable to the retention of phosphorus in the sediments, hence controlling the eutrophication process of the water column. We suggest future works focusing on sequential extraction procedures for the determination of phosphorus forms in sediment to better understand the burial and diagenesis of P in sediments. Anyway, the geochemical data were effective for detection of impacts in the Paiva Castro drainage basin. We recommended that human activities in the river basin should be managed carefully, in addition to improving sewage treatment. The approaches in this research could be extended to other locations, especially in mesotrophic and oligotrophic reservoirs, to provide information on historical human impacts in those ecosystems.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Fig. 8 Fe/Mn molar ratio and Fe content for the sediment core from the limnetic area of the Paiva Castro Reservoir

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