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ORIGINAL PAPER

The eutrophication history of a tropical water supply reservoir in Brazil

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Abstract Guarapiranga Reservoir is the second most important public water supply in São Paulo, Brazil and has been eutrophic for several decades. We inferred the major ecological shifts for the period 1919–2010 related to multiple stressors (forest flooding, hydrological change, use of algicide and eutrophication), using geochemistry (TOC, TN, TP, C/N, δ^{15}N, δ^{13}C) and diatom assemblages in a short (75-cm) sediment core. Thirty-two diatom species were abundant in the core and stratigraphically constrained incremental sum of squares analysis enabled identification of three diatom zones and four subzones, i.e. depths at which marked changes in species composition occurred. Early diatom assemblages were dominated by benthic, oligotrophic taxa, mainly *Eunotia*, influenced by flooded vegetation after dam construction. A shift to dominance by a planktonic species (*Eunotia tukanorum*) occurred ca. 1932, during the period of initial physical disturbance and early use of the water body as a public water supply. Diatoms and geochemical variables show that the reservoir was oligotrophic from ~1919 to 1947. Eutrophication began ~1975 and by the early 1980s the reservoir had become eutrophic, in response to an explosive increase in human population in the watershed. Severe cultural eutrophication has persisted since ~1990. Higher concentrations of copper in the sediments, beginning in 1991, reflect the increased use of copper sulfate to

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control cyanobacteria blooms and provide a chronological marker. Higher $\delta^{15}N$ values in recent sediments indicate greater sewage inputs and low C/N values reflect the predominant contribution of algae to sediment organic matter. Eutrophic taxa *Cyclotella meneghiniana* and *Nitzschia* sp. dominate recent diatom assemblages, along with *Aulacoseira granulata*, a species that is tolerant of copper sulfate. Diatom assemblages reflect multiple stressors, however, geochemical information provides a better understanding of the early phase of the reservoir. Paleolimnologically documented trophic state changes in this important drinking water supply are largely attributable to increased urbanization of the drainage basin and inputs of sewage. Management efforts should focus on mitigating this nutrient source.

Keywords Diatoms · Eutrophication · Geochemistry · Guarapiranga reservoir · Land-use change · Multiple stressors

Introduction

Reservoirs in densely populated, industrialized regions receive discharges of nutrients, organic compounds and heavy metals that impair water quality and threaten aquatic biota and human health (Ishii and Sadowsky 2008). Guarapiranga Reservoir, São Paulo, Brazil, was constructed in 1909 and is the second most important public water supply reservoir in the city, supplying two million people in one of the world's largest urban areas. This reservoir has experienced a pronounced decline in water quality, from excessive nutrient inputs delivered in untreated sewage effluent (Whately and Cunha 2006), pollution by metals (Moura and Sígolo 2002), unplanned land development, physical disturbances and other human impacts (Whately and Cunha 2006).

The agency in charge of the public water supply in São Paulo State began regular monitoring of the reservoir in 1970, long after intensification of anthropogenic impacts in the drainage basin. Pre-disturbance water quality conditions were therefore unknown. To set realistic restoration goals, it is important to identify the causes, timing and extent of water quality deterioration (Smol and Cumming 2000). For this purpose, long-term monitoring data are essential, though rarely available (Battarbee et al. 2005). Paleolimnological approaches have been used successfully to infer pre-impact limnological conditions as well as post-disturbance trajectories of environmental change (Battarbee and Bennion 2011; Liu et al. 2012).

Diatoms are one of the most widely used biological indicator groups in paleolimnological studies, particularly for investigation of past trophic state (Bennion et al. 2004; Costa-Böddeker et al. 2012). The diatom record is a useful tool for assessing water quality and defining pre-disturbance chemical and ecological conditions in water bodies (Räsänen et al. 2006). There have been, however, few paleolimnological studies in reservoirs used to supply drinking water (Shotbolt et al. 2001; Liu et al. 2012). In Brazil there has been only one paleolimnological study of a shallow tropical urban reservoir (Costa-Böddeker et al. 2012). The study reported here is the first contribution on a large public water supply reservoir in South America.

We documented the eutrophication history of the second most important public water supply reservoir in São Paulo, southeast Brazil. We used geochemistry, stable isotopes and diatom assemblages in a 75-cm sediment core to infer when the main shifts in trophic state occurred over a period of ~91 years (1919–2010) and to define pre-eutrophic conditions in this system. This study also contributes to the understanding of how multiple stressors (hydrologic changes, eutrophication, and heavy metal contamination) influence diatom communities. The Guarapiranga study is the first to investigate: (1) initial water quality conditions following reservoir construction and flooding of a large area of Atlantic forest, (2) the ontogeny of a reservoir under changing hydrological/physical conditions, (3) trophic state shifts associated with rapid population growth in the watershed, and (4) impacts on the system from copper sulfate applications for control of cyanobacterial blooms. This is the first paleolimnological study in a large public water supply reservoir in South America, which lies in one of the most densely populated cities worldwide. Considering that most of the rivers (70 %) in Brazil have been dammed (Kelman et al. 2002), the paleolimnological data and interpretation in this work will be useful for agencies that must formulate plans to manage this and other reservoirs in Brazil. Most such water bodies lack historical documentary information and long-term monitoring studies. Moreover this study provides valuable information to better understand limnological changes in tropical reservoirs, particularly those susceptible to urbanization pressure.

Study site

Guarapiranga Reservoir is located in the metropolitan area of São Paulo city, in São Paulo State, southeast Brazil (23°41′S, 46°43′W) at an altitude of 737 m asl (Fig. 1). The reservoir has an area of 36.18 km^2, a mean depth of 7 m and a water volume of 253×10^6 m^3 (Mozeto et al. 2001). It was built in 1909 for energy production, and dam construction flooded a large portion of Atlantic forest (Whately and Cunha 2006). In 1927 the city of São Paulo began to use the reservoir as a public water supply (Whately and Cunha 2006). Today, the reservoir is the second major water source for the city, supplying about two million people, i.e. 25 % of the population. About 1970, the population in the drainage basin increased rapidly. Much of the new housing was sub-standard and untreated sewage from these developments was discharged to the reservoir (Whately and Cunha 2006). Monitoring of the reservoir was initiated at that time. By 1980, cyanobacterial blooms were very common and studies in the 1990s concluded the reservoir was eutrophic to hyper-eutrophic (Beyruth 2000). Since 1991, the agency in charge of the public water supply has intensified the use of copper sulfate to control increasing cyanobacterial blooms (Beyruth 2000). Nevertheless, the reservoir continues to receive untreated sewage from the drainage basin.

Materials and methods

Core collection and sampling

Refraction seismology, using a Stratabox™ 3510 (Ocean Data Equipment Corporation, Providence, Rhode Island), was used to identify the best core sampling location in the reservoir. The northern area of the basin, close to the dam, is the deepest point in the reservoir and has been affected by human activities. It was therefore selected for sampling (Fig. 1). Divers collected a 75-cm core (GUA10-01) in February 2010, using an acrylic tube that was 15 cm in diameter and 100 cm long. The lithology (color and texture) was described using the Munsell Color (1975) scheme. The core was sectioned in the field at 1-cm intervals for chemical (TOC, TN, TP), isotopic (δ^{15}N, δ^{13}C), physical (grain size, dry mass, water content) and diatom analyses. Percent dry mass and water content were determined immediately after sampling the core by weighing sub-samples, drying them at 45–50 °C, and re-weighing.

Core chronology

The core chronology was determined by ^{210}Pb dating. The total ^{210}Po activity ($\alpha = 5.31$ MeV, $t_{1/2} = 138$ d) in samples was measured by alpha spectrometry, according to Flynn (1968). The ^{210}Po activity was assumed to be in secular equilibrium with ^{210}Pb activity. Supported ^{210}Pb activity was estimated from ^{226}Ra activity, which was found from ^{234}U activity measured by alpha spectrometry. We measured homogenized portions of 1-g dry samples, taken at 10 depths (5, 10, 20, 26, 34, 40, 48, 52, 64 and 72 cm) in core GUA10-01. Excess ^{210}Pb was calculated as total ^{210}Pb activity minus supported ^{210}Pb activity. The CIC (Constant Initial Concentration) model was used to calculate sedimentation rates by linear regression between excess ln ^{210}Pb activity and core depth (Appleby and Oldfield 1978), with an estimated error of 5 %. Documentary information, in the form of maps and library archives on activities in the basin, was collected to complement the radioisotope-based chronology.

Sediment chemistry

Total phosphorus (TP) and copper (Cu) were analyzed by multi-element ICP-OES (inductively coupled plasma-optical emission spectroscopy). Grain size analysis was performed using a CILAS Automatic Analyzer and the result was calculated by GRADSTAT software (Blott and Pye 2001). Total organic carbon (TOC), total nitrogen (TN) and their stable isotopes (δ^{13}C, δ^{15}N) were analyzed using an ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) at the University of California, Davis, Stable Isotope Facility. N_2 and CO_2 were separated using a molecular sieve adsorption trap before entering the IRMS. Values for stable isotope data are expressed relative to international standards V-PDB (Vienna PeeDee Belemnite) and air, for carbon and nitrogen, respectively.

Diatoms

Diatom samples were prepared using a modification of the method described by Battarbee (1986). Weighed

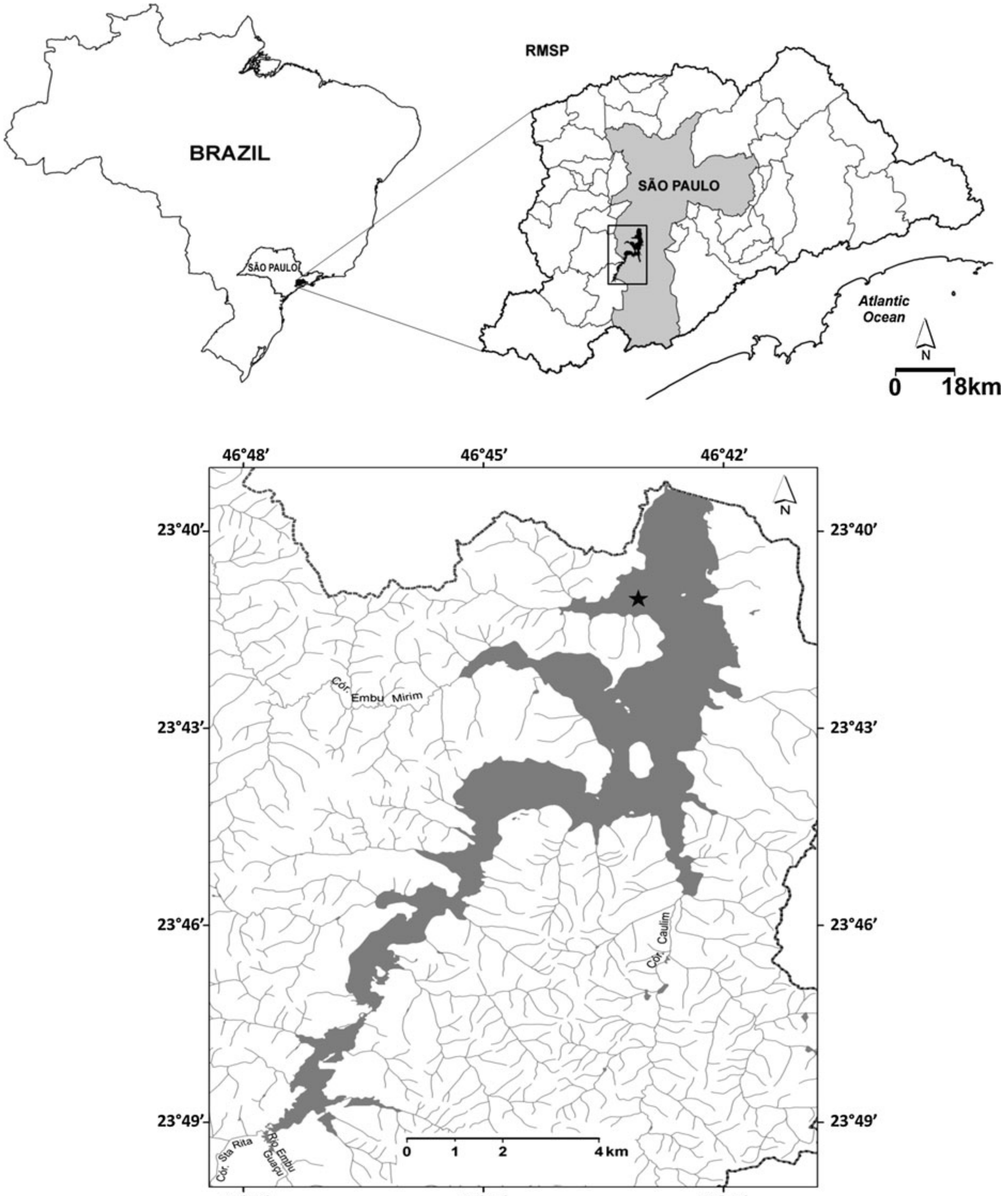

Fig. 1 **a** Map showing the location of the state of São Paulo in Brazil, **b** map of the city of São Paulo metropolitan urban region (RMSP) and municipality, showing the location of Guarapiranga Reservoir, and **c** enlarged map of the Guarapiranga Reservoir showing the site where core GUA10-01 was collected

aliquots of dry sediment were heated to boiling (~100 °C) in 30 % H_2O_2 for 30 min. Concentrated HNO_3 was then added to remove organic material, resulting in a rapid reaction. After the oxidation reaction was complete, the material was washed several times with distilled water, by settling and decantation to remove acid and oxidation by-products. Permanent slides were prepared using Naphrax (refractive index 1.73). Counts were made at 1,000× magnification, using a Zeiss® Microscope (Axioskop 2 *plus* Type) with an oil-immersion objective. At least 500 valves were counted per slide (sub-sample) according to Battarbee et al. (2001). Species abundances were calculated as percentages of the total counts. Taxonomy and nomenclature followed classic works and new publications (e.g. Round et al. 1990; Rumrich et al. 2000; Metzeltin and Lange-Bertalot 2007), and the on-line catalogue of valid diatom names (Site of California Academy of Sciences 2012). Diatom names were coded according to the OMNIDIA® software (Lecointe et al. 1993). Diatoms were assigned to habitat categories (benthic or planktonic) based on literature sources (van Dam et al. 1994; Moro and Fürstenberg 1997).

Data analysis

Major stratigraphic changes in sediment chemistry were identified using the C2 program, version 1.3 (Juggins 2003). The C/N ratio and stable isotope composition ($\delta^{13}C$, $\delta^{15}N$) were used to characterize the main changes in organic matter, and serve as evidence for when eutrophication began in the reservoir.

The diatom relative abundance diagram was produced using TILIAGRAPH 1.7.16 (Grimm 1991), and the main phases in the diatom assemblages were identified by stratigraphically constrained incremental sum of squares (CONISS). Thirty-two species with relative abundances ≥5 % were used. Rare species (<5 %) were removed prior to analysis, as they were considered not to be representative of ecological shifts in the reservoir. Major shifts in the diatom assemblages were also analyzed using non-metric multidimensional scaling (NMDS) with Bray-Curtis distance for abundant species (≥5 %). NMDS analysis is based on ranked distances between points and is of theoretical interest in ecology because it involves simple mapping of resemblance structure into a space of specified dimensionality (Kenkel and Orloci 1986).

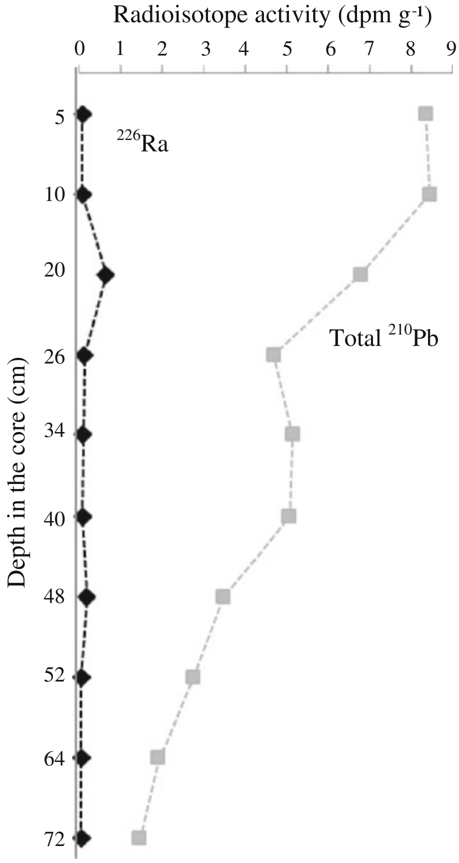

Fig. 2 ^{210}Pb and ^{226}Ra activity (dpm g^{-1}) versus depth in the GUA10-01 core

Results

Core chronology

The ^{210}Pb results indicate that the 75-cm core represents sediment deposited over the last ~91 years, i.e. since about 10 years after the construction of the Guarapiranga Reservoir. ^{226}Ra activity, i.e. supported ^{210}Pb activity (Fig. 2), was very low throughout the sediment profile (0.05–0.67 dpm g^{-1}). The total ^{210}Pb activity profile showed a fairly consistent decrease with sediment depth, from ~8 dpm g^{-1} at the top of the core to 2 dpm g^{-1} near the bottom (Fig. 3). Application of the CIC model was considered appropriate, given the linear relation and strong correlation ($r = 0.98$; $r = 0.93$) between the natural log of $^{210}Pb_{excess}$ activity and cumulative mass in two core segments (Fig. 3). A historically documented event in the basin also served as a good chronological marker (Table 1). Copper sulfate was initially used to control cyanobacterial blooms in

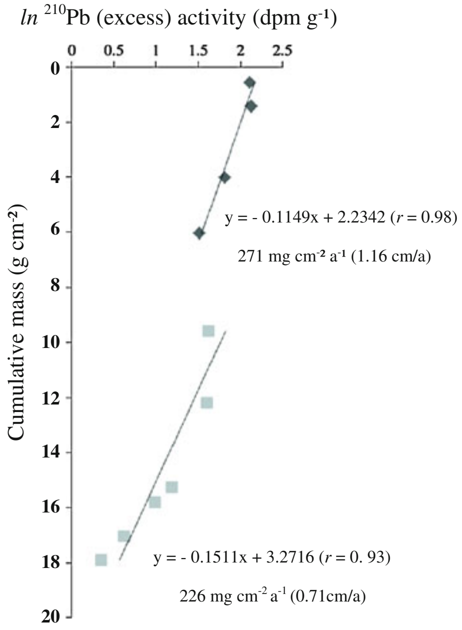

Fig. 3 ln ^{210}Pb (excess) activity (dpm g^{-1}) versus cumulative mass (g cm^{-2}) in the GUA10-01 core

1991 and is first detected at 24 cm (~1991) depth in the sediment profile, providing a chronological marker. It displays concentrations as high as 900–6,000 mg kg^{-1} above that depth (Fig. 4).

Sediment physical and chemical characteristics

The core was divided into three major zones using sediment lithology. Basal sediments (75–51 cm) are brown (2.5Y 4/4), with fragments of leaves, roots and bark, have high water content (88 %), and the highest organic matter concentration (80 %) in the core. Overlying sediments (51–26 cm) are olive gray (5Y 4/2) and clayey. Above that (26–0 cm), sediments are black (5Y 3/1) and characterized by homogenous silty gyttja. Silt-size grains prevailed throughout most of the record (mean 56.2 %), compared to mean percentages of clay (21.3 %) and sand (10.0 %), except in samples from 30 and 28 cm, which contained 100 % very coarse sand.

The sediment chemistry (Fig. 5) revealed three major core zones, closely related to the lithology: zone 1 (75–50 cm, ca. 1919–1934), zone 2 (50–25 cm, ca. 1934–1991) and zone 3 (25–1 cm, ca. 1991–2010). TOC and TN profiles display similarly fluctuating concentration profiles over the length of the core and have their highest values, 3.0 and 0.20 mg g^{-1}, respectively, in zone 1. Concentrations of both decreased dramatically in zone 2, to values of about 0.5 and 0.05 mg g^{-1}, respectively, but rise again slightly in zone 3. The C/N ratio shows a fairly consistent decrease above the top of zone 1 to the

Table 1 ^{210}Pb dates for Guarapiranga Reservoir core GU10-01 and some key historical events recorded by monitoring data and land use records

Depth (cm)	Chronology			Sedimentation rate (g cm^{-2} a^{-1})	Key historical events
	Cumulative mass (g cm^{-2})	Date AD	Age (years)		
5	0.58	2008	2	0.27	
10	1.43	2005	5	0.27	
20	4.02	1995	15	0.27	Initial copper application (~1991); copper-tolerant diatom species and taxa associated with eutrophic environments
26	6.05	1988	22	0.27	Marked increase in the population in the drainage basin after ~1980; 45 % increase in sewage input; replacement of oligo-mesotrophic species by taxa indicative of eutrophy
34	9.57	1964	46	0.21	
40	12.18	1951	59	0.21	
48	15.24	1936	74	0.21	
52	15.82	1933	77	0.21	
64	17.03	1927	83	0.21	Initial public water supply use
72	17.89	1923	87	0.21	

middle of zone 3, dropping from >17 to <8. TP values are lower and rather consistent in zone 1 (~1.0 mg g^{-1}), but rise dramatically through zone 3, beginning about 1992, and show the highest values (~4.5 mg g^{-1}) in the topmost deposits (Fig. 5).

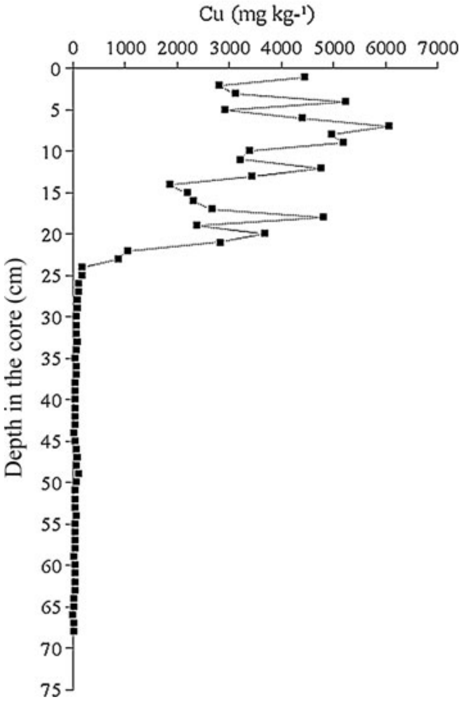

Fig. 4 Copper concentration (mg kg^{-1}) versus depth in the GUA10-01 core

Stable isotopes

In the early deposits of the core (zone 1), $\delta^{13}C$ values range from −29 to −28 ‰ and C/N values are

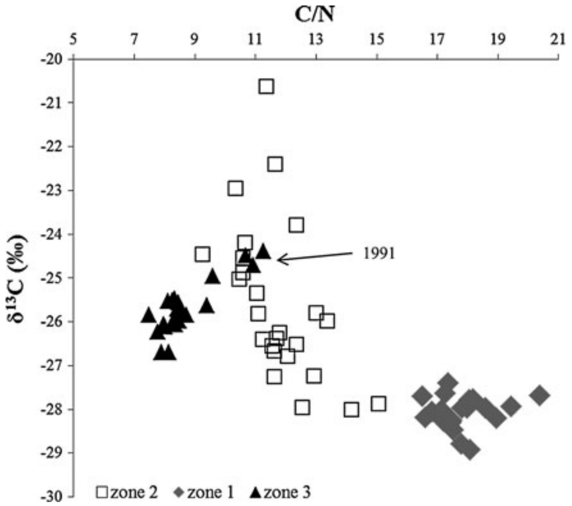

Fig. 6 C/N ratio versus $\delta^{13}C$ of organic matter in the GUA10-01 core, showing values for the three zones in the core delimited using changes in the sediment chemistry. *Arrow* indicates 1991, the beginning of the use of copper sulfate to control cyanobacterial blooms

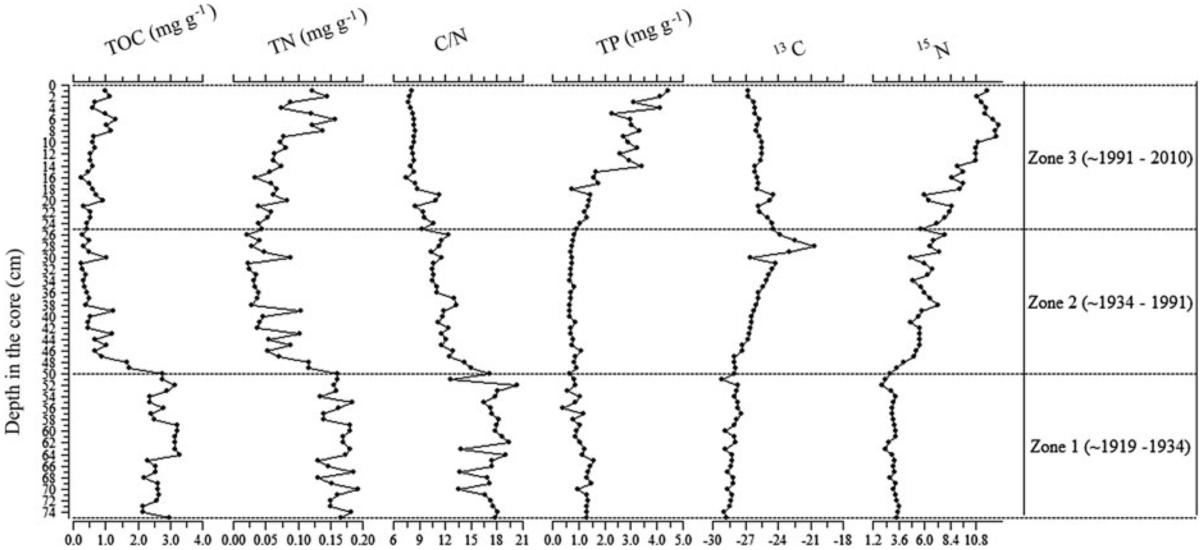

Fig. 5 Total organic carbon (TOC), total nitrogen (TN) and total phosphorus (TP) concentrations (mg g^{-1}), C/N ratio, $\delta^{13}C$ and $\delta^{15}N$ versus depth in the GUA10-01 core. Three zones were delimited using changes in the sediment chemistry

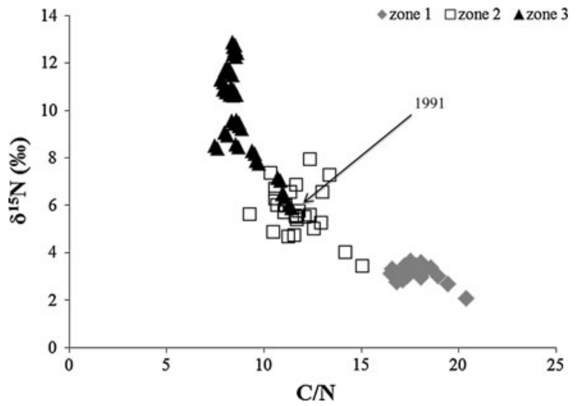

Fig. 7 C/N ratio versus δ^{15}N of organic matter in the GUA10-01 core, showing values for the three zones in the core delimited using changes in the sediment chemistry. *Arrow* indicates 1991, the beginning of the use of copper sulfate to control cyanobacterial blooms

relatively high (17–20). The δ^{13}C values increase in zone 2, ranging from −28 to −21 ‰ (Fig. 6), associated with a decrease in the C/N ratio (16–10), but decline again in zone 3 (−25 to −27 ‰), following an abrupt, further decline in C/N ratio (7) (Fig. 6). The δ^{15}N values are positive and display an increasing trend upcore (Fig. 7), ranging from 2 ‰ in zone 1, associated with high values of C/N ratio (17–20), to as much as 10 ‰ in zone 3, associated with low values of C/N ratio (7), increasing after ∼1991 (Fig. 7).

Diatoms

A total of 77 diatom species were identified in the core, but only 32 species had $\geq$5 % representation in at least one sample and they are plotted in the TILIAGRAPH diagram and were used for calculations in the CONISS program (Fig. 8). Diatoms were well preserved throughout the core and fell into three major assemblages (zones 1, 2 and 3) that are related to zones defined by lithological and chemical changes. In addition, four diatom subzones (1a, 1b, 3a, 3b) were identified using constrained cluster analysis.

Subzone 1a (75–55 cm; ca. 1919–1932) is dominated (∼45 %) by 10 *Eunotia* species that display high abundance at some time in the subzone (>5–40 %): *Eunotia* sp. 1, *Eunotia* sp. 2, *E. maior* (W. Smith) Rabenhorst (EUMA), *E. praerupta* var. *bidens* (Ehr.) W. Smith (EUPRB), *E. indica* Grunow (EUIN), *E. monodon* Ehrenberg (EUMO), *E. rabenhorstii* Cleve and Grunow (EURB), *Eunotia tukanorum* Wetzel and Bicudo (EUTK), *E. camelus* Ehrenberg (EUCA) and *E. botuliformis* Wild Nörpel and Lange-Bertalot (EBTU). Other species of this genus (e.g. *Eunotia valida* Hustedt) (EUVA) were present during this period in smaller percentages (5 %). *Luticola muticoides* (Hust.) Mann (LTMU) and *Fragilaria javanica* Hustedt (FJAV) also occurred almost throughout this entire subzone, with low to moderate abundances (15–20 %). Three other species were present in relatively low abundances: *Frustulia crassinervia* (Bréb.) Lange-Bertalot & Krammer (FRUC) (5–15 %), *Fragilaria vaucheriae* (Kützing) Petersen (FVAUC) (10 %) and *Kobayasiella micropunctata* (Germain) Lange-Bertalot (KOBAY) (5 %). The benthic/plankton (B/P) ratio was about 8 in this subzone.

The second distinct assemblage corresponds to subzone 1b (55–42 cm; ca. 1932–1947) and is characterized by the dominance ($\geq$80 %) of *E. tukanorum* (EUTK). Other species occur in low abundances (<5 %) in almost the entire subzone: *Eunotia praerupta* var. *bidens* (EUPRB), *Brachysira microcephala* (Grunow) Compère (BRC1), *Frustulia saxonica* Rabenhorst (FRUSX) and *Aulacoseira ambigua* (Grunow) Simonsen (AAMB). The B/P ratio decreased substantially (0–1), remaining low after this zone.

The third distinct assemblage, in zone 2 (42–29 cm; ca. 1947–1974), is characterized by moderate to high abundances ($\leq$40 %) of two species, *Aulacoseira pusilla* (Meister) Tuji et Houki (APSL) and *Aulacoseira tenella* (Nygaard) Simonsen (AUTE).

Zone 3 was subdivided into subzones 3a and 3b. Subzone 3a (29–25 cm; ca. 1974–1988) possesses three common species (30–60 %): *A. ambigua* (AAMB), *Cyclotella meneghiniana* Kützing (CMEN) and *Aulacoseira granulata* (Ehr.) Simonsen (AUGR). After ∼1989 (25 cm), in subzone 3b, there is a marked expansion of *A. ambigua* (AAMB), *C. meneghiniana* (CMEN) and *A. granulata*, which reach highest abundances (40–60 %). Deformed *Fragilaria crotonensis* Kitton (FCROD) valves were observed only in this subzone, in four subsamples that constituted up to 5 % of the total diatom count. A probably new species of *Nitzschia* (NTSP) appeared in all zones of the Guarapiranga core, but was abundant only in the topmost subzone (3b), from 25 to 0 cm (ca. 1988–2010), particularly above 10 cm (∼2005), where this species often represented 20–40 % of the total diatom count.

There is good agreement between the core divisions produced by CONISS (Fig. 8) and NMDS analysis (Fig. 9). In the latter, stress values converged after 117

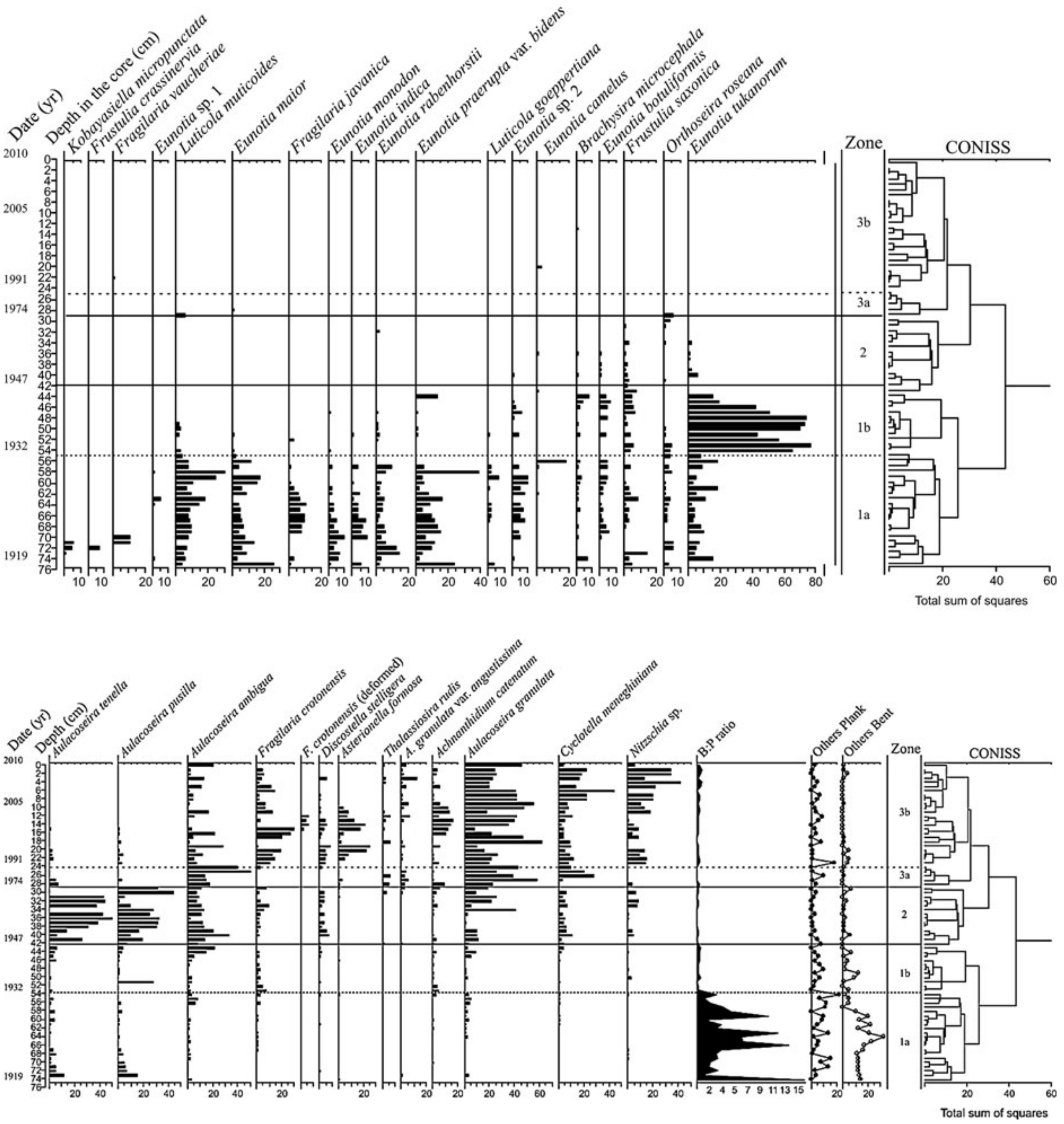

Fig. 8 CONISS diagram of the diatom assemblages from Guarapiranga Reservoir core GUA10-01. Only species with abundances in a sample of ≥5 % were included. *Horizontal lines* define diatom zones 1, 2, 3 and subzones 1a, 1b, 3a, 3b

iterations, at a value of 0.476, and a two-dimensional solution was recommended. Samples were clearly grouped over time, from subzone 1a (ca. 1919–1932) to subzone 3b (ca. 1989–2010). The NMDS analysis also showed substantial changes in diatom assemblages over time ($p = 0.0196$), with the greatest difference between zones 1 and 3 (Fig. 9).

Discussion

The 75-cm sediment core (GUA10-01) from Guarapiranga Reservoir shows rapid, marked changes in lithology, geochemistry and diatoms over the last ~91 years. The main changes in the lithologic, geochemical and diatom data occur more or less

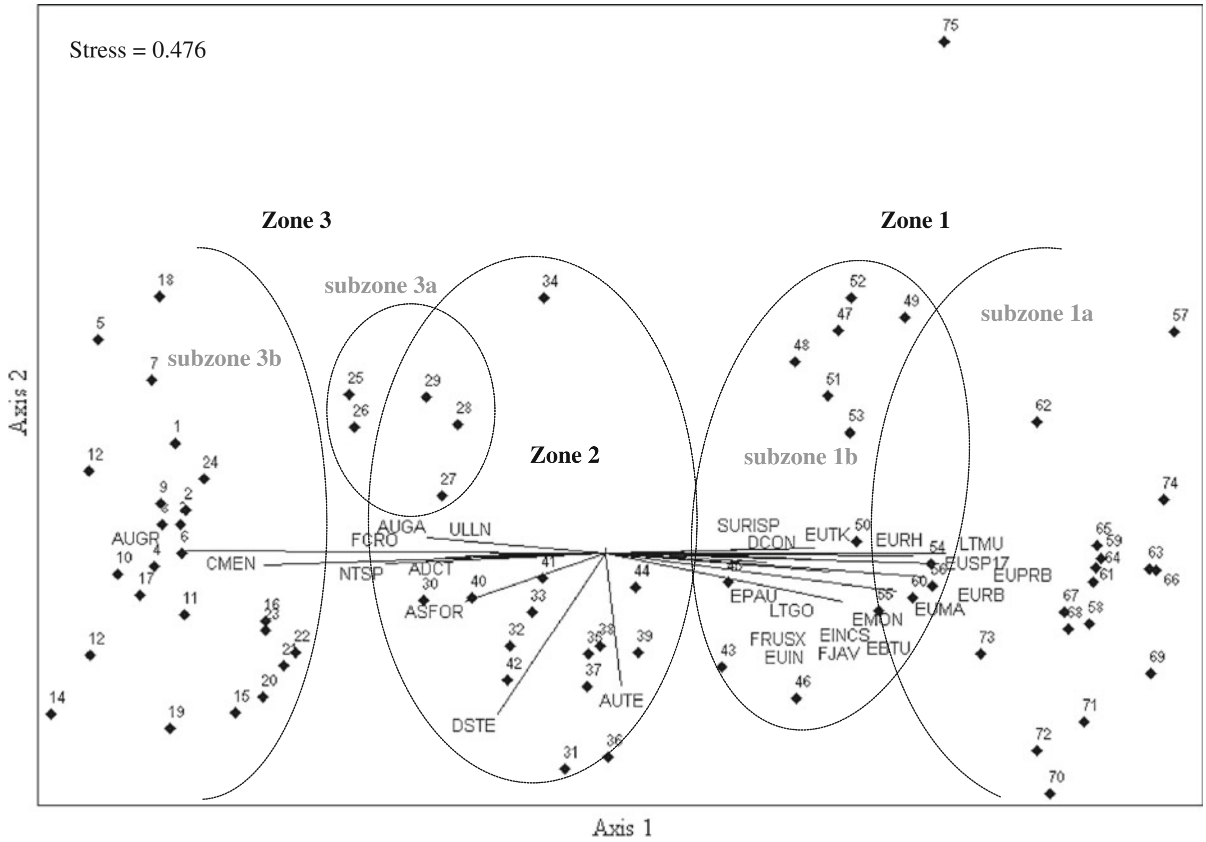

Fig. 9 Two-dimensional, non-metric multidimensional scaling (NMDS) ordination of diatom communities from Guarapiranga Reservoir core GUA10-01. NMDS also identified assemblage zones 1, 2, 3 and subzones 1a, 1b, 3a, 3b

synchronously and at times consistent with key events in the local land-use history (Table 1). The diatom assemblages, however, enabled finer-resolution division of the core into subzones, which appear to be related to specific historical events (e.g. use of the reservoir for public water supply after ~1928 [subzone 1b], onset of eutrophication from sewage discharge in ~1974 [subzone 3a] and use of copper sulfate to control cyanobacteria blooms after ~1991 [subzone 3b]).

Subzone 1a (ca. 1919–1932): initial phase, flooded vegetation, minor cultural eutrophication

The Guarapiranga Reservoir was constructed in 1909 for energy production, about 10 years before the period represented by subzone 1a. Subsequently, a large area of Atlantic forest was flooded (Whately and Cunha 2006). High C/N ratios and low δ^{13}C signatures indicate the predominant source of organic matter in this zone was C3 terrestrial plants (Meyers 2003). Much of the organic matter in the basal zone of the core came from vegetation that was flooded by the dam construction.

The relatively low total phosphorus concentrations and low δ^{15}N values (mean 2 ‰), compared with the overlying zones, suggest this was a period of minor anthropogenic eutrophication, without substantial sewage input to the water. Stable nitrogen isotopes (δ^{15}N) have been used to distinguish among different nitrogen sources in aquatic food webs, and identify sewage, which usually has high values (Wayland and Hobson 2001).

The first diatom assemblage in subzone 1a was dominated by benthic, oligotrophic and slightly acidic taxa, with ten relatively abundant species of *Eunotia*. Species of this genus usually live attached to a substrate by mucilage, and form colonies (van Dam et al. 1994; Furey 2010). Other species (*K. micropunctata*, *F. saxonica* and *B. microcephala*), commonly reported in low-pH and oligotrophic waters (DeNicola 2000), were also abundant in some subsamples. Additionally, *L. muticoides*, often found with lichens in terrestrial habitats (Lakatos et al. 2004), occurred with moderate abundance, and is probably a good indicator of substrate availability in this subzone.

The abundant species in subzone 1a suggest a well-illuminated water column, with light either penetrating to the bottom or reaching available surfaces, thereby favoring benthic/periphytic species, under acidic and oligotrophic conditions. The assemblage of this subzone was very similar to the diatom assemblage reported in acidic, oligotrophic, dark water of the Rio Negro, Amazonas, Brazil (Wetzel 2011). The diatom assemblage of this subzone was probably influenced by the flooded vegetation, which increased the availability of surfaces for benthic species and promoted acidic conditions that were a consequence of decomposition of organic matter from C3 terrestrial plants.

Subzone 1b (ca. 1932–1947): large physical impact, minor cultural eutrophication

In 1928, the city of São Paulo began to use Guarapiranga Reservoir as a public water supply (Whately and Cunha 2006). From 1940 to 1950, the Pinheiros River was channelized and partly diverted to the reservoir to cope with a water shortage in the metropolitan region of São Paulo (Beyruth 2000). Subzone 1b reflects the impacts of these major hydrological changes, under conditions of low urbanization.

Marked changes in the diatom assemblage occurred in subzone 1b, mainly the abrupt disappearance of benthic taxa and replacement by one dominant planktonic species, *E. tukanorum*. This species was found in abundance in the plankton of a large river in the Amazon Basin (Wetzel et al. 2010), which displays large water level fluctuations (~15 m) between the dry and wet seasons (Sioli 1984). Despite the fact that the vast majority of *Eunotia* species are attached forms (Siver et al. 2006), there are a few exceptions, e.g. *E. asterionelloides*, *E. zasuminensis* and *E. tukanorum*, which are common in phytoplankton assemblages, and their colonies can be found as dominant components of lakes and rivers (Eloranta 1986; Wetzel et al. 2010). High densities of *E. tukanorum* were also encountered in the Amazon River during the period of rising water in the annual cycle, and in the floodplain lakes during the low-water period, when water transparency was also low (Raupp et al. 2009). This corroborated the fact that this species prefers environments with low light transparency (Moro and Fürstenberg 1997).

In Guarapiranga Reservoir, dominance of *E. tukanorum* and disappearance of the benthic taxa, account for the marked decrease in the B/P ratio (Fig. 9), and probably reflect the nearly seven-fold increase in water discharge (from 1.3 to 9.5 m^3/s) associated with the use of the reservoir as a public water supply. A decrease in the proportion of benthic to planktonic diatoms over time also occurred after the formation of Liuxine Reservoir in China, associated with fluctuations in water retention (Liu et al. 2012), and in the paleo-reconstruction of a complex reservoir in South Australia (Kangaroo Creek Reservoir), related to an increase in water level (from 26 to >35 m deep), a consequence of substantial inflow and rapid volume increases (Tibby et al. 2007). These studies indicate the utility of tracking changes in the relative abundance of benthic species as a result of physical and hydrologic changes.

Considering that *E. tukanorum* has been reported in slightly acidic, oligotrophic rivers in Brazil (Laux and Torgan 2011), and that TOC, TN and TP concentrations show little change in this subzone, we suspect that there were physical and hydrologic impacts, but still find no evidence of cultural eutrophication.

Zone 2 (ca. 1947–1974): transitional phase with moderate cultural eutrophication

Channelization of the Pinheiros River was completed in ~1950 and this impacted the Guarapiranga Basin, causing the disappearance of wetlands. Population density near the reservoir increased, but remained low relative to the time represented by subzones 3a and 3b (Whately and Cunha 2006). In 1958 the "Alto da Boa Vista" Water Treatment Station for the public water supply was completed, and the water level of Guarapiranga Reservoir increased (Whately and Cunha 2006). Zone 2 represents the transitional phase in the reservoir, characterized by a mix of two organic matter sources, i.e. algae and terrestrial C3 plants (Meyers 2003), and is associated with a decrease in C/N ratio and an increase in $\delta^{13}C$ signature.

A sharp shift in the diatom assemblage occurred, with dominance of *A. tenella* and *A. pusilla*, both oligo-mesotrophic, planktonic species (Lepskaya et al.

2010). *Aulacoseira pusilla* (commonly reported as *A. subborealis*) is reported to have an optimum conductivity of 432 μS cm^{-1}, somewhat higher than the modern surface water conductivity in Guarapiranga Reservoir (151 μS cm^{-1}), and is a major component of the plankton assemblage (Tibby and Reid 2004). Furthermore, this species has a wide tolerance with respect to several environmental variables, including TP (Tibby et al. 2007). *Aulacoseira tenella* is an abundant planktonic species in oligo-mesotrophic reservoirs in the State of São Paulo and is probably a good indicator of non-eutrophic conditions (unpublished data). By the end of zone 2, TP and $\delta^{15}N$ values were becoming progressively higher, and this trend continued into zone 3, with a marked shift in the diatom community, indicating the onset of cultural eutrophication.

Subzone 3a (ca. 1974–1988): onset of marked cultural eutrophication

The onset of cultural eutrophication is related with the abrupt increase in urbanization of the drainage in the mid-1970s, which had profound impacts on the sediment lithology, geochemistry and diatom assemblages. The granulometric texture (100 % sand), especially in the 28–30 cm interval (~1980), indicates the explosive increase of urbanization and deforestation in the Guarapiranga basin. The lithology, characterized by homogenous, black gyttja and silty sediments, suggests higher organic carbon content. An abrupt increase in TP and a marked decrease in the C/N ratio, indicate a rapid increase in trophic state. These shifts were associated with higher $\delta^{15}N$ values (mean 10 ‰), indicating the onset of untreated sewage discharge to the reservoir. Typically, bacteria discriminate against ^{15}N in favor of ^{14}N because the lighter isotope is easier to metabolize (Heaton 1986). Hence, the remaining nitrogen from the sewage effluent is enriched in ^{15}N (Costanzo et al. 2005). Nitrogen isotopes are therefore useful for tracking sewage inputs (Tucker et al. 1999).

Following the onset and expansion of unplanned settlements in the 1970s, oligotrophic and mesotrophic diatoms were rapidly replaced by eutrophic taxa such as *A. granulata, C. meneghiniana* and *A. ambigua*. These taxa are all associated with higher nutrient concentrations in lakes (Dong et al. 2008) and have been reported in eutrophic waters (Zalat 2000). In particular, *C. meneghiniana* was associated with a marked shift to hypereutrophic conditions in a tropical reservoir in southeast Brazil (Costa-Böddeker et al. 2012). In addition, both *A. granulata* and *A. ambigua* were also reported in different productive water bodies, as well as associated with high hydrological/physical changes resulting from deforestation and erosion. They also appear as a consequence of changes in light climate in response to shifts in land use in the drainage basin (Costa-Böddeker et al. 2012).

Subzone 3b (ca. 1988–2010): major cultural eutrophication phase

Subzone 3b represents the major eutrophication period in the reservoir, with higher $\delta^{15}N$ values (14 ‰) and TP concentrations relative to previous zones. After ~1980, the population in the drainage basin increased rapidly, with rapid expansion of slum dwellings that lacked adequate sewage treatment (Whately and Cunha 2006). This led to common cyanobacterial blooms (Beyruth 2000). Many cyanobacteria taxa are known to produce toxic compounds as well as substances that impart a foul taste and odor to drinking water (Falconer 1999). Because of frequent gastroenteritis infections in the local population, the agency in charge of the public water supply began to use copper sulfate to control cyanobacterial blooms in ~1991 (Beyruth 2000), and copper concentration rises abruptly at about 24 cm in the sediment, marking the first widespread use of this algicide. Concentrations rise sharply and are very high in the upper 20 cm of the profile (typically 2,000–5,000 mg kg^{-1}). Copper is very persistent in aquatic ecosystems (Gunn et al. 1989) and becomes toxic at concentrations higher than those required for growth (Fargašová 2001). Many species of diatoms are sensitive to metals, sometimes even in small quantities, and frustule deformities can be caused by metal contamination (Cattaneo et al. 2004). In general, the effects of heavy metals on diatom assemblages are observed in the disappearance of the most sensitive taxa and an increase in relative abundance of the most tolerant ones, and appearance of teratological forms or deformed individuals (Falasco et al. 2009). Valve deformities in *Fragilaria crotonensis* were observed only in this subzone, albeit in low percentages (≤5 %). Nevertheless, they were probably caused by high copper concentrations in the water.

This subzone was characterized by diatom assemblage shifts. In general, the assemblage showed an increase in species associated with eutrophic conditions [*C. meneghiniana*, *A. granulata*, *A. ambigua* and *Achnanthidium catenatum* (Bily and Marvan) Lange-Bertalot], which reached highest abundances in this subzone. One taxon, *A. granulata*, has low sensitivity to copper (Viana and Rocha 2005) and has typically been reported in eutrophic waters (Stoof-Leichsenring et al. 2011). This species has also been associated with physical alterations in water bodies (depth variation, turbulence, deforestation, and hydrological changes), regardless of trophic state (Dong et al. 2008; Costa-Böddeker et al. 2012). Thus, the increase in *A. granulata* in this subzone is probably a response to multiple stressors. *Cyclotella meneghiniana* is commonly associated with high TP concentrations (Yang et al. 2008), is tolerant of wastewater and industrial pollution (Sabater and Sabater 1998), and was also associated with a sharp shift to a hypereutrophic state (after ~1999) in a paleolimnological study of an urban shallow reservoir in Brazil (Costa-Böddeker et al. 2012). Although *A. catenatum* was not a major component of the diatom assemblage, it clearly achieved higher abundances in this subzone, and in other Brazilian reservoirs highlighted the onset of a marked eutrophication phase (Costa-Böddeker et al. 2012). Another taxon, which is probably a new *Nitzschia* species, appeared in all sediment zones of the Guarapiranga core, but was most abundant in the topmost subzone (3b), particularly after ~2005. This *Nitzschia* species was also abundant in the surface sediments of other eutrophic reservoirs in the same drainage basin (unpublished data).

Major cultural eutrophication occurred during this period, particularly after ~1990. Other paleolimnological studies in Brazil (Costa-Böddeker et al. 2012, Garças Reservoir) and China (Jinglu et al. 2007, Lake Taihu) also report accelerated eutrophication, with the highest trophic status in the 1990s, mainly as a consequence of urbanization and/or industrialization in the catchment.

Conclusions

We examined a sediment core from a large, tropical public water supply reservoir in one of the most urbanized cities worldwide, Guarapiranga Reservoir, São Paulo, Brazil. We inferred the major ecological shifts in the water body over the last ~90 years, which were related to multiple stressors, including the influence of forest flooding (initial phase), hydrologic change (shift in residence time), metal contamination (algicide application) and eutrophication (increased sewage inputs). The reservoir was oligotrophic from ~1919 to 1947 and underwent an initial physical disturbance period in the early ~1930s, caused by the first use of the reservoir as a public water supply. The onset of eutrophication in the mid-1970s was associated with the abrupt increase in urbanization of the drainage basin, followed by rapid expansion of slum dwellings after 1980, leading to the increase of sewage inputs and contamination by copper, i.e. use of algicide since 1990. Since ~1990, the reservoir has been eutrophic to hyper-eutrophic. The period of pre-eutrophic conditions occurred around 1947–1950 (beginning of zone 2), when Guarapiranga Reservoir displayed more stable conditions. This period occurred after the initial influence of flooding and the marked hydrological changes, but before there were major changes in the drainage basin, such as the dramatic increase in population and channelization and diversion of the Pinheiros River into the reservoir.

Our findings show the ability of diatom assemblages to track major perturbations, including hydrological changes, use of copper-based algicides and eutrophication. Geochemical information, however, provided better insights into conditions during the early phase of the reservoir, revealing the effects of the flooded vegetation on diatom changes. This study highlights the utility of a multi-proxy approach for tracking ecological shifts in a large public water supply reservoir. Furthermore, our results indicate that interpretation of shifts in the benthic/planktonic (B/P) diatom ratio in reservoirs must be used with caution because factors other than eutrophication may influence the B/P value.

This paleolimnological study contributes to the understanding of limnological changes in a tropical reservoir that was subject to profound urbanization pressure. Such investigations will continue to be useful in Brazil, where most such water bodies lack long-term water-column data. Indeed, paleolimnological methods have great potential for management of tropical reservoirs worldwide. The approach can provide insights into the trophic state trajectory of reservoirs, determine if a pollution problem exists, help identify the cause(s) of nutrient enrichment, and perhaps set target conditions for improved water quality. This is one of only a few paleolimnological studies on the trophic state history of low-latitude reservoirs. One goal for future studies will be to improve autoecological information on diatoms in tropical regions to enable quantitative trophic state inferences for both tropical lakes and reservoirs.

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