Acta Limnologica Brasiliensia, 2011, vol. 23, no. 2, p. 200-216

Spatial evaluation of water quality in an urban reservoir (Billings Complex, southeastern Brazil)

Avaliação espacial da qualidade da água em reservatório urbano (Complexo Billings, sudeste do Brasil)

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Abstract: Aim: The study aimed at (a) contributing to a spatial evaluation of the Billings Complex water quality; (b) associating information on the geochemistry of the surface sediments; and (c) providing, based on previous studies, a temporal evaluation of the Complex's water quality since the Pinheiros River pumping restriction; Methods: sampling was performed at 12 sites: 2 in the Central body (CB), 3 in the Taquacetuba branch (TQ), 3 in the Rio Pequeno branch (RP) and 4 in the Rio Grande Reservoir (RG). Water samples were taken along a vertical profile during the winter (August 2009) and summer (February 2010) and in the surface sediments (2 cm) during the winter. Physical and chemical characteristics of water and sediments were evaluated. Lamparelli's Trophic State Index (TSI) was calculated; Results: limnological variability was mostly affected by the season. The spatial heterogeneity of the Complex was more pronounced during winter, with greater differences among its compartments. Nitrogen was higher in the winter, whereas in the summer there was a substantial phosphorus increase along with a nitrogen decrease. The most degraded compartments, associated with the highest nutrient levels, were CB and TQ. In contrast, the upstream region of the RP branch was considered a reference site (the least impacted) for the Complex; Conclusion: The Billings Complex ranged from mesotrophic (RP) or eutrophic (RG) to super-eutrophic (CC, TQ). High TSI variation also occurred within compartments and/or depending on the season, mainly associated with the human management of the Complex. The surface sediments underlined the differences observed between the extremes in the Billings Complex water quality, as well as providing additional information on other impacts that was not observed from the water analysis. A slight improvement in the water quality of the Central body and the Taquacetuba branch has been observed since 2009, possibly associated with the Pinheiros River flotation project.

Keywords: eutrophication, reservoir, surface sediments, trophic state index.

Resumo: Objetivos: Este estudo visa a (a) contribuir com a avaliação espacial da qualidade da água do Complexo Billings; (b) associar informações sobre a geoquímica dos sedimentos superficiais e (c) com base em literatura, fornecer uma avaliação temporal da qualidade da água no Complexo desde a restrição do bombeamento do Rio Pinheiros; Métodos: As amostragens foram realizadas em 12 locais: 2 no Corpo Central (CB), 3 no Braço Taquacetuba (TQ); 3 no Braço Rio Pequeno (RP) e 4 na Represa Rio Grande (RG). A coleta da água foi realizada ao longo do perfil vertical no período de inverno (agosto/2009) e verão (fevereiro/2010) e a dos sedimentos superficiais (2 cm), no inverno. Foram avaliadas características físicas e químicas da água e dos sedimentos, e foi calculado o índice de estado trófico (IET) de Lamparelli; Resultados: As condições limnológicas foram primordialmente influenciadas pelos períodos climáticos. No inverno, a heterogeneidade no Complexo foi mais definida com separação de seus compartimentos espaciais. Maior disponibilidade das formas nitrogenadas ocorreu no inverno, enquanto que, no verão, estas diminuíram e o fósforo apresentou aumento substancial. Os compartimentos mais degradados e associados aos maiores valores de nutrientes foram CB e TQ. De forma inversa, destaca-se o RP, cuja região a montante foi considerada de referência (menos impactada) no Complexo; Conclusão: Complexo Billings variou de mesotrófico (RP), eutrófico (RG) a supereutrófico (CB e TQ). Variação marcada do IET também ocorreu dentro dos compartimentos e dependendo do período climático, principalmente, associada ao manejo antrópico do Complexo. Os sedimentos salientaram os extremos de qualidade da água e forneceram informações adicionais sobre impactos antrópicos não detectados pela análise da água. Houve leve melhora da qualidade da água do CB e TQ a partir de 2009, possivelmente associada ao projeto de flotação do Rio Pinheiros.

Palavras-chave: eutrofização, índice de estado trófico, reservatório, sedimentos superficiais.

1. Introduction

The deterioration of lake and reservoir waters was one of the 20th century's largest and most wide-spread environmental problems, and is one of the greatest challenges that humanity faces in the present century (MA, 2008). The water crisis is of global extent, since it hampers public health and social and economic development, as well as endangering the ability to sustain life on this planet (Tundisi, 2005; UNDP, 2006; Ribeiro, 2008). Among the environmental issues, eutrophication is a worldwide problem that is still far from being solved, despite the huge number of studies documenting its causes (Sayer and Robert, 2001, Battarbee et al., 2005). Even so, eutrophication is often considered a local issue (Carpenter and Bennett, 2011).

The São Paulo Metropolitan Region (SPMR) is the largest South American megalopolis and at present the second in the world with respect to scarcity of adequate water resources for consumption (PROAM, 2006; Whately and Cunha, 2006). This situation is of great concern since the SPMR already imports almost 50% of its water supply from another hydrographic basin, the Piracicaba River basin.

The Billings Complex is the largest water-storage facility in the SPMR, and has multiple uses, including public water supply, energy generation, and recreation (Carvalho et al., 1997). Considering its natural discharge of 14 m^3/s, the Complex could provide water for about 4.5 million people, but this number dropped to one million people due to its severe water contamination (Capobianco and Whately, 2002). One of the Billings Complex's greatest problems is its conflicting uses, especially related to water supply and energy generation. Since the 1940s, the Complex has received a large part of the SPRM sewage via the Tietê and Pinheiros rivers, in order to augment the discharge for electricity generation. Since 1992, pumping from these rivers has been limited to periods of flood risk and energy crises (Capobianco and Whately, 2002). From 1958 on, the SPRM has received additional water supplies from the Rio Grande Reservoir, which has been totally isolated from the Billings Reservoir since 1982; and from the Taquacetuba branch (via water transfer to the Guarapiranga Reservoir) since 2000, whenever necessary (Capobianco and Whately, 2002). During the last four years, two important events had negative and positive impacts on the Complex basin: the Pinheiros River flotation (2007-2009), aiming at improving its water quality for pumping to the Billings Reservoir (EMAE, 2011); and the construction of the southern part of the Rodoanel, a perimeter highway. from 2007 to 2010 (GESP, 2011).

Limnological studies of the Billings Complex started only 20 years after the pumping from the Pinheiros River, triggered by pollution, the appearance of algal blooms, and the need for potable water (Branco, 1959, 1966). Since then, the Rio Grande Reservoir and the Taquacetuba branch, both used for domestic water supply, have been more intensively studied (Maier et al., 1997; Beyruth and Pereira, 2002, Moschini-Carlos et al., 2009, 2010). The Billings Central body, the area that receives the Pinheiros River, has also been investigated (Carvalho et al., 1997, Lamparelli, 2004). These three sites are part of a monitoring program (e.g., Cetesb 1996, 2010). The Rio Pequeno branch has received much less attention (Souza et al., 1998).

Regarding the reservoir bottom sediments, contributions are more recent and focused mainly on the Central body and the Rio Grande Reservoir. These studies aimed mainly at evaluating the sediment quality and metal contamination (e.g., Soares and Mozeto; 2006; Fávaro et al., 2007, Mariani and Pompêo, 2008). Particularly, information on carbon, nitrogen and phosphorus is very scarce (Silvério, 2003) and mostly provided by the Cetesb monitoring program, in operation since 2002 (e.g., Cetesb, 2003, 2010).

Therefore, wider spatial studies on the water quality of the Billings Complex, as well as on the geochemistry of the surface sediments, are practically nonexistent. Carvalho et al. (1997) characterized the Billings Complex water quality with emphasis on the phytoplankton community, and Capobianco and Whately (2002) provided a comprehensive characterization of the Billings drainage basin, including land use and socio-environmental implications.

The present paper aims at contributing to a more complete spatial evaluation of the Billings Complex water quality, including the Rio Pequeno branch, as well as the spatial variation within the Billings compartments. It also endeavors to associate information on the geochemistry of the surface sediments, since the sediments integrate information on a larger time scale. Finally, based on the literature, this paper presents an evaluation of the Complex water quality since the restriction on pumping from the Pinheiros River.

2. Material and Methods

2.1.Study area

The Billings Complex is located in the State of São Paulo, southeast Brazil (23° 47' S, 46° 40' W), in a highly populated (~14 million people) urban area (Figure 1). It was built in the 1920s, and has a drainage area of 560 km^2, surface area of 120 km^2, volume of 1.20 × 10^9 m^3, maximum depth of 18 m and water residence time of 392 days (Carvalho et al., 1997; Cetesb, 2007). The Complex has a dendritic pattern, with a narrow and elongated Central body and several compartments (branches), of which one, the Rio Grande, is independent. The water output through the Summit Control channel connects the Billings Reservoir to the cascade Rio das Pedras Reservoir. Due to this configuration, the principal water flow passes mainly through the longest central axis of the reservoir (Cetesb, 2003). The water volume control for the Billings Complex is done by Sabesp (by pumping out water and controlling the volume of the Rio Grande reservoir, and transferring water from the Taquacetuba branch) and by EMAE (water input through the Pinheiros channel and output through the Summit Control channel).

2.2.Sampling data

Twelve sampling stations were defined (Figure 1), distributed along the Rio Grande reservoir (1-4), Rio Pequeno branch (5-7), Central body (8-9) and Taquacetuba branch (10-12). The depth of sampling sites varied within and among compartments (Z_{max} for RG1 = 12 m, RG2 = 10 m, RG3 = 9 m, RG4 = 5 m, RP5 = 8 m, RP6 = 6 m, RP7 = 2 m, CB8 = 14 m, CB9 = 9 m, TQ10 = 12 m, TQ11 = 4 m, and TQ 12 = 8 m).

Sampling was carried out during the winter (August 2009) and summer (February 2010). Water samples were collected with a van Dorn sampler along the reservoir vertical profile (euphotic zone, mean depth, and 1 m above the sediments), and were transferred to acid-rinsed polyethylene vials.

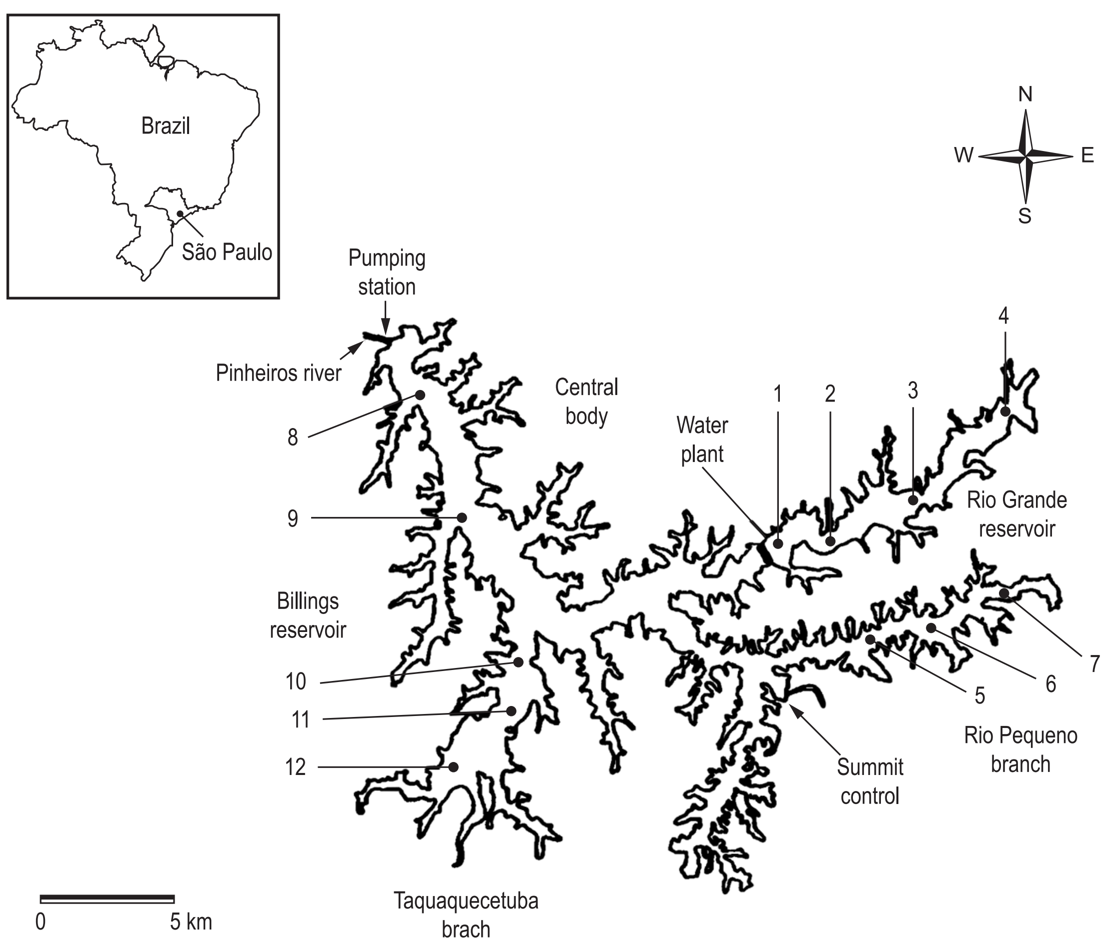

Figure 1. Billings Complex and locations of sampling sites: Rio Grande Reservoir (1-4), Rio Pequeno branch (5-6), Central body (8-9), and Taquacetuba branch (10-12). Adapted from Carvalho et al. (1997).

Temperature, pH and electrical conductivity were measured in the field at every 50-cm depth, using standard electrodes (Eureka Amphibian). The following water variables were also measured on the day of sampling: water transparency (Secchi disk), alkalinity (Golterman and Clymo, 1969), free CO_2, HCO_3^- and CO_3^{2-} (Mackereth et al., 1978), dissolved oxygen (Winkler modified by Golterman et al., 1978), ammonium (N-NH_4) (Solorzano, 1969), nitrate (N-NO_3^-) and nitrite (N-NO_2^-) (Mackereth et al., 1978), soluble reactive phosphorus (SRP) and total dissolved phosphorus (TDP) (Strickland and Parsons, 1965), and soluble reactive silica (Golterman et al., 1978). Chlorophyll-*a* corrected for phaeophytin analysis was measured within at most one week from the day of sampling, using 90% ethanol as the organic solvent (Sartory and Grobbelaar, 1984). Unfiltered samples were frozen and later used within at most 30 days from the collection date, for total nitrogen (TN) and total phosphorus (TP) determinations (Valderrama, 1981). Nitrogen–ammonium concentrations were added to obtain the final TN levels.

Surface sediments (2 cm) were collected during the winter, with a gravity corer. The geochemical analyses included total phosphorus (TP), total organic carbon (TOC) and total nitrogen (TN). TP was analyzed by the colorimetric method (Valderrama, 1981) after acid digestion with nitric and perchloric acids (Andersen, 1976). TOC and TN concentrations were analyzed using a Carlo Erba EA 1110 elemental analyzer (Hedges and Stern, 1984). Grain size was determined by a CILAS 1064 L laser granulometer (Blott and Pye, 2001).

2.3. Data analysis

Multivariate Principal Components Analysis (PCA) was used to ordinate sampling stations and periods in relation to environmental data. Before computation, variables were transformed by ranging, to more closely approximate the linear relationship assumed during the PCA. Data transformation and PCA were carried out using the FITOPAC program (Shepherd, 1996) and PC-ORD, version 5.15 (McCune and Mefford, 2006), respectively.

The Trophic State Index (TSI) was calculated according to Lamparelli (2004) without considering the Secchi disk transparency, since this parameter was not always associated with biogenic transparency (Equation 1).

$$TSI = [TSI (Chl) + TSI (TP)]/2 \quad (1)$$

where:
TSI (Chl) = 10{6-[(0.92-0.34 ln Chl)/ n 2]};
TSI (TP) = 10{6-[(1.77-0.42 ln TP)/ln 2]};
TP = total phosphorus ($\mu g.L^{-1}$); and
Chl = Chlorophyll-*a* ($\mu g.L^{-1}$);

Limits used are: ultra-oligotrophic (TSI ≤ 47), oligotrophic (47 < TSI ≤ 52), mesotrophic (52 < TSI ≤ 59), eutrophic (59 < TSI ≤ 63), super-eutrophic (63 < TSI ≤ 67) and hypereutrophic (> 67).

For literature data comparison, TSI was also calculated according to the above equation.

3. Results

3.1. Limnological variables

Sampling periods were not typical, considering the precipitation regime. The winter was rainier than the historical average for the region (53 mm), with an increase of 71% (90.8 mm). During the summer, precipitation was also more intense, with an increase of 50% (314.7 mm) over the historical average (208.6 mm) for the region (Sabesp, 2011). Nevertheless, the water surface temperature followed a regular pattern for the two climate periods, with higher means during the summer (27.3 °C) than in the winter (17.9 °C).

The depth of Secchi disk disappearance was usually greater during the winter than in the summer. In winter, it was especially deep in the branches used for public supply (Rio Grande branch: 1.1 to 3.0 m, and Taquacetuba branch: 1.0 to 2.3 m). During the summer there was little variation among the Billings Complex branches (RG: 1.1-1.6 m; RP: 1.0-1.5 m; CB: 1.0-1.3 m; TQ: 0.7-0.9 m).

The dissolved oxygen concentration (Tables 1 and 2) decreased toward the bottom of the Central body (mainly at CB8) and the Taquacetuba branch during the winter. During the summer, this trend was observed at all sampling stations, with oxygen contents at the bottom close to anoxia, except for stations RP6 and RP7. The pH varied from slightly acid to alkaline, and the lowest values were observed in the upstream section of the Rio Pequeno branch (RP7: ~5.0) during both seasons, whereas the highest pHs were measured at stations RP5 (8.8), TQ10 (8.2), TQ10 (8.1) and TQ11 (8.6). Electrical conductivity was considerably higher during the winter in the Central body, and much lower in the Rio Pequeno branch, mainly in the upstream region (RP7) (Tables 1, 2).

Table 1. Limnological variables in the Billings Complex during the winter period. RG: Rio Grande Reservoir, RP: Rio Pequeno branch, CB: Central body, TQ: Taquacetuba branch, S: water surface, M: mean depth, B: 1 m above the sediments; < Below the method detection limit.

	Sampling stations	Chl-*a* ($\mu g.L^{-1}$)	Temp. (°C)	Conductivity ($\mu S.cm^{-1}$)	pH	DO ($mg.L^{-1}$)	$N\text{-}NH_4$ ($\mu g.L^{-1}$)	$N\text{-}NO_3$ ($\mu g.L^{-1}$)	$N\text{-}NO_2$ ($\mu g.L^{-1}$)	TN ($\mu g.L^{-1}$)	TP ($\mu g.L^{-1}$)	CO_2 ($mg.L^{-1}$)	HCO_3 ($mg.L^{-1}$)
RG	1S	16.48	17.79	225.95	7.41	6.08	88.28	72.75	20.48	688.47	17.43	1.92	28.57
	1B	7.69	17.14	224.90	7.08	5.43	137.25	82.26	17.66	706.98	23.98	4.64	29.40
	2S	12.63	17.30	225.64	7.10	5.71	118.44	95.78	16.08	699.89	19.98	4.24	28.12
	2B	13.73	17.08	225.60	6.95	5.07	169.19	87.52	13.80	749.47	16.95	6.26	29.41
	3S	18.67	17.30	196.86	7.14	7.66	566.29	76.86	17.43	1220.36	19.82	4.00	29.12
	3B	10.98	16.92	206.10	6.91	7.71	654.66	79.12	14.47	1493.79	18.23	6.29	29.56
	4S	33.50	17.11	141.57	7.11	8.52	1190.35	48.65	39.67	2143.09	71.42	4.25	28.88
	4B	36.80	17.05	142.00	7.26	7.31	1267.59	49.97	38.70	2144.20	75.57	3.02	28.99
RP	5S	37.90	18.05	143.83	8.85	8.33	28.66	68.24	<5	1166.11	18.71	0.08	32.70
	5M	39.54	16.87	150.50	7.90	6.50	38.95	67.09	<5	1137.71	23.34	0.84	35.12
	5B	36.80	16.66	139.10	7.45	5.34	303.33	65.86	<5	1146.87	18.07	2.17	32.22
	6S	42.84	17.63	73.38	7.55	7.50	27.95	18.03	<5	397.55	20.78	0.80	16.35
	6M	41.19	16.74	73.30	7.48	6.84	33.27	22.45	<5	1044.27	17.25	0.99	15.69
	6B	42.29	16.56	74.00	7.26	6.38	41.79	20.70	<5	272.23	17.91	1.60	15.38
	7S	6.59	18.08	31.70	5.11	5.21	126.60	171.60	<5	610.04	<4	37.40	2.81
	7B	0.00	17.42	32.00	5.18	5.20	148.96	158.97	<5	655.84	<4	73.79	5.89
CB	8S	26.36	18.04	291.42	6.93	4.25	3259.10	955.23	10.81	4291.90	46.34	13.02	64.06
	8M	9.89	17.49	287.90	6.93	2.46	2414.50	1098.31	9.56	3648.75	31.64	13.53	60.68
	8B	12.08	17.35	288.20	6.88	1.63	2645.16	1032.57	12.17	3974.62	31.64	16.43	65.69
	9S	64.26	18.62	276.95	7.24	6.36	1490.01	868.49	45.39	2976.35	51.77	5.51	55.79
	9M	21.97	18.20	276.70	7.15	4.53	1664.04	1009.00	50.38	3991.85	27.97	6.60	53.89
	9B	12.63	17.63	275.35	7.00	2.70	1362.51	1199.61	25.39	3964.16	23.18	9.28	52.99
TQ	10S	44.82	18.72	240.53	8.24	7.23	44.98	706.08	11.97	1452.291	32.60	0.48	48.33
	10M	5.27	18.25	239.70	7.81	6.47	48.89	442.60	6.43	1052.20	16.63	1.26	47.18
	10B	0.00	17.41	231.10	7.23	3.64	59.18	429.48	6.73	886.14	15.19	5.31	47.55
	11S	7.69	18.22	238.53	7.25	4.99	41.43	624.83	9.03	1302.81	17.11	4.88	49.82
	12S	59.32	18.72	209.26	7.33	6.22	32.21	327.96	<5	1410.85	55.44	3.53	43.83
	12M	3.95	18.52	212.20	7.33	5.52	155.71	332.32	<5	897.66	15.67	3.54	43.77
	12B	6.15	17.34	201.60	6.98	2.65	258.62	247.07	<5	1074.78	14.55	8.78	44.19

Table 2. Limnological variables in the Billings Complex during the summer period.

Sampling stations		Chl-*a* ($\mu g.L^{-1}$)	Temp. (°C)	Conductivity ($\mu S.cm^{-1}$)	pH	DO ($mg.L^{-1}$)	$N\text{-}NH_4$ ($\mu g.L^{-1}$)	$N\text{-}NO_3$ ($\mu g.L^{-1}$)	$N\text{-}NO_2$ ($\mu g.L^{-1}$)	TN ($\mu g.L^{-1}$)	TP ($\mu g.L^{-1}$)	CO_2 ($mg.L^{-1}$)	HCO_3 ($mg.L^{-1}$)
RG	1S	17.14	26.86	44.00	6.99	6.17	13.40	<8	<5	204.14	13.47	4.00	24.19
	1M	7.47	23.84	52.00	6.43	0.97	529.59	<8	<5	920.001	<4	16.02	26.71
	1B	1.76	22.01	98.00	6.59	0.32	482.02	<8	16.29	3254.65	15.00	22.10	49.7
	2S	15.38	27.79	43.00	6.50	6.49	<10	<8	<5	130.46	<4	11.95	24.51
	2M	21.53	23.64	53.00	6.32	4.38	135.87	<8	<5	355.54	<4	19.04	24.64
	2B	26.36	22.77	68.00	6.40	0.24	254.29	<8	10.43	1848.28	<4	23.01	35.8
	3S	21.53	27.32	43.00	6.20	6.16	11.37	<8	<5	198.44	<4	23.18	22.75
	3M	29.88	26.17	43.20	6.39	5.11	22.51	<8	<5	185.94	<4	17.05	25.92
	3B	6.15	25.28	49.00	6.06	0.97	468.86	<8	8.37	895.13	25.00	39.03	27.75
	4S	30.76	26.38	51.67	6.68	3.08	460.77	<8	8.40	1473.60	108.94	9.50	28.17
	4B	11.42	24.34	67.00	6.22	0.65	1054.44	<8	<5	2731.89	115.95	34.30	35.25
RP	5S	32.51	27.76	50.83	6.05	6.25	<10	26.81	<5	201.33	<4	26.15	19.03
	5M	24.61	24.92	46.00	6.15	3.65	52.87	72.90	<5	195.22	<4	22.31	19.52
	5B	11.42	24.18	35.00	5.78	1.06	262.39	12.39	<5	495.13	<4	45.12	16.83
	6S	14.94	27.30	36.00	5.53	5.92	<10	<8	<5	270.20	<4	90.41	18.97
	6M	27.24	25.27	38.00	5.59	3.08	43.76	<8	<5	194.40	<4	66.33	15.98
	6B	21.97	24.77	34.00	5.56	2.59	82.22	<8	<5	189.92	<4	66.47	14.94
	7S	28.56	27.49	35.33	5.28	5.52	<10	<8	<5	206.22	<4	114.24	13.48
	7B	28.12	26.49	29.00	5.34	4.38	<10	<8	<5	390.00	4.00	98.60	13.36
CB	8S	41.74	25.97	99.71	5.98	4.87	347.41	224.43	95.47	4448.02	107.67	43.63	25.8
	8M	45.04	25.24	101.00	6.33	4.95	364.61	207.60	100.26	3981.07	102.35	37.63	49.83
	8B	24.17	24.94	100.00	6.49	3.97	507.33	191.20	109.13	3844.83	96.51	26.93	51.53
	9S	37.35	26.77	93.17	6.80	3.33	262.39	85.30	58.88	4001.76	128.71	14.82	57.91
	9M	4.39	26.63	93.00	6.79	1.05	370.69	<8	7.93	4928.02	149.59	16.54	63.16
	9B	12.08	26.19	94.00	6.77	0.41	621.70	<8	6.24	5743.82	214.62	17.07	62.24
TQ	10S	53.82	27.57	91.20	8.14	6.49	24.53	305.22	57.19	1636.38	87.42	0.55	47.07
	10M	71.40	26.52	91.00	7.37	3.17	20.48	82.17	56.49	1250.10	63.04	3.40	49.35
	10B	5.49	25.05	91.00	7.04	0.98	487.08	33.75	22.57	1651.10	71.80	6.34	43.08
	11S	54.92	28.07	93.00	8.38	7.14	<10	78.15	50.72	1637.30	90.77	0.31	47.95
	11B	47.23	27.78	92.00	8.58	6.98	<10	83.04	55.36	1644.48	90.61	0.19	47.58
	12S	50.53	28.14	94.25	7.98	6.00	<10	81.37	24.40	933.76	68.77	0.74	45.76
	12M	51.63	27.82	93.00	7.90	5.60	<10	68.25	22.71	1280.96	75.31	0.90	46.58
	12B	25.26	26.61	89.00	7.32	3.40	<10	52.99	25.66	1481.24	75.31	3.59	46.44

RG: Rio Grande Reservoir, RP: Rio Pequeno branch, CB: Central body, TQ: Taquacetuba branch, S: water surface, M: mean depth, B: 1 m above sediments; < Below the method detection limit.

Regarding nutrients, the nitrogen series (NH_4, NO_3 and TN) was markedly higher in the Central body during the winter (Table 1, Figure 2). In summer, ammonium concentrations (Figure 2b) were higher in the Central body as well as at the bottom of all other compartments, whereas nitrate levels (Table 2, Figure 2a) were below the method detection limit in the Rio Grande reservoir and part of the Rio Pequeno branch. The highest values were usually observed in the Central body. Total nitrogen levels showed a similar trend during the winter, however with consistently higher levels in the Central body (Table 2, Figure 2c). Dissolved phosphorus fractions were mostly below the method detection limit during the winter, except for the Central body (TDP: 10.2-30.4 $\mu g.L^{-1}$), Taquacetuba branch (TDP: 10.8-23.0 $\mu g.L^{-1}$) and upstream in the Rio Grande Reservoir (TDP: 35.0-35.4 $\mu g.L^{-1}$; SRP: 27.6-28.4 $\mu g.L^{-1}$). During the summer, values above the method detection limit were only observed at the bottom at the Rio Grande Reservoir sampling stations, and in the upstream region (PDT: 10.3-23.4 $\mu g.L^{-1}$; SRP: 8.8-17.3 $\mu g.L^{-1}$), as well as at the Central body sampling station CB9 (TDP: 12.4-94.0 $\mu g.L^{-1}$; SRP: 9.9-90.5 $\mu g.L^{-1}$). Total phosphorus concentrations increased markedly during the summer, mainly in the Central body, the Taquacetuba branch and station RG4 (Table 2, Figure 2d). The lowest chlorophyll-*a* levels were measured in the Rio Grande branch (RG1, RG2 and RG3) and upstream in the Rio Pequeno branch (RP7), whereas the highest levels were usually observed in the Central body (CB9) and the Taquacetuba branch (TQ10-12) (Tables 1-2, Figure 3).

The PCA performed with 14 limnological variables explained 55.8% of data variation on the first two axes (Table 3, Figure 4). The scores relative to the seasons were clearly separated by axes 1 and 2, mainly by the first component. Winter samples were mostly ordered on the positive side of axis 1, being positively correlated with the higher conductivity (r = 0.9), nitrate (r = 0.8), ammonium (r = 0.7) and total nitrogen (r = 0.5) values. On the negative side of this axis, summer samples were ordered, mainly from the Rio Pequeno branch, being associated

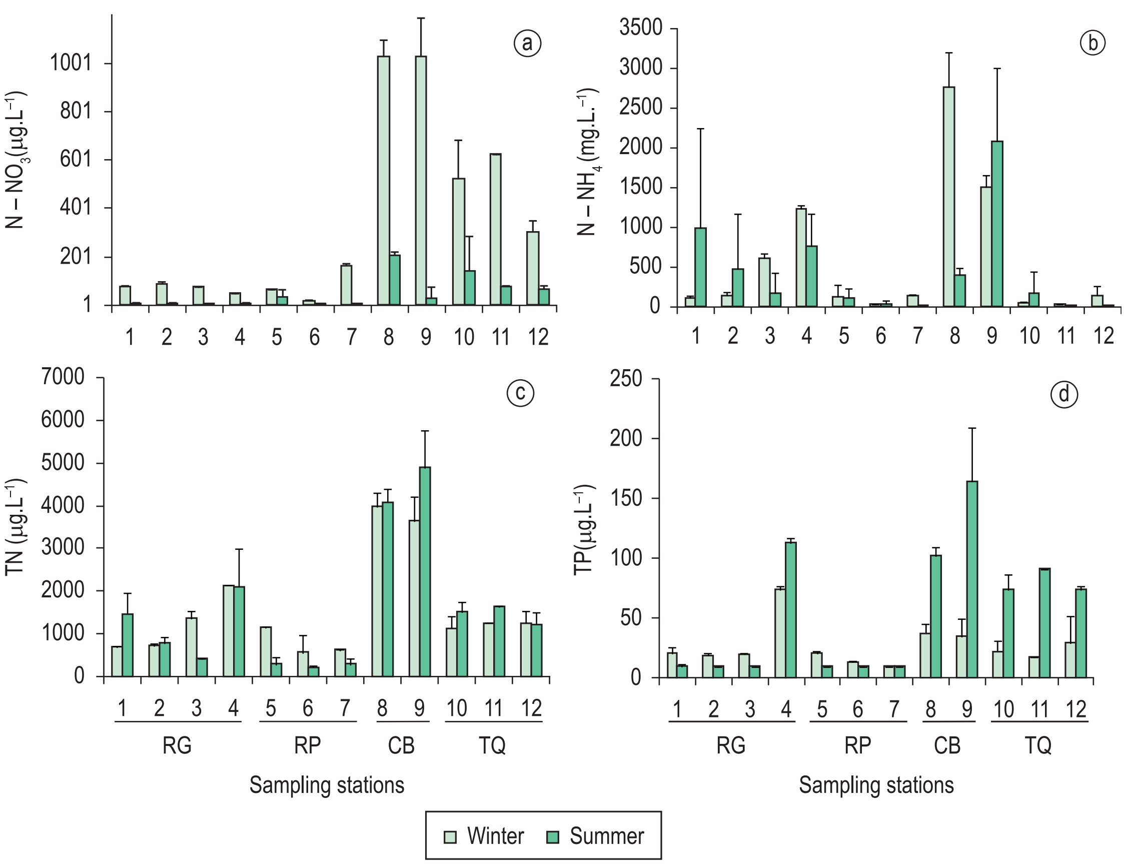

Figure 2. Mean nutrient concentrations for the water profile (and standard deviations) for the Billings Complex during winter and summer periods. Sampling sites: RG: Rio Grande Reservoir, RP: Rio Pequeno branch, CB: Central body, TQ: Taquacetuba branch: a) nitrate, b) ammonium, c) total nitrogen, d) total phosphorus.

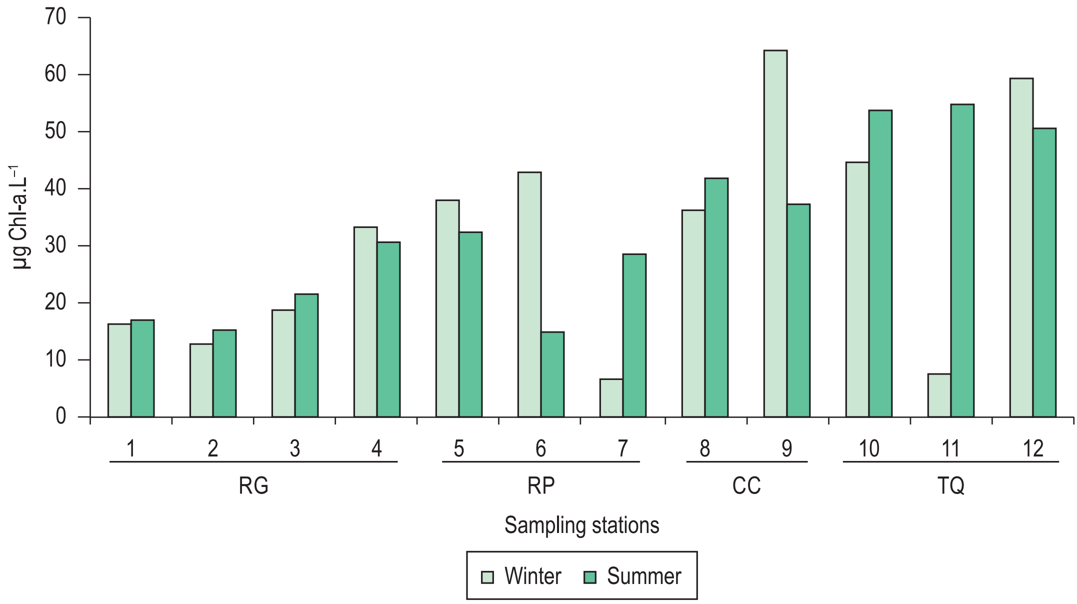

Figure 3. Chorophyll-a concentrations at the water surface in the Billings Complex during winter and summer periods. Sampling sites: RG: Rio Grande Reservoir, RP: Rio Pequeno branch, CB: Central body, TQ: Taquacetuba branch.

with the higher temperature and free CO_2 values ($r \geq 0.6$). Axis 2 ordered, on the negative side, the samples from the Central body (CB8, CB9) and the Taquacetuba branch (TQ10, TQ11) taken during the summer, which were mainly associated with the higher TP ($r = 0.8$), and TN values ($r = 0.7$). Despite the lower correlation ($r = 0.3$), these sampling units were also associated with the higher values of phytoplankton biomass (Table 3).

Considering the climate periods separately, two gradients were observed, represented by the dotted lines in Figure 4. During the winter, samples from the Central body (CB8, CB9) were associated with the greatest nitrogen availability, whereas those of the Rio Pequeno branch (RP6, RP7) were associated with the lowest nutrient (N and P) availability. During the summer, samples from the Central body (CB8, CB9) and the Taquacetuba branch (TQ10, TQ11) were associated with the greatest P and N availability, whereas at the opposite extreme, samples from the Rio Pequeno branch (RP7, RP6) were associated with the lowest availability of both N and P.

The trophic state index classified the Billings Complex as mesotrophic to hypereutrophic, depending on the sampling site and the climate period (Figure 5). The lowest indexes (mesotrophic) were always found in the Rio Pequeno upstream region (RP7). The mesotrophic condition was also found during the summer in the Rio Grande reservoir (RG2, RG3), which contributed to the decline in the TSI annual mean at these sites. The Rio Pequeno branch (RP5, RP6) was also mesotrophic during the summer. The highest indexes (super-eutrophic to hypereutrophic) occurred in the Central body and the Taquacetuba branch (except for TQ11, during winter), and in the upstream region of the Rio Grande reservoir (RG4).

3.2. Surface sediment variables

The granulometry showed a dominance of fine grains (< 63 µm) in the entire Billings Complex, with a prevalence of silt (2-31 µm), ranging from very fine to very coarse silt (80-90%). Larger sand grains and very coarse silt were found at station TQ10 (44%).

The highest percentages of TOC, TN and TP were observed in the Central body, mainly at station CB8, while the lowest occurred in the Rio Pequeno branch (Figure 6a-c). A higher TP contribution was also found in the upstream region of the Rio Grande Reservoir (RG4), where the level was 50% higher than at the remaining sampling stations of this compartment (RG01 to RG3) (Figure 6a). Two sites (TQ12 and CB8) showed the greatest TOC contribution (Figure 6c). Substantial reduction of TOC, TP and TN contributions was observed at station CB9 compared to CB8, and of TOC and TN at station TQ10 compared to the other stations in the Taquacetuba branch. The C:N atomic ratio

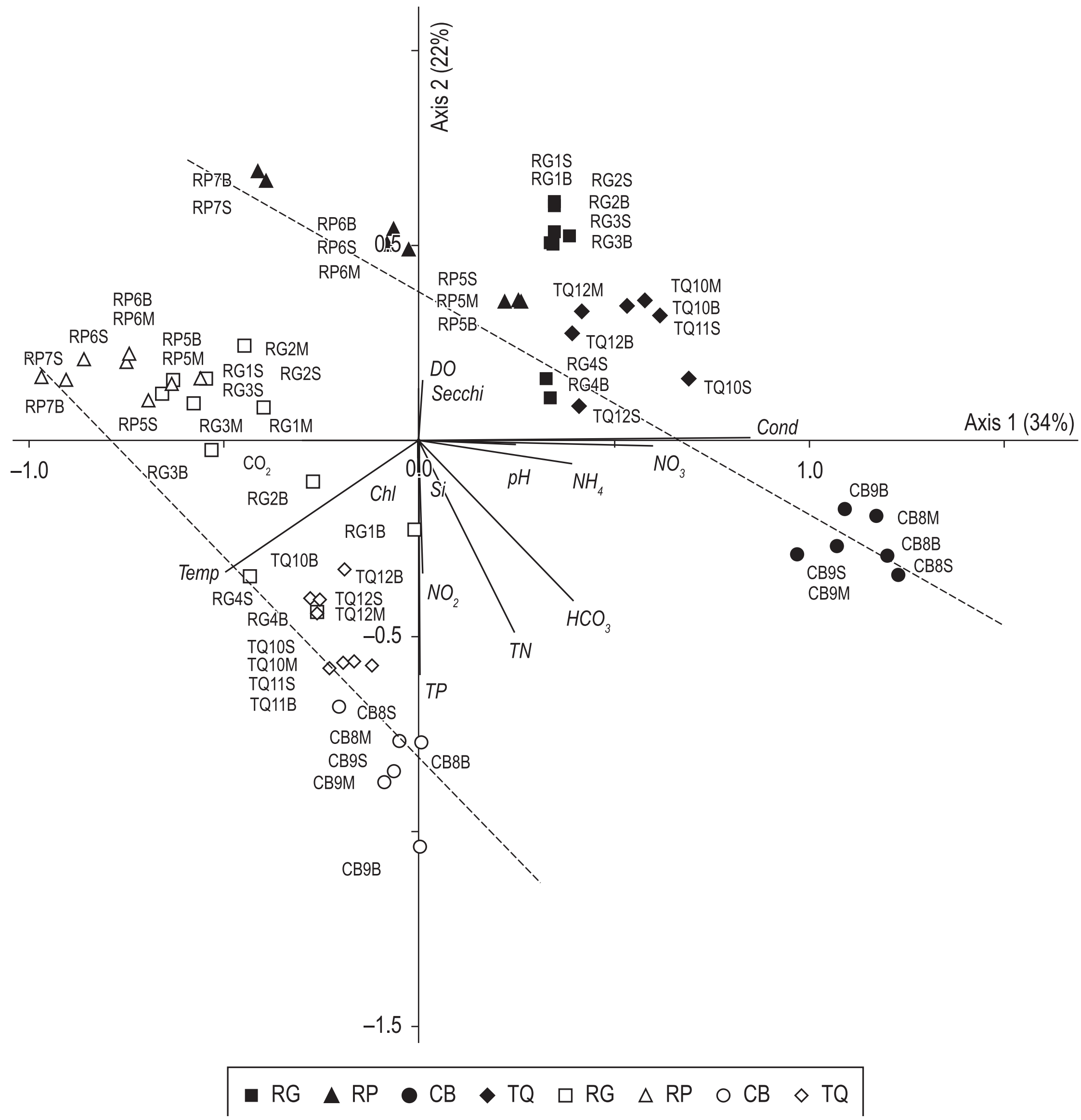

Figure 4. PCA biplot of limnological variables and scores for the sampling sites during the winter (solid symbols) and summer (open symbols). RG: Rio Grande Reservoir, RP: Rio Pequeno branch, CB: Central body, TQ: Taquacetuba branch; S: water surface, M: mean depth, B: 1 m above sediment. For correlation of variables with principal components and respective codes see Table 3.

was either lower than or close to 10 at the majority of the sampling stations (Figure 6d).

The PCA (85% variance) showed a clear-cut separation of the samples from Rio Pequeno and Taquacetuba (TQ10), which were ordered on the positive side of axis 1, associated with the highest sand contribution. On the negative side of this axis, CB8 was ordered associated with the highest carbon, nitrogen and phosphorus contribution (Table 4, Figure 7). Axis 2 mainly separated two sampling stations (TQ12 and RG4), due to their higher C: N ratio than at the Central body sites and TQ10.

4. Discussion

The limnological variability of the Billings Complex was mostly affected by the seasons, despite the atypical precipitation regimen, i.e., a rainier winter (dry season) and precipitation above the historical average for the summer period (Sabesp, 2011). The precipitation regime has important implications for the management of the Billings Complex, due to changes in the Pinheiros River sewage pumping (restricted to flooding control since 1992) and the Complex's water output, which is considered among the main driving forces in the main channel (Carvalho et al., 1997).

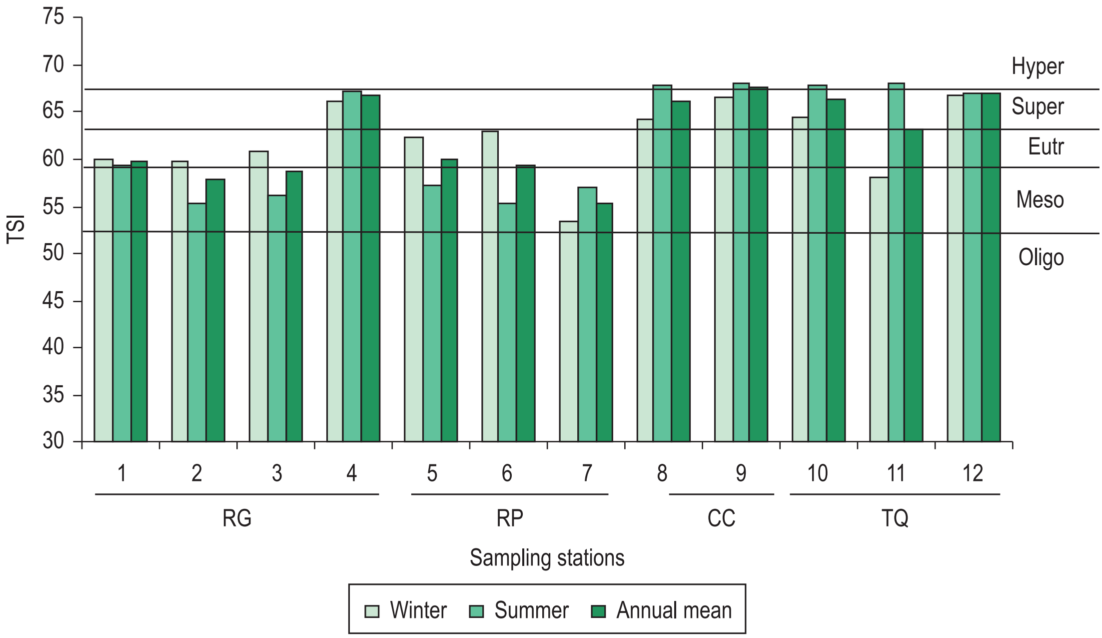

Figure 5. Trophic State Index (TSI) according to Lamparelli (2004) based on the average of chorophyll-*a* and total phosphorus for the Billings Complex (RG: Rio Grande Reservoir, RP: Rio Pequeno branch, CB: Central body, TQ: Taquacetuba branch). Values refer to winter (2009), summer (2010) and the annual mean.

Table 3. Loadings of limnological variables on the first two principal components (PC) and the proportion of variance explained by each component.

Variable	PC 1	PC 2
Temperature: Temp	–0.73	–0.60
Conductivity: Cond	0.95	0.09
pH	0.52	–0.12
Secchi depth	0.05	0.38
Dissolved oxygen: DO	0.10	0.40
Ammonium: NH_4	0.65	–0.26
Nitrate: NO_3	0.80	–0.13
Nitrite: NO_2	0.12	–0.61
Total nitrogen: TN	0.53	–0.72
Total phosphorus: TP	0.08	–0.80
Orthossilicate: Si	0.05	–0.21
Chlorophyll-*a*: Chl	–0.05	–0.31
Free CO_2: CO_2	–0.57	0.05
Bicarbonate: HCO_3	0.65	–0.65
Observed eigenvalue	18.7	11.9
Broken-stick eigenvalue	12.7	8.8
% of variance	34.2	21.63

Table 4. Loadings of geochemical variables on the first two principal components (PC) and the proportion of variance explained by each component.

Variable	PC 1	PC 2
Total organic carbon: TOC	–0.89	–0.28
Total phosphorus: P	–0.77	0.47
Total nitrogen: N	–0.92	0.31
C:N	0.05	–0.96
Sand	0.76	0.36
Observed eigenvalue	2.75	1.48
Broken-stick eigenvalue	2.26	1.27
% of variance	55.49	29.78

Limnological characteristics during the summer were more similar between the Central body and the Taquacetuba branch, most probably due to the Pinheiros River pumping, together with the greater connectivity of these compartments. On the other hand, the spatial heterogeneity was more pronounced during winter, with greater differences among the compartments. As indicated by the PCA, the main trends were a substantial increase in nitrogen availability during the winter (mainly in the Central body), and during the summer a decline in inorganic nitrogen (NO_3, NH_4) along with a pronounced increase in phosphorus availability, mostly in the Central body and the Taquacetuba branch.

According to the TSI estimated by Lamparelli (2004), Billings Complex sampling stations ranged from mesotrophic to hypertrophic, depending mainly on the compartment's location, thus reinforcing the Complex's spatial heterogeneity. The TSI also changed within compartments, particularly in the Rio Grande Reservoir and the Rio Pequeno branch, and also depended on the seasonal scale.

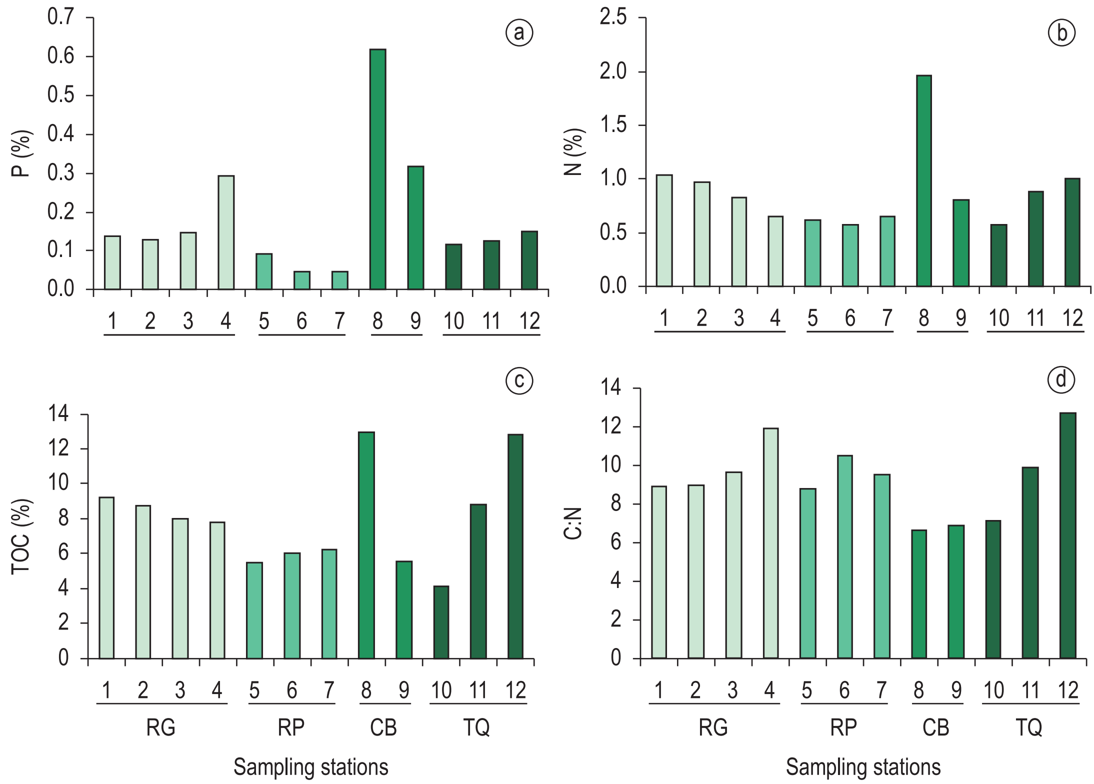

Figure 6. a) Total phosphorus %; b) total nitrogen %; c) total carbon organic matter % and d) C/N atomic ratio values for surface sediments in the Billings Complex (RG: Rio Grande Reservoir, RP: Rio Pequeno branch, CB: Central body, TQ: Taquacetuba branch).

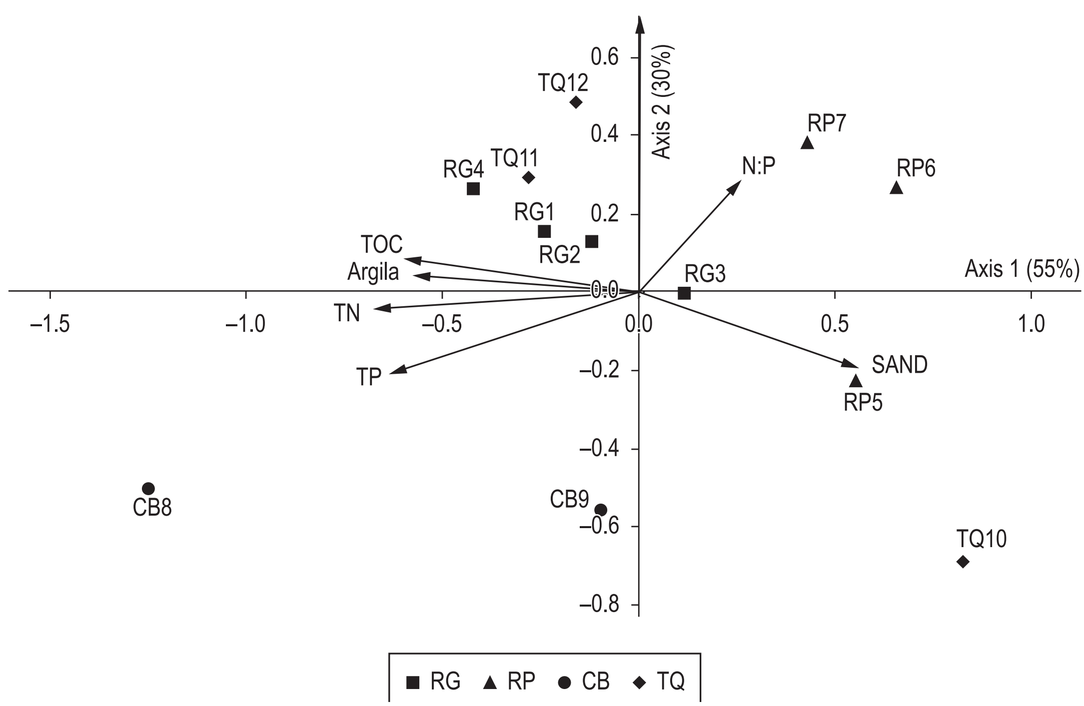

Figure 7. PCA biplot of surface sediment variables and scores for the sampling sites during the winter (RG: Rio Grande Reservoir, RP: Rio Pequeno branch, CB: Central body, TQ: Taquacetuba branch). For correlation of variables with principal components and respective codes see Table 4.

Table 5. Nutrient and chlorophyll-*a* concentrations (range and mean) for the water surface, trophic state index (TSI)*, sampling periods and sample number according to published literature on the Billings Complex since 1992. *TSI (Lamparelli, 2004) values were recalculated here, considering two variables (TP and Chl-*a*).

Compartments		NT (µg.L^{-1})	TP (µg.L^{-1})	Chl-a (µg.L^{-1})	TSI	Sampling period (*n*)	Reference
Central body	CB8	----	~50-4550 (958.3)	~0-65 (25)	hyper (73)	1992–93 (12)	Carvalho et al. (1997)
		2050-3940 (3076.6)	60-200 (86.6)	34.3-150.1 (88.6)	hyper (69)	1999 (6)	Cetesb (2000)
		6500	109	76.2	hyper (69)	1996–2001 (19)	Lamparelli (2004)
		510-5360 (2525)	50-210 (125)	28.9-146.3 (84.8)	hyper (70)	2006 (6)	Cetesb (2007)
		1120–3210 (1778.3)	40–110 (61.6)	32.4-127.5 (60)	super (67)	2009 (6)	Cetesb (2010)
		4291.9-4448.0 (4370.0)	46.4-107.6 (77)	26.4-41.7 (34.0)	super (66)	2009/2010 (2)	this study
	CB9	2976.4-4001.8 (3489.1)	51.7-128.7 (90.2)	37.3-64.2 (50.75)	hyper (68)	2009/2010 (2)	this study
Taquacetuba branch	TQ10	1452.3-1636.4 (1544.4)	32.6-87.4 (60)	44.8-53.8 (49.3)	super (66)	2009/2010 (2)	this study
	TQ11	1302.8-1637.3 (1470.0)	17.1-90.7 (53.9)	7.7-54.9 (31.3)	super (65)	2009/2010 (2)	this study
	TQ12	1360-3990 (2118.3)	30-180 (78.3)	21.3-226.4 (70.6)	hyper (68)	1999 (6)	Cetesb (2000)
		(1900)	(68)	(42.6)	super (66)	1996-2001 (17)	Lamparelli (2004)
		550-3850 (1586.6)	40-380 (136.60)	40.6-78.6 (59.7)	hyper (69)	2006 (6)	Cetesb 2007
		431.6-473.6 (452.6)	54.6-402.2 (228.4)	33.2-867.0 (450.1)	hyper (76)	2007 (2)	Moschini–Carlos et al. (2010)
		500-1180 (811.6)	20-40 (28.3)	5.9-30.4 (17.7)	eutr (62)	2009 (6)	Cetesb (2010)
		933.8-1410.8 (1172.3)	55.4-68.7 (62.0)	50.5-59.3 (54.9)	super (67)	2009/2010 (2)	this study
Rio Pequeno branch	RP5	600-2000 (1200)	30-120 (53,3)	----	----	1992-93 (12)	Souza et al. (1998)
		201.3-1166.1 (683.7)	<4-18.7 (11.3)	32.5-37.9 (35.2)	eutr (61)	2009/2010 (2)	this study
	RP6	270.2-397.5 (333.8)	<4-20.7 (12.3)	14.9-42.8 (28.8)	eutr (60)	2009/2010 (2)	this study
	RP7	206.2-610.4 (408.3)	<4-<4 (<4)	6.6-28.5 (17.55)	meso (56)	2009/2010 (2)	this study
Rio Grande Reservoir	RG1	700-1290 (1170)	30-160 (68.3)	1.53-9.15 (5.4)	eutr (61)	1999 (6)	Cetesb (2000)
		210-1740 (833.3)	25-190 (56.6)	3.4-14.4 (9.9)	eutr (62)	2003 (6)	Cetesb (2004)
		450-1410 (846.6)	< 20-90 (38.3)	6.3-24.3 (15.3)	eutr (62)	2006 (6)	Cetesb (2007)
		162.1-421.1 (291.6)	36.6-40.1 (38.35)	4.7-5.6 (5.1)	eutr (60)	2007 (2)	Moschini–Carlos et al. (2010)
		500-1780 (873.3)	20-80 (36.6)	8.6-22.4 (15.3)	eutr (62)	2009 (6)	Cetesb (2010)
		204.1-688.5 (466.3)	13.4-17.4 (15.4)	16.5-17.1 (16.8)	eutr (60)	2009/2010 (2)	this study
	RG2	130.5-699.89 (415.2)	<4-19.9 (11.9)	12.6-15.38 (13.9)	meso (58)	2009/2010 (2)	this study
	RG3	198.4-1220.4 (709.4)	<4-19.8 (11.9)	18.6-21.5 (20)	meso (59)	2009/2010 (2)	this study
	RG4	1473.6-2143.1 (1808.3)	71.4-108.9 (90.1)	30.7-33.5 (32.1)	super (67)	2009/2010 (2)	this study

Central body - The CB is undoubtedly the most degraded region of the Billings Complex, being super-eutrophic during the winter and hypertrophic during the summer at both sampling stations. Considering the annual average, this compartment is super-eutrophic. The highest levels of phosphorus and total nitrogen (summer) and both inorganic and total nitrogen (winter) occurred in the Central body. Phosphorus levels were 40-fold higher than in the Rio Pequeno branch and in the Rio Grande Reservoir (except for upstream, RG04). Despite the high concentration of nutrients, the chlorophyll-*a* concentrations were not the highest found, most probably because of light limitation and other factors such as aluminum contamination (Carvalho et al., 1997). Eutrophication in the Complex has been reported since 1951 (Rocha and Branco, 1985). This process was accelerated by the almost 70 years of continuous sewage pumping, produced in part by the SPMR (by reversion of the Pinheiros River), and also by the point and diffuse sewage inputs to the Central body as well as the resuspension of contaminated sediments (Capobianco and Whately, 2002). In October 1992, pumping of sewage and industrial effluents was suspended and restricted to flood control (Carvalho et al., 1997). However, based on the literature published from 1992 to 2006, the Central body remained hypereutrophic (Table 5). From 2009 on, the Central body has possibly changed to super-eutrophic, associated with the decline in chlorophyll-*a* and phosphorus levels (Table 5). This slight improvement in water quality may be associated with the Pinheiros River flotation pilot project started in 2007, which showed a ~90% TP removal efficiency (Cetesb, 2008; EMAE, 2010).

Taquacetuba branch – This branch, located near the reservoir's Central body, is also in a highly degraded state. All sampling stations were eutrophic during the winter, hypereutrophic during the summer, and, on an annual average basis, this branch was super-eutrophic. During the summer, there was a sharp decline in water quality in TQ, mainly due to the greater connectivity between this branch and the Central body, thus receiving a higher organic loading (greater reversion of the Pinheiros River during the flooding period), as well as additional loadings from its polluted tributaries (Capobianco and Whately, 2002). Furthermore, oxygen depletion towards the reservoir bottom provides suitable conditions for phosphorus internal loading, which along with the temperature increase and greater thermal stability favor the onset of cyanobacteria blooms (Bicudo et al., 2007). In fact, cyanobacteria blooms have been consistently reported for the Taquacetuba branch (Moschini-Carlos et al., 2009; Cetesb, 2010). On the temporal scale and similar to the Central body, from 2009 on, both phosphorus and chlorophyll-*a* concentrations have decreased, and the Taquacetuba branch changed from hypereutrophic to eutrophic/super-eutrophic (Table 5).

Rio Pequeno branch - This branch ranged from mesotrophic (RP7, upstream region) to eutrophic (RP5, RP6) during the winter, and was mesotrophic along the entire branch in summer. Considering the annual average, this compartment is mesotrophic. The greatest influence of the Central body on the Rio Pequeno branch (higher connectivity) occurred during the winter, not during the summer as observed for the Taquacetuba branch. Most probably, the decrease in the water discharge through the Summit Control (Figure 1) in a dry period (winter), associated with the increase of the Complex retention time, allowed the influx of the Central body waters into part of the Rio Pequeno branch (RP5, RP6). According to Capobianco and Whately (2002), the region next to the Central body (up to the Rio Pequeno mid-region) was eutrophic and contaminated with aluminum. Those authors considered that from this point (mid-region) on, there was no influence of the Central body waters, an interpretation not confirmed in the present study. In fact, *Cylindrospermopsis raciborskii* blooms have been reported for these regions (Carvalho et al., 1997; Souza et al., 1998). Our present findings demonstrated that only the upstream section of the Rio Pequeno branch (RP7) remained mesotrophic during both seasons. Two main factors combined to produce this limnological condition, the good water quality of the main tributary (Rio Pequeno) and the well protected surroundings (Capobianco and Whately, 2002; SET, 2005). Information on the Rio Pequeno branch is very sparse, and does not allow an evaluation on the temporal scale. To our knowledge, the only report available (Carvalho et al., 1997) classified one sampling station of this branch (the present RP6) as eutrophic for the period 1992-1993; however, no quantitative data were presented.

Rio Grande Reservoir – For the purpose of improving the Rio Grande Reservoir water quality, this branch was completely isolated from the Billings Reservoir in 1981. Since then, the greatest pollution source for the reservoir comes from the Rio Grande da Serra and Ribeirão Pires tributaries, with dilution from the upstream section

(RG4) until the dam (RG1) (Cetesb, 2004, 2008). Cyanobacteria control has been accomplished by the frequent application of algaecides (copper sulfate and hydrogen peroxide), since the reservoir has been used for public water supply (Carvalho et al., 1997; Moschini-Carlos et al., 2010). During this study and based on the annual average, the upstream station (RG4) was super-eutrophic, the intermediate ones (RG2, RG3) were mesotrophic, and the downstream region (RG1), where the water pumping occurs, was meso-eutrophic, clearly caused by the addition of algaecides to its Central body region (RG2, RG3). Thus, chlorophyll-*a* values were low in spite of the nutrient availability, in agreement with previous studies (Carvalho et al., 1997, Moschini-Carlos et al., 2010). Most probably, without algaecides, the limnological conditions in this branch would be similar to the upstream region classified as super-eutrophic. Considering the temporal scale, the water-pumping region (RG1) has been eutrophic since 1999 (Table 5).

The surface sediments represent a spatial and temporal integrated sample of the cumulative recent past events. Particularly the first 2 cm usually integrate the last two years of sedimentation and up to four years (for systems with very low sedimentation rates) (Smol, 2008). The present results reflected the differences in the water quality of the Billings Complex, i.e., separating the Rio Pequeno branch from the Central body, mostly from its highly degraded station (CC8). Furthermore, the surface sediments provided additional information about other impacts on the Complex, such as the input of allochthonous organic matter and the Rodoanel ring road construction.

In comparison with the findings of Silvério (2003), our results indicated substantial increases of the total geochemical organic carbon (122%), total phosphorus (63%) and total nitrogen (63%) in the Central body region. The same trend was observed for the Rio Grande Reservoir when compared to data from 2008 (Cetesb, 2009). The observed C:N atomic ratios lower than 10 are in agreement with the prevalence of autochthonous productivity (Meyers, 2003) in the Billings Complex. In the Taquacetuba branch, a higher total organic carbon contribution occurred at the site near the water transfer to the Guarapiranga Reservoir (TQ12), reinforcing the consideration of Capobianco and Whately (2002) that this branch is influenced by the Central body as well as by additional nutrient loadings from its tributaries. Our observation was not detected by the water analysis, since the sampling stations were not located near the tributary mouth, and therefore indicates the spatial-integrator role of the surface sediments. The impact of the Rodoanel construction very probably occurred in the Central body (CC9) and the Taquacetuba branch (TQ10). In the former, a short core showed a 10-cm light-brown and coarse-grained surface layer deposited over dark layers, indicating a recently eroded deposition. This impact was noted in the Taquacetuba branch, from the prevalence of sand and very coarse silt in the region located just after the main bridge crossing the Central body (TQ10). Similar effects on lithology and granulometry were observed in a paleolimnological study of an urban reservoir located in the SPRM (Costa, 2008). Finally, the recently eroded material and the larger particles in the surface sediments diluted the geochemical nutrient contribution in both localities (CC9, TQ10), which attained the lowest levels within their respective compartments.

5. Conclusion

The Billings Complex is a highly heterogeneous environment, ranging from mesotrophic (Rio Pequeno branch) and eutrophic (Rio Grande reservoir) to super-eutrophic (Central body and Taquacetuba branch). The trophic state varies widely within the compartments and/or depending on the season, mainly due to the human management of the Complex (pumping station operation, hydrodynamic changes, and algaecide applications). The highly degraded Central body has been compromising the water quality in areas where the soil use is not intense and human occupation is sparse. Therefore, only the upstream region of the Rio Pequeno branch has remained mesotrophic, and is presently considered a reference location (the least degraded) for the Billings Complex.

The differences found in the surface sediments underlined the differences observed between the extremes of water quality in the Billings Complex, besides providing additional information on other impacts (not identified by the water analyses) such as allochthonous organic matter input, and the Rodoanel construction. Consequently, the use of surface sediments as a complementary tool for water monitoring is reinforced by the present findings.

Finally, a slight improvement in the water quality of the Central body and the Taquacetuba branch has been observed since 2009 (changing from hypertrophic to super-eutrophic), possibly associated with the Pinheiros River flotation pilot project.

Acknowledgements

This work was supported by funds provided by FAPESP, Fundação de Amparo à Pesquisa do Estado de São Paulo (2009/53898-9), and was undertaken as part of a M.Sc. thesis (FAPESP fellowship 04/08675-8 to SW) at the Instituto de Botânica (São Paulo, Brazil). Funding was also provided by CNPq, Conselho Nacional de Desenvolvimento Científico e Tecnológico (Grant 305072/2009-9 to DCB). We are deeply grateful to the staff of Sabesp (Divisão de Recursos Hídricos Metropolitanos Sudoeste) for their valuable logistical support during the fieldwork. We also thank the students and technicians involved in the laboratory and in the fieldwork.

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Received: 12 June 2011
Accepted: 14 October 2011