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RESEARCH ARTICLE

Geochemistry and sedimentary photopigments as proxies to reconstruct past environmental changes in a subtropical reservoir

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Abstract

Sediment cores were used to establish past environmental impacts associated with eutrophication, erosion and metal contamination in the subtropical Atibainha reservoir (São Paulo State, Brazil). We hypothesize that: (1) the levels of nutrients, determined by a spectrophotometric method, reflect the contributions of these elements over time and (2) changes in sedimentation rates, determined by ^{210}Pb geochronology, and metal flows, determined by ICP-AEOS, are related to anthropic activities. Stratigraphic changes in the analysed variables were used to divide the sediment cores into three intervals, according to PCA and cluster analysis (Euclidian distances, Ward's method). Interval I, composed by the period prior to operation of the reservoir, was influenced by organic matter levels. Interval II, between 1967 and 1993 (PC2: 14.94% of the total variability), a period of minor impacts, was mainly influenced by Mn (eigenvalue of 0.71) and Zn (0.74). Interval III, which included sediment deposited between 1993 and 2015 (PC1: 60.28% of the total variability), was influenced by the highest levels of the pigments lutein (0.86), zeaxanthin (0.90) and fucoxanthin (0.65), together with total nitrogen (0.78) and sedimentation rate (0.91), suggesting changes in the phytoplankton community composition probably associated to the intensification of eutrophication and erosion processes. Despite the limitations of applying paleolimnological techniques in reservoirs and the use of pigments as proxies in regions with higher temperatures, it was observed that the anoxic conditions and the aphotic environment in the hypolimnion acted to preserve pigments associated with the groups Chlorophyta (lutein), Cyanobacteria (zeaxanthin) and Bacillariophyta (fucoxanthin). The isolated analysis of nutrients was not sufficient to make conclusive inferences regarding the eutrophication history, since the levels of TP tended to decrease over time, in contrast to an increase in the levels of TN. Despite intensification of eutrophication and erosion, associated to anthropic activities, no signs of metal contamination were recorded.

Keywords Sediments · Eutrophication · Erosion · Sedimentation rate · Nutrients · Lutein · Zeaxanthin

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Introduction

Paleolimnological techniques have the potential to fill data gaps in environmental monitoring (Paterson et al., 2020; Reavie, 2020), enabling assessment of long-term ecological trends, which can assist water resource management decisions (Tse et al., 2015). Such studies are rare for reservoirs, because these ecosystems have sedimentation patterns that can hinder accurate interpretation of stratigraphic data (Shotbolt et al., 2006; Tse et al., 2015). However, despite the limitations, it is possible and important to apply the technique in reservoirs, which can shed light on ecosystem dynamics and processes such as eutrophication, metal accumulation, erosion and changes in biological communities.

The eutrophication in lakes and reservoirs is a natural process intensified by human activities that increases the loading of nutrients as phosphorus and nitrogen from domestic, agricultural or industrial sources (Halac et al., 2020). It has become a global environmental problem (Smith and Schindler, 2009) and has been intensified with the synergistic effect of climate change and human activities. Although eutrophication processes have been widely described, it remains an area of scientific research, due to the various consequences in the abiotic and biotic environment and water quality degradation. Furthermore, our understanding of eutrophication history is still often limited (Zhuo et al. 2014), because monitoring is commonly absent or deficient in most aquatic ecosystems. These gaps in scientific knowledge can be overcome, for example through paleoenvironmental research.

Paleoenvironmental studies focused on trophic state reconstruction generally include the use of geochemical parameters, such as nutrients, as well as biological proxies such as diatoms and photopigments (Soares-Silva et al., 2020; Halac et al., 2020). Among the nutrients, phosphorus (P) plays a key role in eutrophication, because it is the principal limiting element in freshwater ecosystems. In addition to total P analysis, it is important to elucidate the different forms of P, since not all of them are likely to be released from the sediment and thereby increase eutrophication (Ruban et al., 2001). Among biological proxies, photosynthetic pigments have the advantage of presenting a wide range of structures (Romero-Viana et al., 2009), most with a chemotaxonomic association (Roy et al., 2006). For example, carotenoids such as fucoxanthins are considered markers of diatoms, while zeaxanthin reflects cyanobacteria (Jeffrey et al., 1997; Roy et al., 2006; Wright, 2005; Reuss et al., 2005; Buchaca et al., 2019), and lutein indicates chlorophytes (Wright, 2005; Reuss et al., 2005; Buchaca et al., 2019). On the other hand, chlorophyll-a and β-carotene act as indicators of algal biomass, because they are present in all phytoplankton groups (Wright, 2005; Borghini et al., 2007; Makri et al., 2019). Thus, pigments can provide information about changes in trophy as well as variations in phytoplankton community.

One of the challenges of using photopigments as proxies is the rapid degradation of these substances in the water column, due to zooplankton grazing or photo- and chemical oxidation (the rates of which vary with temperature, light and oxygen) (Sanger, 1988; Zhang et al., 2019). In the tropics and subtropics, the higher temperatures and accelerated metabolism may make the preservation of pigments even more problematic, restricting their use as bioindicators of ecosystem changes (Buchaca et al., 2019). Consequently, there have been only a few studies focusing on the analysis of pigments in these regions. Some examples can be observed in African Lakes: El-Monem and Ahmed (2009), Meyer et al. (2017), Loakes et al. (2018) and Saulnier-Talbot et al. (2018); and in Latin American reservoirs: Soares-Silva et al. (2020), Halac et al. (2020) and Gangi et al. (2020).

Sedimentation rates determined by geochronological techniques, applied with other proxies, can also be used to elucidate the history of environmental changes. Sedimentation rates are specific to each water body and may be influenced by human activities that can result in increased erosion and eutrophication processes (Moss et al., 2003; Scharf et al. 2010). They are also used to infer the fluxes of contaminants such as metals in the aquatic environment (Cochran et al., 1998). Metals are well-known environmental contaminants, due to their potential toxicity, with a tendency to accumulate in sediments, so they are good indicators of human activities in the watershed. Much of what is known about the dynamics of these elements has been obtained by paleolimnological studies (Smol, 2008). Despite their toxic character, some metals are essential in biological metabolism, acting as micronutrients (Devesa-Rey et al., 2009). Hence, their absence may result in deficiencies in the metabolic functions of organisms at all trophic levels.

In this work, using a subtropical reservoir as a study model, evaluation was made of sediment profiles in terms of nutrients, organic matter, sedimentation rate, metals and fossil photopigments (chlorophyll-a, β-carotene, fucoxanthin, zeaxanthin and lutein). The data were analysed to identify past environmental impacts associated with eutrophication, erosion and metal contamination. We hypothesize that: (1) the levels of nutrients (N and P) may reflect the contributions of these elements over time and (2) changes in sedimentation rates and metal flows may be related to anthropic activities. This work is a contribution to studies of pigments and nutritional element status in subtropical reservoirs.

Materials and methods

Study area

Sediment cores were obtained on October 1, 2015, in the Atibainha reservoir in São Paulo State, Brazil (Fig. 1). The Atibainha reservoir is the fourth of five reservoirs in the Cantareira cascade multisystem, which is the primary source of drinking water for the São Paulo metropolitan region (Cardoso-Silva et al., 2017; Pompêo et al., 2017). The reservoir lies in the Piracicaba watershed, at an altitude of 787 m, where annual mean rainfall is 1642.0 mm. The reservoir has an area of 21.8 km^2, a mean depth of 4.8 m, a volume of 104 m^3/s and a residence time of 105.8 days (Cardoso-Silva et al., 2021). The Atibainha watershed has been the scene of agricultural activities since the mid-seventeenth and nineteenth centuries. Industrialization began in the region only in the mid-1930s and was intensified during the 1960s and

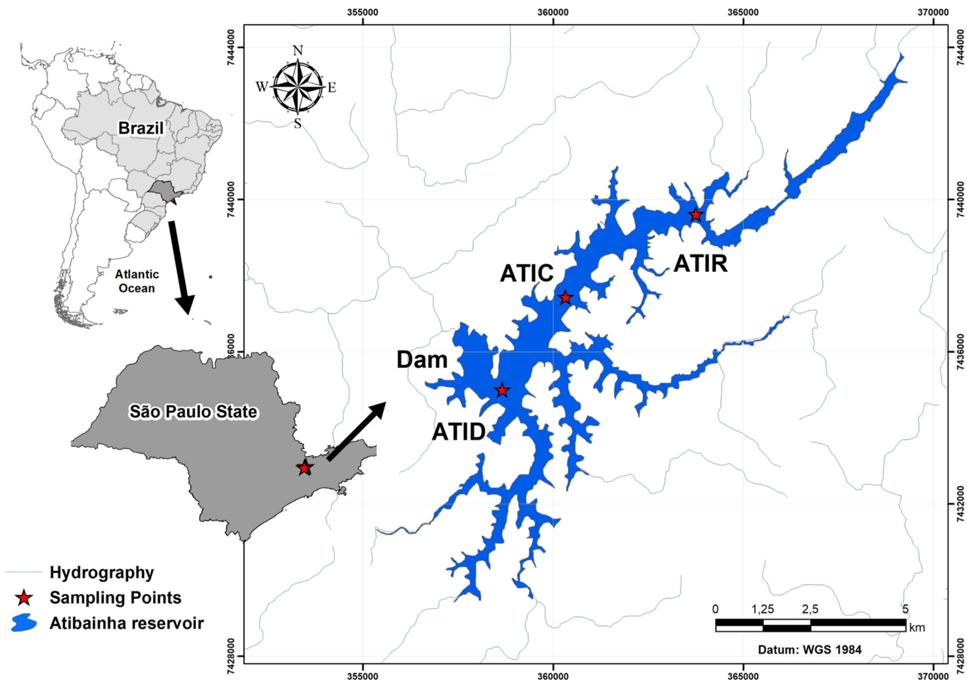

Fig. 1 Atibainha reservoir in São Paulo State, Brazil. The sediment cores were obtained in the dam area (ATID). ATID, limnetic area; ATIC, transitional area; ATIR, fluvial area

1970s when the construction of the D. Pedro I Highway took place. During this period, the cultivation of eucalyptus was also started, which continues to this day. Of the total area of the reservoir, 98.5% is located in rural areas (Andrade et al, 2015) and in Nazaré Paulista, the municipality in which most of the reservoir basin is located, the percentage of rural area is 68% (FF, 2020).

The type of land use around the Atibainha watershed has a major impact on the water quality of this reservoir (Vieira and Vieira, 2016; Cardoso-Silva et al., 2017). The occupation register for the Atibainha reservoir reveals a growing urban development of residential and recreation centres around the reservoir (Andrade et al, 2015). One of the greatest management challenges concerns inadequate infrastructure for sewage collection and treatment. In the urban area of Nazaré Paulista, about 60% of the collected sewage is treated, while no systems for sewage disposal exist in rural areas, so there is the potential for high inputs of nutrients into the watershed. Eutrophication has recently intensified, resulting in the reservoir being classified as oligo-mesotrophic (CETESB, 2017; Cardoso-Silva et al., 2017). The monitoring program performed by the local environmental agency Cetesb, in Atibainha reservoir initiated only in 2014 leaving an information gap about limnological conditions during the first 40 years of dam operation.

Sampling

A gravity corer was used to collect four sediment cores from the deepest part of the reservoir, in the dam region (17 m depth), where sedimentation is generally higher and there is less potential for bioturbation or other mixing processes (Smol, 2008). Each core was sectioned at 2-cm intervals and the samples were stored in sealed plastic bags, which were kept in thermally insulated bags until the laboratory analyses were performed. One core (core 1) was used for metal determination and geochronological analysis. Another core (core 2) was used for the determination of organic matter, particle size and nutrients. A third core (core 3) was used for pigment analysis. A fourth core (core 4) was preserved at – 15 °C for possible future analyses. The core slices were numbered in ascending order, from the top to the bottom of the core. The cores had total depths ranging between 20 and 36 cm.

To characterize the reservoir, water and surface sediments were also sampled in the three theoretical zones in reservoirs (riverine, transitional and lacustrine) (Kimmel et al., 1990) (Fig. 1), as described by Frascareli et al. (2018). For sediment collection, a 400 cm^2 Lenz-type grab was released three times at each site. The fraction from 0 to 4 cm deep was collected in each release, followed by removal of an aliquot for the determination of metals and another aliquot for analyses of organic matter, particle size, and total nitrogen and phosphorus. The sediments were transferred to previously cleaned vials and kept in the dark at low temperature. For each site, samples were collected in triplicate, followed by replicate analyses in the laboratory.

Measurements of temperature, dissolved oxygen, percentage of dissolved oxygen saturation, pH and electrical conductivity were taken throughout the vertical profiles at all the sampling sites, using a multiparameter probe (U52, Horiba). The maximum depth (Echotest II, Plastimo) and the water column transparency (30 cm Secchi disc) were also determined in situ. The euphotic zone was estimated according to Cole (1979), by multiplying the Secchi disc values by 2.7. Integrated water samples were collected at each sampling site using a 2 cm diameter garden hose (Navarro et al., 2006; Becker et al., 2010). The hose was repeatedly launched until a 5 L volume of water had been collected. The integrated water column represented the depth of the photic zone (Pompêo et al., 2017; Frascareli et al., 2018). The samples were stored in plastic bottles and kept in a cooler bag until arrival at the laboratory.

Laboratory analyses

Geochronology and metal analyses (core 1 and surface sediments)

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

A second aliquot of sediment was used for metal analysis (in duplicate), according to US EPA method SW-846 3050 B (US EPA, 1996). The samples were stored at 4 °C, prior to analysis of Al, Cr, Cu, Fe, Mn, Ni, Pb and Zn by inductively coupled plasma atomic emission spectrometry (ICP-AES), using an Agilent Series 720 instrument (Cardoso-Silva et al., 2021). Analytical grade reagents (obtained from Merck and Sigma-Aldrich) were used in all the analyses. All items of glassware and equipment used for the storage and processing of the samples for metal analysis were left in 10% nitric acid for at least 24 h, followed by rinsing with ultrapure water. The accuracy of the data obtained was evaluated in recovery assays performed using sample solutions fortified with the metals. These assays employed SpecSol® G16 V standard solutions containing 100 mg/L of the metals in 2% HNO_3. A value between 75 and 125% was considered as the acceptance criterion. The recovery efficiencies ranged from 79.8 to 116.9%. The same procedures were used for analysis of the metals in the surface sediments.

Organic matter, carbon and nutrients (core 2 and surface sediments)

The core 2 and surface sediment samples were dried in a forced aeration oven at 50 °C, until constant weight, followed by grinding using a glass mortar and pestle. The organic matter (OM) content was determined by the loss-on-ignition method, which involves combustion of the organic matter in an oven at 550 °C (Meguro, 2000). The organic carbon (Corg) content was estimated from the OM value, assuming that the OM contained 58% carbon by weight (Meguro, 2000). Another portion of the sediment was used for analyses of total Kjeldähl nitrogen (TKN) (APHA, 2002) and total phosphorus (Andersen, 1976), as described by Pompêo and Moschini-Carlos (2003). Sequential chemical extraction was used to obtain the different P fractions: organic and inorganic, bioavailable P, NaOH-extractable P (P bound to Al, Fe and Mn oxides and hydroxides) and HCl-extractable P (P associated with Ca) (Ruban et al., 2001). The same procedures were applied to the surface sediments (except analysis of the P fractions).

Pigment analyses (core 3)

Photosynthetic pigments were analysed following the recommendations of Airs et al. (2001) and Squier et al. (2002), as described by Soares-Silva et al. (2020). About 1 g of the fresh sediment was sonicated together with 10 mL of acetone (100%) for 10 min at 25 W, followed by centrifugation for 5 min at 2000 rpm. The supernatant was filtered (0.45-µm syringe filter, Merck) and transferred to 1.5-mL vials for HPLC analysis. The HPLC analyses employed a C18 column (250 × 4.6 mm, 5 µm) and an ultraviolet detector (Soares-Silva et al., 2020). The eluent flow rate was 1 mL min^{-1} and the injection volume was 100 µL. The mobile phases were as follows: (phase A) 80:20 methanol:0.5 M ammonium acetate, at pH 7.2; (phase B) 90:10 acetonitrile:water and (phase C) ethyl acetate (Chen et al., 2001). The total analysis time was 20 min (Soares-Silva et al., 2020). Determination was made of the concentrations of chlorophyll-a and β-carotene, which are indicators of algal biomass (Wright, 2005; Borghini et al., 2007; Makri et al., 2019), and fucoxanthin, lutein and zeaxanthin, which are pigments characteristic of diatoms, chlorophytes and cyanobacteria, respectively (Wright, 2005; Reuss et al., 2005; Buchaca et al., 2019). The last two groups of organisms are favoured during the eutrophication process. Standard pigments for chlorophyll-a, β-carotene, lutein, zeaxanthin and fucoxanthin, were purchased from Sigma-Aldrich Company. Pigment identification was determined by comparison with retention times of the standards.

Water analysis

The water samples were filtered (AP40, Millipore) within 24 h after sampling. The filters were used for the determination of chlorophyll-*a* and photopigments (Lorenzen, 1967). The total phosphorus concentration was determined using unfiltered samples (Valderrama, 1981). The trophic state index (TSI) was calculated based on the TSI of Carlson (1977), adapted for tropical aquatic ecosystems by Lamparelli (2004). Transparency was not used in the TSI calculation, because the water bodies in São Paulo State are affected by high turbidity, caused by high levels of suspended particulate matter derived from the predominant clay soils in the region.

Data analysis

Enrichment factors

The metal concentrations were used to obtain enrichment factors (*EF*s), calculated as follows:

$$EF = \frac{M}{El}/(\frac{Mr}{Elr}) \quad (1)$$

where *M/El* is the ratio between the concentrations of the analysed metal and the conservative element in the sample, and *Mr/Elr* is the ratio of the background values for the metal analysed and the conservative element. Al was used as a conservative element, as recommended by Förstner and Wittmann (1981) and Luoma and Rainbow (2008). The *EF* classifications were as follows (Sutherland, 2000): (a) $EF < 2$ (absent/very low); (b) $2 \leq EF < 5$ (moderate); (c) $5 \leq EF < 20$ (considerable); (d) $20 \leq EF < 40$ (high) and (e) $EF > 40$ (very high).

Flux calculation

The rates of accumulation of the metals and nutrients in the cores were calculated as follows (Cochran et al., 1998; Cardoso-Silva et al., 2018):

$$Fx = Rx\rho xCx \quad (2)$$

where *Fx* is the species accumulation rate for the *x*th depth interval (mg cm^{-1} $year^{-1}$); *Rx* is the ^{210}Pb-derived sedimentation rate for the *x*th interval (cm $year^{-1}$); ρx is the dry bulk density of the *x*th interval (g cm^{-3}) and *Cx* is the species concentration for the *x*th interval (mg g^{-1}). The use of accumulation rates is more appropriate than simply reporting the concentrations of nutrients or other species, because such concentrations are determined by the accumulation of the nutrient/species of interest, relative to the accumulation of other sediment components (Cardoso-Silva et al., 2018).

Molar ratios

Molar ratios were employed to reconstruct past environmental information concerning the oxi-reduction potential, using the Mn/Fe ratio (Mackereth, 1966) and the Cu/Zn ratio (Vaalgamaa, 2004). As described by Cardoso-Silva et al. (2018), under oxic conditions, Fe and Mn are highly insoluble (Mackereth, 1966), while under anoxic and reducing conditions, 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 the mobilities of these elements are associated with the reducing potential of the environment (Mackereth, 1966; Boyle, 2001; Smol, 2008). Analogous to Fe and Mn, Zn and Cu also compose a pair of elements that occur in the reduced form in solution at different threshold oxi-redox levels (Vaalgamaa, 2004).

Statistical analysis

Basic descriptive and multivariate statistical analyses were performed for the entire dataset. Before statistical analysis, the data were standardized using the amplitude of variation method $[(x-x_{min})/(x_{max}-x_{min})]$ (Legendre and Legendre, 1998). Relationships between the chemical and physical variables were firstly evaluated using Spearman correlations. Principal component analysis (PCA) was used for data ordination (Legendre and Legendre, 1998). A cluster analysis was performed with the two main PC axes to identify the formation of groups. The Kruskal–Wallis (KW) test was applied for each parameter, in the two main groups (period 1967–1993 and 1993–2015), according to the cluster analysis. The KW test was used to evaluate significant differences between the periods ($p < 0.05$, df = 1). The calculations were performed using PAST 2.7 software (Hammer et al., 2001).

Results

Reservoir general characteristics: water and surface sediments

The levels of metals and nutrients in the surface sediments differed significantly among the sampled areas (Kruskal–Wallis test, $p < 0.05$), with the dam area presenting the highest levels of Fe and TN. Despite the differences, no site was considered contaminated by metals, with $EF < 2$ (Table 1). Likewise, the levels of TN and TP (Table 1) were below the maximum limits established for uncontaminated sediments, with values of 4.8 and 2.0 mg/g, respectively (Persaud et al., 1993). The water column was stratified, with DO concentrations of up to 0.5 mg/L in the hypolimnion. Values for depth, TN, TP and Chl-a were 8.9 m, 2.9 mg/L, 11.19 µg/L and 7.64 µg/L respectively in ATIR; 19.1 m, 1.4 mg/L, 10.36 µg/L and 5.51 µg/L respectively in ATID and 17.0 m, 0.8 mg/L, 2.8 µg/L and 2.17 µg/L respectively in ATIC. All the sampled areas were classified as mesotrophic.

Geochronology, sedimentation rate, metals and oxidation–reduction potential (core 1)

The sediment profiles had a brownish colour, with no visible signs of stratification. The ^{210}Pb geochronological analyses revealed episodes of dilution of unsupported ^{210}Pb, which could be causally related to sedimentation rate increases (Fig. 2). The highest SR values were observed for the uppermost layers, in the years 2012 and 2015 (0.48 cm/year) (Table 2).

The metal concentrations showed no significant changes over time, remaining close to background, as reported by Cardoso-Silva et al. (2021). *EF* values < 2 were indicative of geogenic sources of the metals (Table 2). Figure 3 shows the metal fluxes for the sediment profiles. The Fe/Mn and Cu/Zn molar ratios were used to indicate the oxi-reduction potential (Fig. 4). The increase in Fe/Mn molar ratios and the decrease in Mn levels since 1993 suggested the existence of anoxic conditions, which was further supported by the changes in the Cu/Zn ratios since the 1990s.

Organic matter and nutrients (core 2)

The reservoir could be classified as organic (Ungmack, 1960), since OM exceeded 10% (18.26 ± 2.22%, Table 2), with the Corg distribution profile shown in Fig. 5. The TP concentrations (0.97 ± 0.16 mg/g) decreased over time (Figs. 5A and B), although the changes were not significant (coefficient of variation of 17.07%, Table 2). The P linked to Fe, Mn and Al (bioavailable P) was the predominant fraction, accounting for 81.21 ± 5.14% (Fig. 6). There was a predominance of inorganic fractions (59.64 ± 2.85%), with a slight decrease in the period associated with the beginning of reservoir operation (47.29%), probably due to the decomposition of OM in the flooded area (Fig. 6). The total nitrogen contents, on the other hand, showed a more pronounced increasing profile, with a slight decrease in the surface layer and a coefficient of variation of 62.9% (Fig. 5A and B, Table 2). Considering the Redfield ratio (C:N:P = 106:16:1), a mean value of 113.07:1 for the Corg/P ratio indicated that the sediment was not polluted by phosphorus.

Pigments (core 3)

There were increases in the levels of lutein and zeaxanthin, which are pigments associated with the Chlorophyta and cyanobacteria groups, respectively (Fig. 5C and D), especially from the 1990s onwards. The concentrations of chlorophyll-a and β-carotene, which are indicators of algal biomass, and fucoxanthin, a pigment characteristic of the diatoms group, showed significant coefficients of variation over time (63.38, 31.98 and 84.77%, respectively). No clear increases of Chl-a were observed. The highest Chl-a, β-carotene and fucoxanthin values were found for the period

Table 1 Descriptive statistics for variables in surface sediments from three areas of the Atibainha reservoir. *SD*, standard deviation; *BG*, background (Cardoso-Silva et al., 2021); *EF*, mean enrichment factor; *CV*, coefficient of variation; *OM*, organic matter

	Unit	ATIR		ATIC		ATID		Reservoir			BG	*EF*
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	CV		
Al	g/kg	44.71	0.81	52.25	0.67	40.98	0.92	45.98	5.02	10.91	44.7	1.00
Fe	g/kg	34.86	0.53	45.20	0.86	53.84	2.65	44.63	8.35	18.71	71.8	0.60
Cu	mg/kg	14.66	0.35	25.80	1.02	24.91	4.19	21.79	5.78	26.52	23.1	0.92
Cr	mg/kg	44.20	0.51	43.51	0.50	30.66	0.62	39.46	6.62	16.79	32.3	1.19
Ni	mg/kg	12.87	0.58	10.49	0.27	8.79	0.36	10.72	1.81	16.93	10.6	0.98
Zn	mg/kg	66.15	0.75	42.48	0.65	39.47	0.64	49.37	12.67	25.66	50.6	0.95
Mn	mg/kg	770.44	45.40	162.58	14.37	231.02	29.30	388.01	289.70	74.66	289.8	1.30
TP	mg/g	0.38	0.01	0.36	0.08	0.37	0.00	0.37	0.05	12.50	–	–
TN	mg/g	1.16	0.37	1.72	1.41	3.16	0.72	1.87	1.17	62.88	–	–
OM	%	11.21	0.68	16.92	2.04	13.99	0.33	11.21	0.68	16.92	–	–

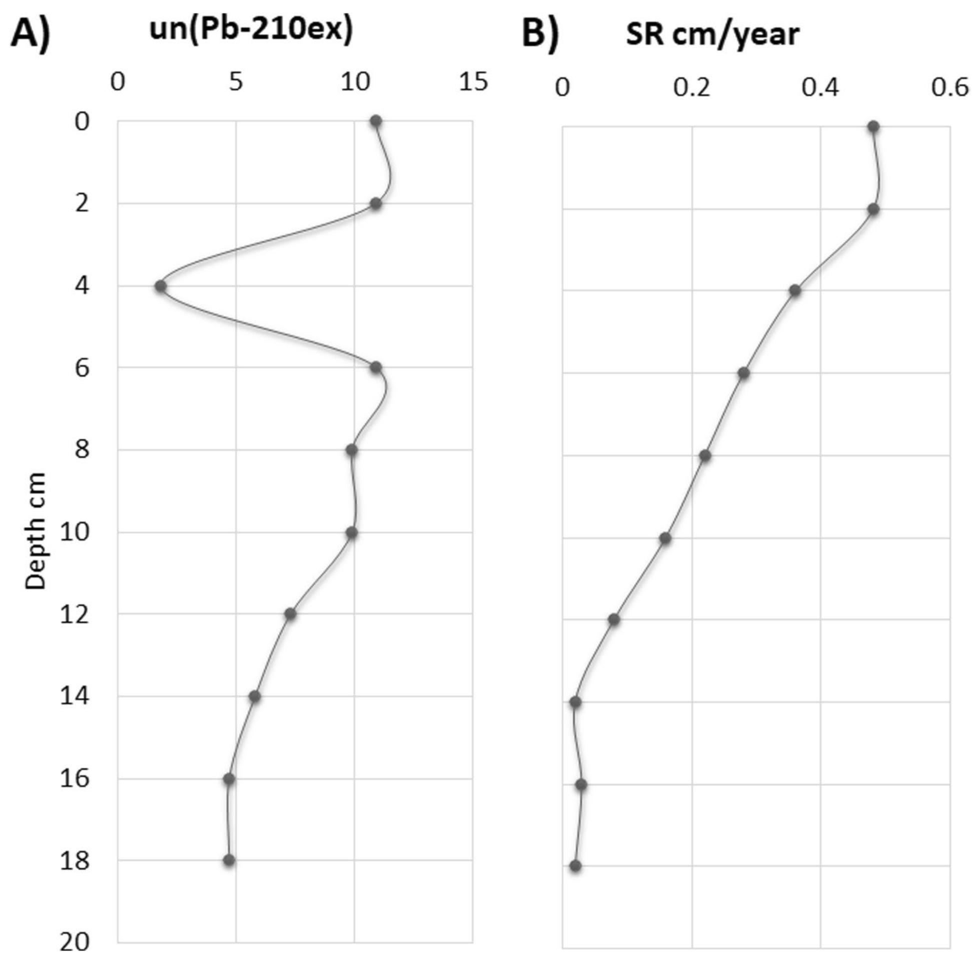

Fig. 2 Vertical profiles of unsupported ^{210}Pb (**A**) and vertical sedimentation rate (SR) profiles (**B**) for sediment cores at Atibainha dam area

Table 2 Descriptive statistics for parameters in the sediment cores from the Atibainha reservoir. *BG*, background (Cardoso-Silva et al., under review); *EF*, enrichment factors for metals, where $EF > 2$ indicates geological origin or minor impact (Sutherland, 2000); *SD*, standard deviation; *CV*, coefficient of variation; *SR*, sedimentation rate; *TP*, total phosphorus; *TN*, total nitrogen; *P-Mn*, bioavailable P; *OM*, organic matter; *Chl-a*, chlorophyll-a; *Lut*, lutein; *Zea*, zeaxanthin; *Fuc*, fucoxanthin; *Bet*, β-carotene

	Unit	Range		Mean	SD	CV	BG	*EF*
Al	g/kg	10.87	48.13	36.00	15.50	42.99	44.7	–
Cr	mg/kg	6.77	35.6	25.87	11.86	45.83	32.3	0.95 ± 0.06
Cu	mg/kg	2.42	28.84	19.34	10.56	54.60	23.1	0.90 ± 0.26
Fe	g/kg	8.56	58.21	41.58	20.72	49.83	71.8	–
Mn	mg/kg	18.88	310.91	192.79	117.92	61.16	289.8	0.46 ± 0.74
Ni	mg/kg	1.27	10.42	7.53	3.69	49.06	10.6	0.87 ± 0.15
Zn	mg/kg	15.94	54.73	38.10	13.80	36.2	50.6	0.97 ± 0.16
SR	cm/year	0.02	0.48	0.33	0.13	40.5	–	–
TP	mg/g	0.72	1.20	0.97	0.16	17.07	–	–
TN	mg/g	0.52	3.13	1.90	1.19	62.90	–	–
P-Mn	%	75.53	88.55	81.21	5.41	6.60	–	–
Corg	mg/g	0.26	0.36	0.28	0.03	11.29	–	–
OM	%	16.52	23.44	18.26	2.22	12.15	–	–
C/P	–	7.82	12.00	9.29	1.44	15.45	–	–
Fe/Mn	–	135.64	241.33	200.07	34.48	17.24	–	–
Chl-a	μg/g OM	4.92	32.31	14.68	9.16	62.38	–	–
Lut	μg/g OM	7.80	136.15	72.56	53.10	73.19	–	–
Zea	μg/g OM	6.10	102.30	60.51	41.90	69.24	–	–
Fuc	μg/g OM	1.96	26.98	11.09	9.40	84.77	–	–
Bet	μg/g OM	2.41	41.37	11.36	15.00	131.98	–	–

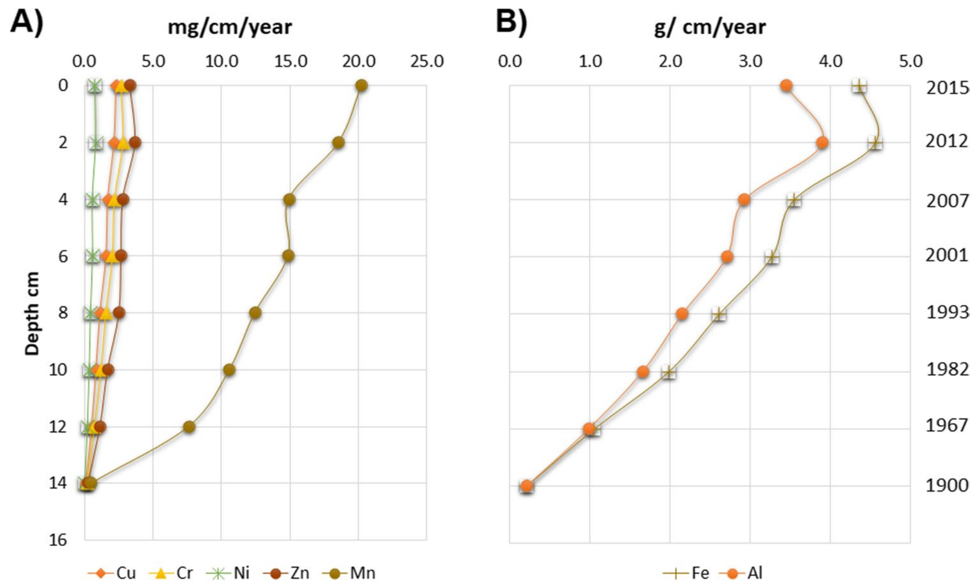

Fig. 3 Metal flux in a dam core at Atibainha reservoir

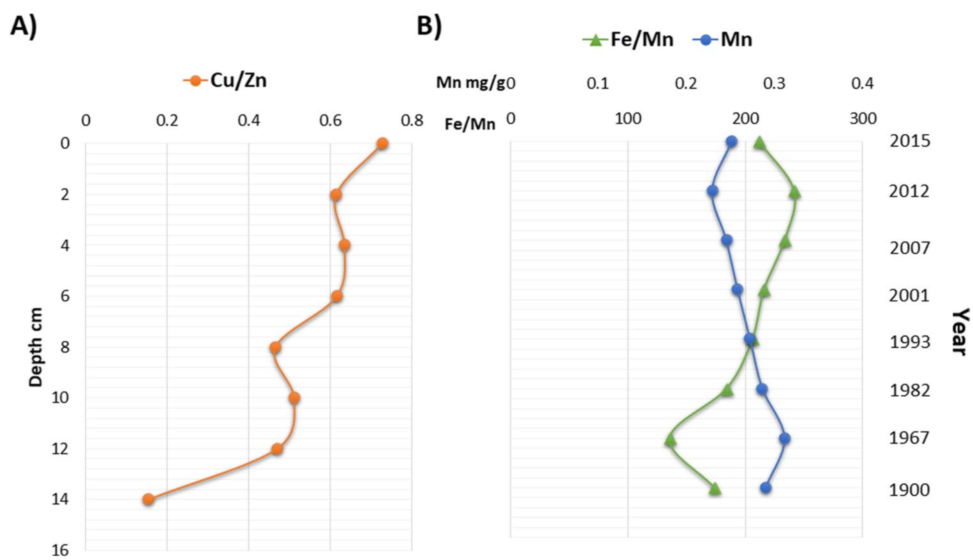

Fig. 4 Vertical profiles of Molar ratios for Fe/Mn and Cu/Zn for sediment cores at Atibainha reservoir

from 2001 onwards (Table 2; Fig. 5C and D). The lower levels of Chl-a and β-carotene, compared to the other carotenoids, could be explained by the different degradation rates of the pigments.

Correlations

Significant Spearman correlations ($p < 0.05$) were observed, especially between variables directly and indirectly associated with the eutrophication process. Lutein, zeaxanthin and fucoxanthin were negatively correlated with TP ($r = -0.57, -0.64$ and -0.69, respectively) and the bioavailable P fraction ($r = -0.87, -0.87$ and -0.57), while positive correlations were obtained with SR ($r = 0.89$, 0.87 and 0.89). The pigments were also positively correlated with TN ($r = 0.69$ for all the pigments) and the population increase ($r = 0.80$ for zeaxanthin and fucoxanthin). Correlation between TN and organic matter ($r = -0.71$) could be explained by the decomposition of organic compounds during diagenesis and nitrogen release during the process.

The positive correlations between SR and the pigments TN ($r = 0.79$), population increase ($r = 0.63$) and the concentration of Al ($r = 0.68$), a constituent element of silt–clay particles, suggested the existence of both eutrophication and erosion processes. Correlations were also observed between the pigments and metals essential to phytoplankton metabolism: Cu and fucoxanthin ($r = 0.76$), zeaxanthin ($r = 0.98$) and lutein ($r = 0.91$), and Fe and lutein ($r = 0.55$), zeaxanthin ($r = 0.68$) and β-carotene ($r = 0.52$).

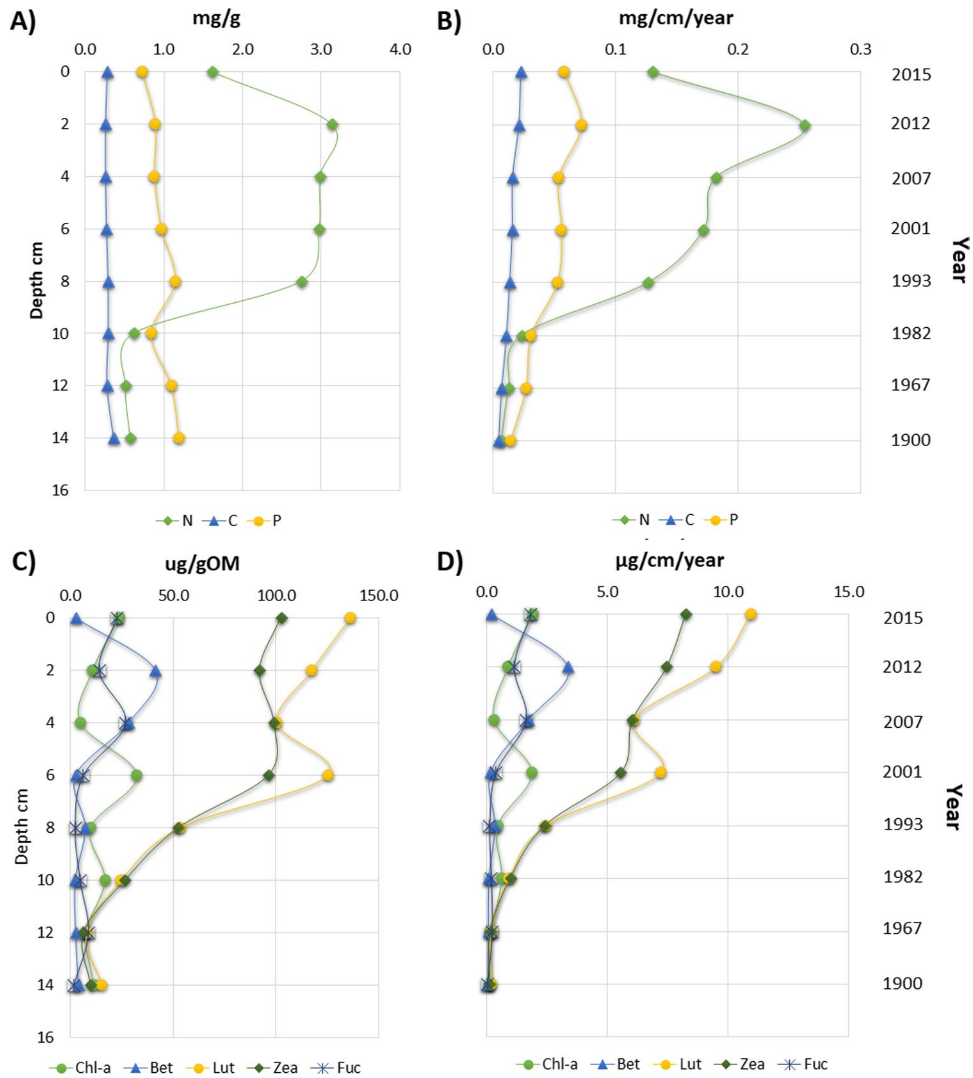

Fig. 5 Concentrations of phosphorus and nitrogen (**A**) and fossil pigments (**C**) and the flux for nutrients (**B**) and sedimentary pigments (**D**) in a dam core at Atibainha reservoir

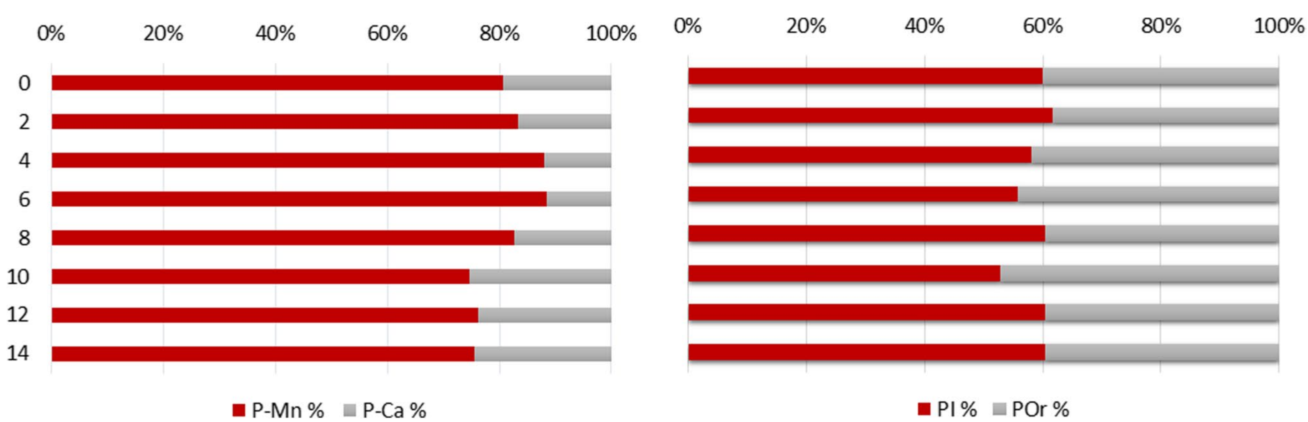

Fig. 6 Sequential chemical extraction of P: (a) the bioavailable P, NaOH-extractable P (P bound to Al, Fe and Mn oxides and hydroxides) and HCl-extractable P (P associated with Ca) and (b) organic (POr) and inorganic (PI) fractions in a dam core at Atibainha reservoir

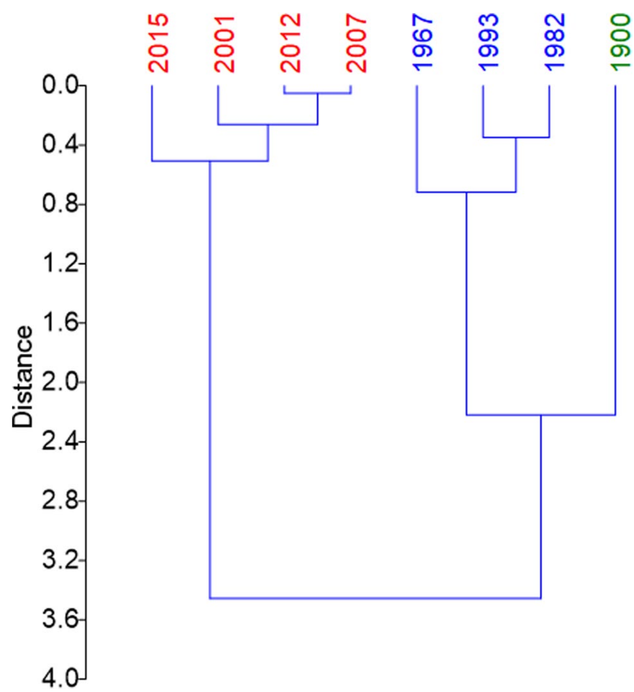

Fig. 7 Cluster analysis distribution (Ward's method, with Euclidean distances) based on the two main axis of a PCA of variables measured in the Atibainha reservoir core sediments

Principal component analysis, cluster analysis and Kruskal–Wallis test

The results of cluster analysis (Fig. 7) and PCA (Fig. 8), where PC1 explained 60.28% of the data variability and PC1 + PC2 explained 75.22% of the variability, revealed three main intervals, with and without significant anthropic impacts. Interval I, composed by the period prior to operation of the reservoir, was influenced by the levels of organic matter. Interval II, between 1967 and 1993 (PC2), was a period of minor impacts, mainly influenced by the variables Mn (0.71) and Zn (0.74), which are metals with geogenic origins ($EF < 2$). Interval III, from 1993 to 2015 (PC1), was mainly associated with the variables SR (0.91), TN (0.78) and the pigments lutein (0.86), zeaxanthin (0.90) and fucoxanthin (0.65) (Table 3), suggesting the intensification of eutrophication and erosion processes. The KW test, between the two main periods (II 1967–1993 and III 1993–2015) indicated significative differences for the variable: lutein, zeaxanthin, TP and P-Mn, variables associated with the eutrophication process and SR and Mn variables associated with the increase in erosion process as well, eutrophication.

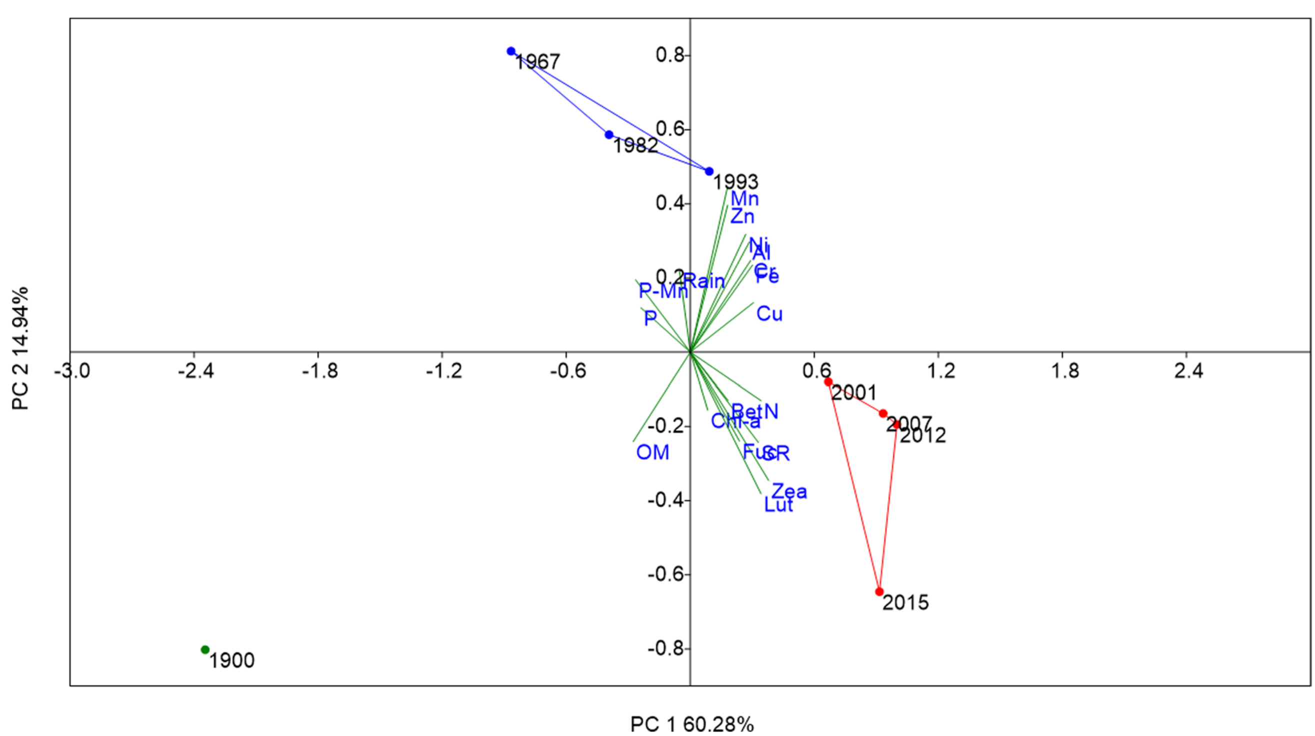

Fig. 8 PCA of variables measured in the Atibainha reservoir core sediments. The scores were related to the variables chlorophyll-a (Chl-a), lutein (Lut), zeaxanthin (Zea), fucoxanthin (Fuc), β-carotene (Bet), total nitrogen (TN), total phosphorus (TP), rain, bioavailable P (P-Mn), organic matter (OM), sedimentation rate (SR) and metals Al, Cr, Cu, Fe, Mn, Ni and Zn

Table 3 Loadings of the variables for the first two principal components obtained in the PCA analysis. *Chl-a*, chlorophyll-a; *Lut*, lutein; *Zea*, zeaxanthin; *Fuc*, fucoxanthin; *Bet*, β-carotene; *TN*, total nitrogen; *TP*, total phosphorus; *Rain*, rainfall; *P-Mn*, bioavailable P; *OM*, organic matter; *SR*, sedimentation rate

	Eigenvalues	
	PC1	PC2
SR	0.91	−0.33
Cu	0.97	0.21
Cr	0.92	0.39
Ni	0.85	0.50
Zn	0.65	0.71
Mn	0.60	0.74
Fe	0.92	0.36
Al	0.88	0.46
OM	−0.89	−0.39
TP	−0.71	0.18
TN	0.78	−0.15
Rain	−0.17	0.36
P-Mn	−0.84	0.31
Chl-a	0.26	−0.24
Lut	0.86	−0.47
Zea	0.90	−0.41
Fuc	0.65	−0.33
Bet	0.49	−0.17

Discussion

Historical trend in nutrients and sedimentary pigments

The analysis of the proxies TN, TP, pigments, molar ratios and SR in the core suggest changes in the dynamics of nutrient content and changes in the phytoplankton community composition probably associated with the eutrophication process. The increase in TN levels could be attributed to the greater contribution of this element resulting from population growth in the Atibainha reservoir basin (IBGE, 2020), leading to greater inputs of effluents in the watershed. Agricultural activities were not the main source of nutrients, because local farmers do not normally use mineral fertilizers (Ditt et al., 2010). The decrease in TN in the uppermost core sediments could be explained by denitrification, involving the decomposition of organic matter and the release of nitrogen in the gaseous form to the water column, which is facilitated in environments with low levels of dissolved oxygen.

The decreases in the levels of TP and its fractions, on the other hand, did not necessarily indicate a lower trophic state (Boyle, 2001; Antoniades, 2007; Smol, 2008; Dittrich et al., 2013). On the contrary, TP and the bioavailable fraction showed significant negative correlations with the pigments, suggesting the release of this element to the water column and a consequent increase in the trophic state. In general, under anoxic and reducing conditions, phosphorus adsorbed to iron oxyhydroxides in the sediment is released to the water column (Perkins and Underwood, 2001; Antoniades, 2007; Wetzel, 2001). Anoxic conditions in the hypolimnion are a common effect of eutrophication, due to the higher rates of productivity and organic sedimentation, with a consequent increase in organic matter decomposition (Antoniades, 2007). The hypolimnion of the reservoir studied currently has low concentrations of dissolved oxygen (0.54 mg/L), providing a favourable environment for the release of P. The Fe/Mn and Cu/Zn molar ratios corroborated the presence of anoxic conditions by indicating changes in the oxi-reduction potential, mainly from the 1990s onwards, favouring the release of P to the water column and consequently increasing phytoplankton proliferation.

The analysis of Chl-a alone did not provide clear evidence of eutrophication. Degradation of Chl-a generally occurs rapidly, so it is poorly preserved in sediment (Sanger, 1988), especially in tropical regions, where the higher temperatures and faster metabolism can hinder the preservation of pigments (Buchaca et al., 2019). Despite the degradation, we observed a slight increase from the 1990s, a subsequent decrease from the 2001 and another increase from the 2007 onwards. In the present work, a slight increase in algal biomass over time could only be better observed by the β-carotene concentrations. The levels of β-carotene are preserved over longer periods, so this pigment is more frequently selected as an indicator of changes in algal biomass (Buchaca and Catalan, 2007; Zhang et al., 2019; Buchaca et al., 2019).

Lutein and zeaxanthin were better preserved and indicated increases in Chlorophyta and cyanobacteria, both favoured in eutrophication process. Lutein is also present in aquatic macrophytes, and the presence of this pigment could be also originated from these water plants. Nowadays, Santos et al. (2018), using a phytoplankton functional groups analysis, observed that the Atibainha dam area showed the presence of groups tolerant to low light availability and high levels of turbidity, typical of eutrophic and mesotrophic environments, with the typical presence of *Synechocystis aquatilis*. Data collected in 2015 found that cyanobacteria including *Cylindrospermopsis* sp. were present at concentrations of over 56,000 cells/mL (CETESB, 2016; Rodrigues et al., 2019), exceeding the limit stipulated in the CONAMA 357/05 regulation (Brasil, 2005), which is 20,000 cells/mL for the Cantareira system reservoirs. Another Brazilian law, Consolidation Ordinance n° 5, of 16/11/2017 (Brasil, 2017), requires monthly water quality monitoring when the cyanobacteria number is below 10,000 cells/mL, while weekly monitoring is stipulated when cyanobacteria exceed 10,000 cells/mL. When cyanobacteria exceed 20,000 cells/mL, analysis of cyanotoxins should be performed, due to the toxic potential of these organisms. These data show the degradation of the Atibainha reservoir and the importance of regular monitoring in the region.

Zeaxanthin pigments are chemically stable (Rolland and Vincent, 2014; Ramírez-Ortega et al., 2019), while fucoxanthin usually degrades faster than Chl-a (Itoh et al., 2003; Rabalais et al., 2004), so its absence does not necessarily mean that diatoms are not present in the water column. However, here increasing levels of fucoxanthin were observed, which were even higher than Chl-a levels, especially during the 1990s. It is possible that the existence of anoxic conditions in the hypolimnion could have favoured its preservation, as observed in other paleolimnological studies (Züllig, 1981; Rabalais et al., 2004).

The significant positive correlations between the pigments and the metals could be explained by the essential roles of these metals in phytoplankton metabolism. Cu and Fe act as cofactors or parts of cofactors in enzymes and are structural elements in proteins (Morel and Price, 2003; Devesa-Rey et al., 2009), so they can act as prime limiting elements for algal growth. In addition, the significant correlations between SR and the variables TN and phytoplankton carotenoids provided further evidence of the influence of eutrophication in increasing SR. The influence of eutrophication on SR in lakes and reservoirs has been reported in several studies (Fávaro et al., 2007; Rose et al., 2010; Zhang et al., 2016; Anjum et al., 2018; Cardoso-Silva et al., 2021) and this phenomenon has increased in the reservoirs of São Paulo State, especially since the 1960s (Fávaro et al., 2007; Cardoso-Silva et al., 2021). We can observe therefore that although the N levels increased over time the P concentrations in the evaluated area did not to reflect the contributions of this element in the eutrophication process. Eutrophication was suggested only when both, nutrients, and pigments, as well as SR were analysed together. Also, metal flows did not indicate significative enrichment associated to anthropic activities.

Increases in sedimentation rates

Besides the influence of eutrophication, the increase in SR could have been related to a series of other factors. In the early 1980s, it was possibly associated with the inclusion of the Jaguari and Jacareí reservoirs in the Cantareira system, when the flow rate of the system increased by 22 m^3/s. The subsequent increases may have been linked to the population growth in the Cantareira system watersheds, with significant correlations observed between these two variables. An important point is that anthropic activities can accelerate erosion processes. In 2016, anthropic uses corresponded to 81.80% of the Cantareira system watersheds (Vieira and Vieira, 2016), which was an increase of 12.4%, compared to 2003 (Whately and Cunha, 2007). Furthermore, the stripping of the Atlantic rainforest in the Atibainha watershed (15.2% during the period 1989–2003) (Whately and Cunha, 2007) may have led to the intensification of sedimentation due to weathering. Also, the growing urban development of residential and recreation centres around the reservoir registered in 2013 can imply in the intensification of erosion process as well as changes in several other process, such as runoff, infiltration and groundwater recharge, and biotic conditions (Andrade et al., 2015).

Ditt et al. (2010) made predictions of the possible outcomes in 2039, in the Atibainha watershed, considering different scenarios related to the maximum expansion of each of the four main land uses: native forest, eucalyptus, pasture and urban area/bare soil. The authors concluded that delivery of sediment to the reservoir would be 9 tons/year if the entire study area was occupied by native forests, 1500 tons/year if occupied by pasture and 36 tons/year if occupied by eucalyptus. For the current land use scenario, the estimated sediment delivery is 1037 tons/year, with restoration of native forest in the study area having the potential to mitigate up to 500 tons/year of sediment. It should be noted that the degree of urbanization in the municipality of Nazaré Paulista was estimated at 87% in 2015, with an increase to 95% expected by 2035, which is likely to intensify discharges of effluents, if sewage collection and treatment are not improved. Consequently, both erosion and eutrophication processes may be exacerbated in the near future. Our data indicated, therefore, increases in SR which were mainly related to anthropic activities.

Conclusions

Despite the limitations associated with the application of paleolimnological techniques to reservoirs, as well as drawbacks in the use of pigments as proxies in regions with higher temperatures, the results of the present work demonstrated that it was possible to perform the reconstruction of impacts for a subtropical mesotrophic reservoir, used as a model system. The anoxic conditions and the aphotic environment allowed the preservation of carotenoid pigments associated with Chlorophyta (lutein), cyanobacteria (zeaxanthin) and Bacillariophyta (fucoxanthin). The use of isolated algal biomass indicators is not recommended, since high rates of degradation may lead to inaccurate interpretation of earlier conditions. It is important to highlight that in oligotrophic reservoirs, under oxic conditions and/or with the presence of light in the hypolimnion, the degradation of pigments can be more intense, so the absence of pigments (or their presence at low levels) does not necessarily imply the absence of a particular phytoplankton group. Therefore, due caution is required in the use of sediment pigments as proxies to reconstruct past environmental changes.

Recent monitoring (started in 2014) has suggested a mesotrophic state of the Atibainha reservoir, while the present results indicate the intensification of eutrophication and erosion processes since the 1990s. Anthropic impacts were suggested only when a multiproxy approach was adopted, nutrients concentrations were not sufficient to predict eutrophication and a biotic was fundamental to observe such environmental changes. Increases in SR were related both to changes in the drainage basin, which led to an increase in erosive processes, and to an increase in the eutrophication process. This study shows the potential of applying paleolimnological techniques to subtropical reservoirs, providing information that can inform appropriate implementation of recovery, restoration and preservation measures.

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Author contribution All authors contributed to the study conception and design as follows: Sheila Cardoso-Silva: conceptualization, writing original draft, formal analysis, investigation. Juliana Oliveira Soares Silva Mizael: formal analysis, investigation, writing review, editing. Daniele Frascareli: formal analysis, investigation, writing review. Rubens César Lopes Figueira: formal analysis, writing review. Eduardo Vicente: formal analysis. Marcelo Pompêo: supervision, funding acquisition, project administration. Viviane Moschini-Carlos: supervision, funding acquisition, project administration. All authors commented, read and approved the final manuscript.

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Data Availability All data generated or analysed during this study are included in this published article and its supplementary information files.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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