Water quality of an urban reservoir subjected to periodic applications of copper sulphate: the case of Ibirité reservoir, southeast Brazil

A qualidade da água de um reservatório urbano sujeito a aplicações periódicas de sulfato de cobre: o caso do reservatório de Ibirité, sudeste do Brasil

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Abstract: Aim: The aim of the work was to identify the stratification patterns and characterize the water quality of Ibirité reservoir considering, among other aspects, the effects of additions of copper-sulphate as a way of controlling algae blooming; **Methods:** Temperature, pH, dissolved oxygen and conductivity were measured in the reservoir and in Pintados and Ibirité streams. Water column samples were taken to determine the concentration of total and dissolved N and P and chlorophyll-*a*. The thermal circulation pattern is warm-monomictic; **Results:** The dissolved oxygen concentration varied between 1 and 14 $mg.L^{-1}$; pH between 6.2 e 9.3; electrical conductivity elétrica between 400 e 500 $\mu S.cm^{-1}$; total P between 8.1 and 164.1 $\mu g.L^{-1}$; total N between 1,350.5 and 5,814 $\mu g.L^{-1}$. Chlorophyll-*a* showed values up to 925 $\mu g.L^{-1}$ during blooming. As a measure of controlling the blooming in October/02, copper sulfate was aspersed resulting in a drastic reduction of chlorophyll-*a* concentration; **Conclusions:** The studied environment is highly eutrophic evidencing the need of adopting a management program of its basin for its recovery.

Keywords: stratification patterns, water quality, eutrophication, algae blooming, sulfating, reservoir.

Resumo: Objetivo: Este estudo teve como objetivo identificar o padrão de estratificação e caracterizar a qualidade da água do reservatório de Ibirité considerando, entre outros aspectos, os efeitos de adições de sulfato de cobre como uma forma de controlar floração de algas; **Métodos:** Temperatura, pH, oxigênio dissolvido e condutividade elétrica foram medidos no reservatório e nos córregos Pintados e Ibirité. Amostras da coluna d'água foram coletadas para determinar as concentrações de nitrogênio e fósforo e clorofila-*a*; **Resultados:** O padrão de circulação da coluna d'água é monomítico-quente. As concentrações de oxigênio dissolvido variaram entre 1 e 14 $mg.L^{-1}$; pH entre 6,2 e 9,3; condutividade elétrica entre 400 e 500 $\mu S.cm^{-1}$; P total entre 8,1 e 164,1 $\mu g.L^{-1}$; N total entre 1.350,5 e 5.814 $\mu g.L^{-1}$. Clorofila-*a* mostrou valores maiores que 925 $\mu g.L^{-1}$ durante a floração. Como medida de controle da floração, em outubro/02 foi feito a aspersão de sulfato de cobre, resultando numa drástica redução da concentração de clorofila-*a*; **Conclusões:** O ambiente estudado é altamente eutrofizado, o que evidencia a necessidade de um programa de gestão da sua bacia visando sua recuperação.

Palavras-chave: padrões de estratificação, qualidade da água, eutrofização, floração, sulfatação, reserevatório.

1. Introduction

The construction of reservoirs is an old and frequent practice due to the increasing need of water for several purposes: human consumption, energy generation, agriculture, cattle breeding and industrial use. According to Matsumura-Tundisi and Tundisi (2005) reservoirs are systems characterized by a spatial gradient produced by tributaries thrown in it with influences on the local physical, chemical and biological characteristics of the water column. Due to several reasons such as lack of sewage treatment, accelerated urbanization among others, several of these water bodies have been suffering impacts by anthropogenic activities of which Pampulha reservoir in Belo Horizonte – MG (Barbosa et al., 1998), Billings (Banco Mundial, 2003) and Guarapiranga (Beyruth, 2000) reservoirs in São Paulo and lake Paranoá in Brasília – DF (Branco and Senna, 1996) are good examples in Brazil.

Despite artificial ecosystems reservoirs are similar to natural lakes in several aspects such as the stratification/mixing patterns of the water column for example. However, the opening/closing system of reservoir´s floodgates can change drastically such patterns resulting in significant changes of the physical and chemical features of the environment altering the structure and functioning of the biological communittes. As a consequence the correct understanding of the stratification/mixing pattern is crucial for the understanding of the whole ecosystem functioning.

The eutrophication appears as one of the greatest threats to the waters all over the world (Padisák et al., 2000) with many adverse effects related to the depletion of oxygen within the hypolimnion (Heo and Kin, 2004) and the blooming of cyanobacteria. Especially in developing countries, where sewage treatment problems have not been adequately solved yet the demographic growth is high and the industrial expansion happens without a proper environmental caution (Rocha et al., 1997).

The loadings with domestic and industrial sewage with high levels of phosphorus and nitrogen, cause changes in the composition and diversity of the plankton community (Matsumura-Tundisi and Tundisi, 2005), increase phytoplankton and macrophytes biomasses (Pinto-Coelho, 1994) and, on extreme cases, blooming of potentially toxic cyanobacteria (e.g. *Microcystis* sp. *Cylindrospermopsis raciborskii*), well known environmental and health problems (Huszar et al., 2000).

The estimation of phytoplankton biomass through chlorophyll concentration is a widespread technique. The correlation between this pigment concentration and that of nutrient (e.g. soluble reactive phosphorus, nitrate-nitrogen) is also largely used as a proxis in the identification of factors responsible for the regulation of phytoplankton community.

The application of copper sulfate (sulfating) has been largely used as a way to control algae blooms. This practice not only changes the water's chemistry but causes considerable impacts on the general biota being also ineffective in controlling the bloomings at a long run (Beyruth, 2000).

The reservoir of Ibirité was built for providing water supply to the Gabriel Passos Refinery-REGAP/PETROBRAS. Since its establishment this environment has been suffering considerable impacts due to both effluent loads from the refinery and the disordered occupation of its drainage basin, accentuating a considerable amount of non-treated domestic sewage, mainly at the municipality of Ibirité – MG (Moreno and Callisto, 2006). As a consequence, the environment exhibits an advanced stage of degradation as demonstrated by frequent bloomings of cyanobacteria, fish mortality, and garbage accumulation at its shores. Because of the importance and severity of the eutrophication problem around the world and its causes and consequences, detailed studies focusing on its control are necessary, considering aspects such as the drainage basin, water uses, usage and occupation of the soil of the region and its impacts, as previously reported by Barbosa and Garcia (2003).

Using water quality parameters, chlorophyll, nitrogen and phosphorus concentrations as indicators of human impacts on the Ibirite watershed, the main objective of this study was to identify i) the patterns of thermal and chemical stratification of the water column; ii) the nutrient-chlorophyll relationships and iii) the trophic state and contribution of human activities to the degradation of the Ibirité reservoir.

Two questions were asked in order to guide this study: i) are there significant spatial-temporal differences in water quality of the Ibirité reservoir and its tributaries? ii) the copper sulphate addition practice is effective in controlling algae blooms in the reservoir?

2. Material and Methods

The Ibirité reservoir (44° 5-7' S and 19-20° 17' W) was built during the 60's with a maximum depth of 18 m at the municipality of Ibirité, metropolitan region of Belo Horizonte, southeast of Brazil (Figure 1). The Ibirité stream, responsible for its formation, drains urban and industrial areas, receiving domestic sewage without any treatment. A major tributary to the Iberite stream is the Pintados stream - also an heavily impacted stream which contributes for the decaying of the water quality. The surrounding area is characterized by a disordered and densely occupied population as demonstrated by garbage deposition on the borders and siltation of the reservoir. A description of the benthic macroinvertebrate´s community within the watershed is provided by Moreno and Callisto (2006).

The samplings and in situ measurements were conducted between March /02 and March/03 in six points within the reservoir and six points on its tributaries being

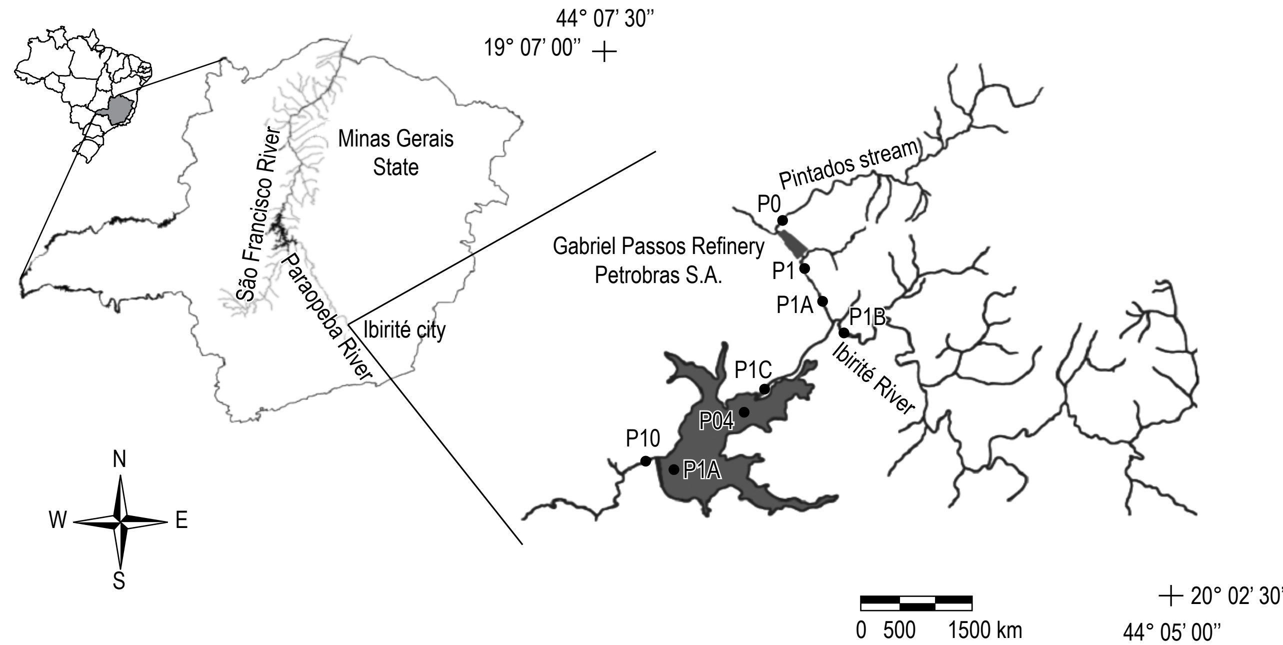

Figure 1. Location of the Ibirité reservoir and the streams Pintado and Ibirité, showing the streams and reservoir sampling stations.

three points in Pintado stream (P0, P1, P1A) and three in Ibirité stream (P1B, P1C, P10), the latter located just downstream the reservoir. Furthermore, measurements of water temperature, pH, dissolved oxygen and conductivity, were done every fortnight on the water column of the reservoir and every two months on the tributaries, through a HORIBA multiprobe (mod. U-22). Bi-monthly samples were also taken in both the reservoir and tributaries to determine total nitrogen, nitrate-nitrogen (Mackereth et al., 1978), total phosphorus and soluble reactive phosphorus (Golterman et al., 1978), ammonium-nitrogen (Grasshorf, 1976) and chlorophyll-a (Lorenzen, 1967, not corrected for pheopigments) concentrations. These samplings were done in 4 depths corresponding to 100% (surface), 10% (Secchi disk deapth), 1% of the surface incident light and at the aphotic zone.

The Kruskal-Wallis H test and Mann-Whitney's U Test (Zar, 1974) were used in order to verify differences between sampling points and seasons of the year. Moreover, Linear Regression was used to establish possible relations between the variables (Zar, 1974). Preliminary analysis did not demonstrate significant differences for the studied variables between the sampling points in the reservoir, which led to the consideration of maintaining only two points: P04, close to the entrance of Ibirité stream in the reservoir and P02, the deepest (18 m) close to the dam.

3. Results

From January/02 to March/03, the climatic seasonality was the typical one for tropical climate with the highest temperature average registered in February/03 (24.3 °C) and maximum precipitation in January/03 (435 mm). The lowest temperature and precipitation averages (19.2 °C and 0 mm, respectively) were recorded in July/02.

High phosphorus (>750 µg.L^{-1}) and total nitrogen (>7,500 µg.L^{-1}) concentrations were registered in Ibirité and Pintados streams (Table 1) with the highest values at points P1 and P1B. High electric conductivity values were registered in both streams at points P1 e P1A (>1,700 µS.cm^{-1}), located downstream REGAP (Table 1). Oxygen concentrations oscillated between 2.9 and 10.4 mg.L^{-1} (Table 1).

3.1 The situation in the reservoir

A warm-monomictic thermal pattern was identified, with stratification of the water column from September until April and circulation from May until August. This pattern demonstrates the influence of the weather on the circulation of the water column with typical consequences on space-temporal distribution of oxygen and water temperature (Figure 2). Dissolved oxygen concentrations varied between 1 and 14 mg.L^{-1} with the lowest values registered at the bottom, during the summer.

The pH ranged between 6.3 and 8.5 at point 02 and between 6.2 and 9.3 at point 04. During the period of stratification the waters remained neutral in the layers near the surface and slightly acidic in the deeper layers. In the period of circulation until the month of November, all the reservoir showed high pH values with higher pH (9.3) being recorded in November/02 as a result of copper sulphate

Table 1. Physical and chemical variables in Pintado stream (P0, P1, P1A) and Ibirité stream (P1B, P1C, P10) (Temp: temperature; DO: dissolved oxygen; Conduct: electrical conductivity; TN: total nitrogen; TP: total phosphorus).

Points		Temp (°C)	DO (mg.L^{-1})	pH	Conduct. (µS.cm^{-1})	TN (µg.L^{-1})	TP (µg.L^{-1})
P0	mean	24	7.9		197	1576	145
	min-max	22-26	6.3-10	6.6-7.3	31-266	587-2874	63-227
P1	mean	25.1	7.8		1049	4936	394
	min-max	22-27	5.7-10.4	4.3-7.4	100-2050	2343-7851	123-774
P1A	mean	25.5	6.9		896	4719	248
	min-max	21-30	4.9-9.3	6.6-7.3	60-1810	2047-7435	20-459
P1B	mean	24.6	6.0		232	5474	423
	min-max	21-28	3.7-8.5	6.6-7.1	32-331	3022-7902	121-916
P1C	mean	22.5	5.5		413	4542	238
	min-max	19-27	2.9-9.6	6.7-7.1	61-690	2366-6474	77-669
P10	mean	24.9	7.1		261	2344	43
	min-max	22-27	5.2-9.9	6.6-7.0	46-394	1668-3078	12-92

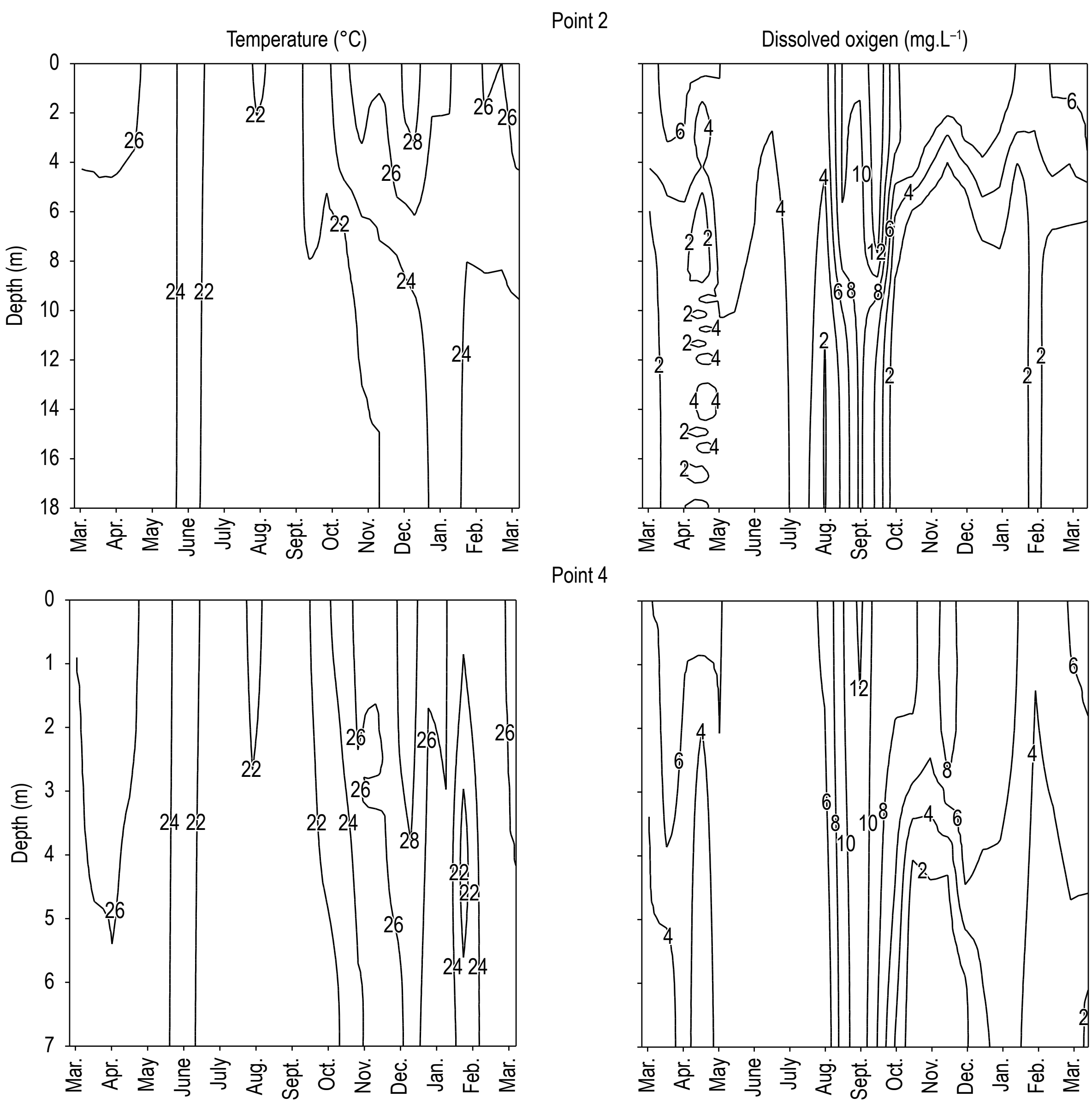

Figure 2. Diagram depth X time for the water temperature and concentration of dissolved oxygen, in the sampling points 02 and 04 of the Ibirité reservoir, MG.

applications, declining from this month and returning to values close to neutrality (Figure 3).

The electric conductivity (Figure 3) ranged between 40 and 500 µS.cm^{-1} in both seasons, with higher values in deeper layers (during the thermal stratification), while low values were observed between the months of August and October in both seasons.

The total P concentrations oscillated between 8.1 and 164.1 µg.L^{-1} and total N between 1,350.5 and 5,814 µg.L^{-1} (Table 2).

Since the nutrients data did not show a normal distribution, nonparametric analyses were performed to verify the differences between sampling periods. The highest concentrations of total nitrogen were registered in September/02 whit significant differences for the other months except July (Figure 4, Tables 2 and 3). The highest concentrations of total phosphorus were registered in September/02, also with significant differences for the other months except January (Figure 5, Tables 2 and 4)

At sampling point 02 e 04 the soluble reactive P varied between 1.3 and 34 µg.L^{-1}, nitrate-nitrogen between 159.6 and 1,551.7 µg.L^{-1}, and ammonium-nitrogen between 3.4 and 834.8 µg.L^{-1} (Table 2). Chlorophyll concentrations varied between 4.3 and 63.6 µg.L^{-1} being higher between July and November/02 reaching 925 µg.L^{-1} at point 04 in September, when blooms of *Microcystis aeroginosa* and *Microcystis* sp were recorded. Variations in concentrations between sampling periods were significant for most cases (Figure 6, Tables 2 and 5).

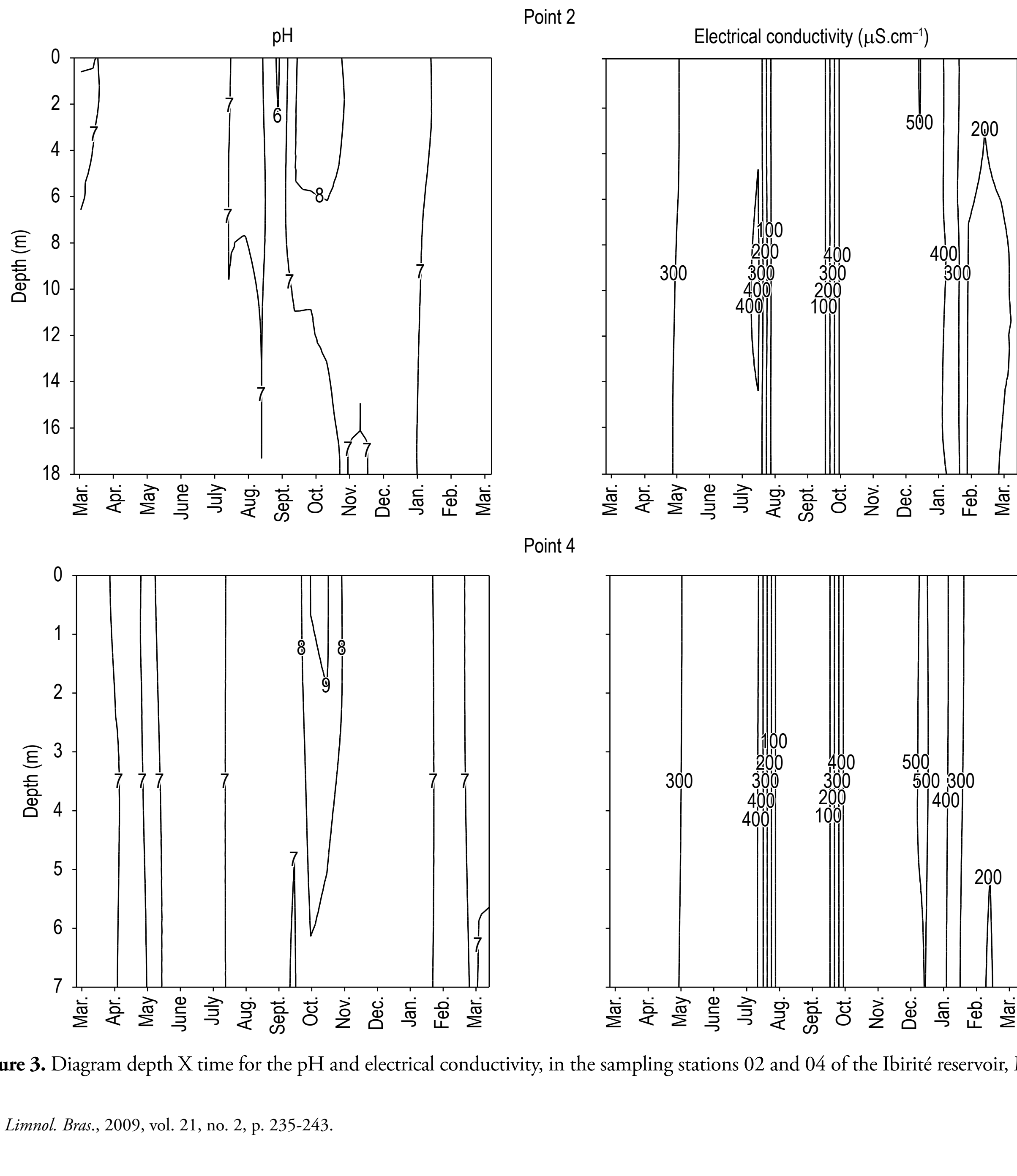

Figure 3. Diagram depth X time for the pH and electrical conductivity, in the sampling stations 02 and 04 of the Ibirité reservoir, MG.

Table 2. Concentrations of nutrients and chlorophyll-a in Ibirité Reservoir (Chlor-*a*: chlorophyll-*a*; TN: total nitrogen; TP: total phosphorus).

Sampling stations		$N\text{-}NO_{3^-}$ ($\mu g.L^{-1}$)	$N\text{-}NH_{4^\pm}$ ($\mu g.L^{-1}$)	TN ($\mu g.L^{-1}$)	$P\text{-}PO_{4^{2-}}$ ($\mu g.L^{-1}$)	TP ($\mu g.L^{-1}$)	Chlor-*a* ($\mu g.L^{-1}$)
P02	mean	1093	239	2429	6.8	39.7	24
	min-max	160-1743	12-835	1350-5337	1.6-17.8	8.3-98.5	4.3-47.2
P04	mean	1033	288	2903	7,1	51	22.5*
	min-max	468-1529	3.4-740	1650-5814	1.3-34	8.1-164	5.9-63.6*

* Medium and maximum values without considering September.

Table 3. Mann-Whitney U Test for the differences in concentrations of total nitrogen between months sampled.

Month	U	Z	p
March/02 and September/02	4.0	–2.94	0.003
May/02 and September/02	0.0	–3.36	<0.001
May/02 and November/02	13.0	–2.00	0.046
September/02 and November/02	8.0	2.52	0.012
September/02 and January/03	4.0	2.94	0.003
September/02 and March/03	6.0	2.73	0.006

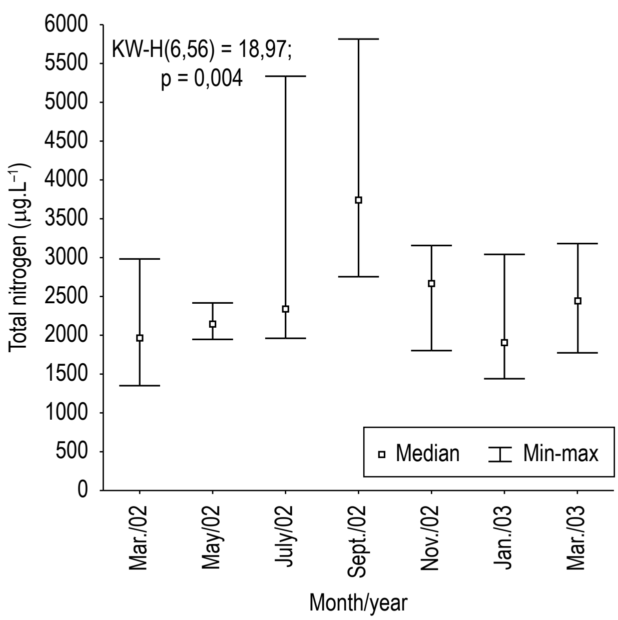

Figure 4. Seasonal variation in the concentration of total nitrogen at Ibirité reservoir-MG. Kruskal-Wallis H test was showing at top of figure.

A chlorophyll peak (925 $\mu g.L^{-1}$) was recorded during the dry period (September), when the highest concentrations of soluble reactive phosphorus and nitrate were registered. This seasonal variation of chlorophyll concentration reflects, in a weak way, the variations of total nitrogen (Spearman Correlations: r = 0.44; N = 56; p = 0.001) and nitrate (Spearman Correlations: r = 0.27; N = 56; p = 0.048), but not that of soluble reactive phosphorus. The drastic reduction observed in November (<50 $\mu g.L^{-1}$) is a consequence of the addition of 5 tons (aqueous solution) of copper sulfate 15% (sulfating).

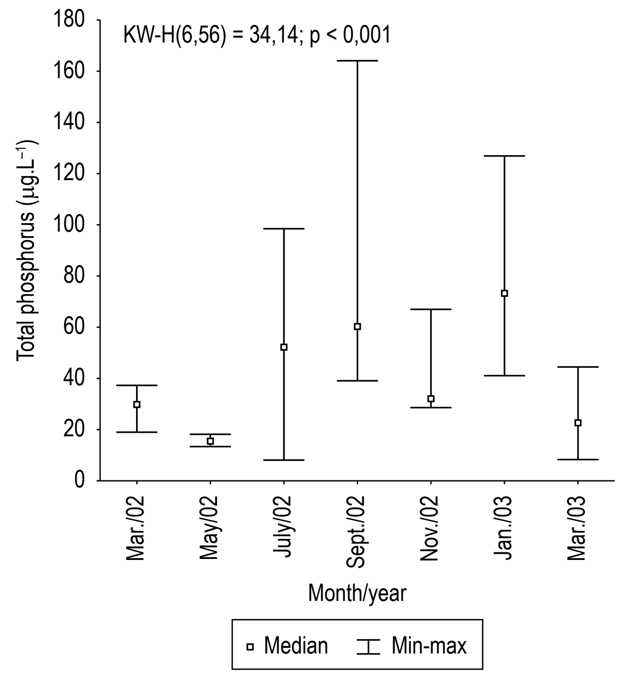

Figure 5. Seasonal variation in the concentration of total phosphorus at Ibirité reservoir/MG. Kruskal-Wallis H test was showing at top of figure.

4. Discussion

In this study, Ibirité and Pintados streams show high values of electric conductivity as well as N and P concentrations suggesting the input of nutrients from non-treated sewage discharges. Significant nutrient contributions from point P1 are evidenced by high values of total N and P observed in Pintados stream. In the same way high concentrations of N and P were also recorded in Ibirité stream (point 1B), indicating a considerable amount of non-treated sewage discharges from the municipality of Ibirité. According to Matsumura-Tundisi and Tundisi (2005) in reservoirs, the contribution of tributaries can be important on the determination of the water quality and the existing biota, in opposite to natural lakes where the composition and richness of species of the plankton as well as the abundance of organisms depend on factors such as the lake's origin, trophic state, colonization process and the presence or absence of toxic substances or pollutants.

Table 4. Mann-Whitney U Test for the differences in concentrations of total phosphorus between months sampled.

Month	U	Z	p
March/02 and May/02	0.0	3.36	0.001
March/02 and September/02	0.0	–3.36	0.001
March/02 and January/03	25.0	–3.36	0.001
May/02 and July/02	12.0	–2.1	0.036
May/02 and September/02	0.0	–3.36	<0.001
May/02 and November/02	0.0	–3.36	<0.001
May/02 and January/03	0.0	–3.36	<0.001
September/02 and November/02	9.0	2.42	0.016
September/02 and March/03	1.0	3.26	0.001
November/02 and January/03	7.0	–2.63	0.009
January/03 and March/03	1.0	3.26	0.001

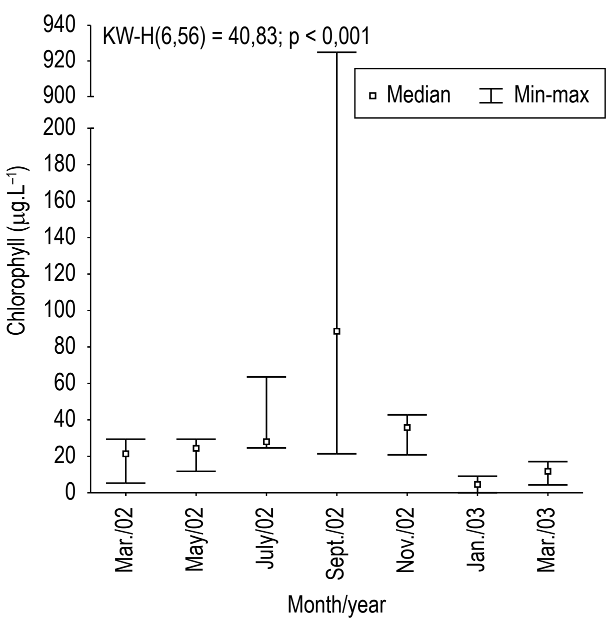

Figure 6. Seasonal variation in the chlorophyll-*a* concentration at Ibirité reservoir-MG. Kruskal-Wallis H test was showing at top of figure.

The role of receptor and accumulator of N and P played by the reservoir is very important as evidenced by the lower concentrations of these nutrients downstream (P10) rendering high concentrations of these nutrients within the reservoir which is classified as eutrophic environment according to the model developed by Salas and Martino (1991). Several studies developed in Pampulha reservoir (e.g. Barbosa et al., 1998) demonstrated that *c.* 70% of the nitrogen and 90% of the phosphorus arriving at that reservoir coming from the tributaries are retained due to both precipitation of these elements and its incorporation into the biota. This retention at the sediment is due to the predominance of aerobic conditions of hipolimnium despite the low concentrations of oxygen at this layer.

Climatic and hydrological events have a strong influence on the physical, chemical and biological processes in

Table 5. Mann-Whitney U Test for the differences in concentrations of chlorophyll-*a* between months sampled.

Month	U	Z	p
March/02 and July/02	7.0	–2.63	0.009
March/02 and September/02	7.5	–2.57	0.010
March/02 and November/02	6.0	–2.73	0.006
March/02 and January/03	4.0	2.95	0.003
May/02 and July/02	8.5	–2.47	0.014
May/02 and September/02	10.5	–2.26	0.024
May/02 and November/02	7.0	–2.63	0.009
May/02 and January/03	0.0	–3.37	<0.001
May/02 and March/03	4.0	2.94	0.003
July/02 and January/03	0.0	3.37	<0.001
July/02 and March/03	0.0	3.36	<0.001
September/02 and January/03	0.0	3.37	0.001
September/02 and March/03	0.0	3.36	0.001
November/02 and January/03	0.0	3.37	0.001
November/02 and March/03	4.5	–2.90	0.004
January/03 and March/03	4.5	–2.90	0.004

reservoir (Mariani et al., 2006), mainly through the interface with nutrient balance (Beyruth et al., 1997). Higher values of total nitrogen and phosphorus as well as of soluble reactive phosphorus and nitrate-nitrogen are registered during the dry period, possibly due to the resuspension of the sediment by the wind action which enriches the water and the sewage loads from the tributaries as demonstrated by Beyruth (2000) for Guarapiranga Reservoir, São Paulo. During the rain period due to dilution, lower concentrations of these nutrients were registered in the reservoir except for ammonium-nitrogen, whose higher concentrations reflect higher flow of allochthonous material and subsequently higher consumption of dissolved oxygen. According to Beyruth et al. (1997) high concentrations of ammonium-nitrogen reflect recent pollution.

Although Ibirité reservoir exhibits a warm-monomictic circulation/stratification pattern as reflected by its dissolved oxygen distribution this pattern was not identified for pH and electrical conductivity. For these variables it was evident a gradient throughout the year showing small variations along the water column.

The seasonal variation of chlorophyll-*a* concentration follows the ones of phosphorus (total and soluble) and nitrogen (nitrate-nitrogen) although it was only found a weak relation with total nitrogen and nitrate. A lower correlation between nutrients (total N and P) and chlorophyll was also demonstrated by Huszar et al. (2006). Furthermore, other mechanisms such as nutrient re-suspension, turbidity, and complex food web interactions could also explain the weak relationship between nutrients and chlorophyll concentrations recorded at Ibirité reservoir.

The peak of chlorophyll was observed in the dry period when the highest concentrations of soluble reactive phosphorus and nitrate-nitrogen were also recorded. The great decrease on chlorophyll-*a* concentration recorded in October/02 is the direct result of copper sulfate application, a widely used algaecide for drastic control of algae blooming. According to Mariani et al. (2006), *Microcystis* is a common alga in eutrophic tropical reservoirs and blooms frequently in Brazilian reservoirs. During the period of the present study *Microcystis aeroginosa* and *Microcystis* sp were the main species registered during the blooms.

The cooper sulfate application, although largely used, has several adverse effects, mainly considerable alterations on the composition and density of the species, as well as on the water quality as demonstrated in studies developed by Beyruth et al. (1997) and Beyruth (2000)

These results constitute a first step for the development of sound management and conservation strategies for Ibirité watershed. The project research in cooperation with REGAP, still continue and other strategies and interventions are now being propose following these preliminary data. So far it was possible to demonstrate the importance of point and non-point pollution sources affecting the quality of the reservoir's water as well as its role on the retention of suspended material and nutrients thus improving the quality of downstream waters as demonstrated previously for upper-medium Tietê reservoir cascade by Barbosa et al. (1998).

In conclusion, a warm-monomictic pattern was identified and, also recorded for dissolved oxygen. Furthermore, it could also be demonstrated a low nutrient-chlorophyll relationship being evident the prevailing eutrophic conditions for the reservoir which exhibits considerable temporal but not spatial differences in water quality.

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