

# **Water Quality in the Tietê River Reservoirs (Billings, Barra Bonita, Bariri and Promissão, SP-Brazil) and Nutrient Fluxes across the Sediment-Water Interface (Barra Bonita).**

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**ABSTRACT: Water Quality in the Tietê River Reservoirs (Billings, Barra Bonita, Bariri and Promissão, SP-Brazil) and Nutrient Fluxes across the Sediment-Water Interface (Barra Bonita).** The quality of the water in the Tietê River reservoirs (Billings, Barra Bonita, Bariri and Promissão) was assessed at different times during 2001 and 2002 in a series of analyses of dissolved chemical constituents (nitrate, nitrite, ammonium, soluble reactive phosphorus, dissolved organic carbon, chloride, fluoride, sulfate and reactive silica), and of the particulate phase (total organic nitrogen and total phosphorus). Physico-chemical variables such as pH, redox potential, electrical conductivity and dissolved oxygen were measured in situ. A study of seasonal variation in the water column was carried out to evaluate the behavior of these variables throughout a complete hydrological year. The majority of the nutrient concentrations determined in the water column increased in the dry season (autumn-winter-spring: April-September), compared to the rainy season (summer: November-March), suggesting that their seasonal cycles were associated with the water residence time and rainfall, as previous studies had already demonstrated. An evaluation of the present water quality status in these reservoirs was made and compared to results from previous studies. It is documented that water quality has deteriorated in the last 2 decades (1979/80 to 2000/2002). Using Fick's first law, diffusive fluxes across the sediment-water column interface were calculated for the studied reservoirs. Specifically for Barra Bonita, results show that sediment acts, for the majority of the elements, as a source to the water column, reaching values such as 284 and 5 mg cm<sup>-2</sup> year<sup>-1</sup> for ammonium and soluble reactive phosphorus, respectively. These are rather critical findings because, even if current nutrient sources were controlled at the Barra Bonita reservoir, the water quality would not necessarily improve as sediment would continue to be an important internal source of nutrient to the water column for a long time.

**Keywords:** water quality, sediment, diffusive fluxes, nutrients, Tietê River reservoirs

**RESUMO: Qualidade da Água das Represas do Rio Tietê (Billings, Barra Bonita, Bariri e Promissão, SP, Brasil) e Fluxos de Nutrientes na Interface Sedimento-Água (Barra Bonita).** A qualidade da água de represas do Rio Tietê (Billings, Barra Bonita, Bariri e Promissão) foi avaliada durante os anos de 2001 e 2002 através de uma série de análises de constituintes químicos dissolvidos (nitrito, nitrito, amônio, fósforo solúvel reativo, carbono orgânico, cloreto, fluoreto, sulfato e sílica reativa), bem como espécies totais (nitrogênio orgânico total e fósforo total). Variáveis físico-químicas como o pH, potencial redox, condutividade elétrica e oxigênio dissolvido foram medidas in situ. Este trabalho foi desenvolvido na forma de uma variação estacional na coluna d'água para avaliar o comportamento dessas variáveis durante um ano hidrológico. Os resultados mostram que a concentração da maioria dos nutrientes determinadas apresentou maiores valores na estação da seca (outono-inverno-primavera; abril-setembro) quando comparada a das chuvas (verão; novembro-março) o que sugere que os ciclos sazonais desses elementos estão intimamente associados ao tempo de residência da água e da pluviometria, como já documentado por outros estudos. A avaliação da qualidade da água desses reservatórios é feita e comparada com aquelas levantadas por outros estudos. Documenta-se que a qualidade vem deteriorando nas últimas duas décadas (período de 1979/80 a 2000/02). Através da 1a. Lei de Fick, fluxos difusivos na interface sedimento-coluna d'água foram calculados para os reservatórios estudados. Os resultados para Barra Bonita mostram que os sedimentos agem como fonte de espécies dissolvidas de nutrientes para a coluna d'água para a maioria dos elementos

estudados alcançando valores como 284 e 5 mg cm<sup>-2</sup> year<sup>-1</sup> para amônio e fosfato solúvel reativo, respectivamente. Essas conclusões são bastante críticas com vistas à qualidade da água neste e outros reservatórios do Rio Tietê, porque mesmo que se as fontes de nutrientes fossem controladas, os sedimentos teriam um potencial de liberação de nutrientes para a coluna d'água por um período de tempo muito longo.

**Palavras-chave:**qualidade da água, sedimento; fluxos difusivos, nutrientes, represas do Rio Tietê.

## Introduction

The assessment of water quality in multiple-use water-bodies has gained great importance in recent years, not only because of their ecological, economic and social roles, but also due to the negative impact of a variety of anthropogenic activities. These water bodies (rivers, lakes and reservoirs), which provide water for human consumption and other purposes, are presently showing signs of severe eutrophication or are already eutrophic in densely populated and highly industrialized cities in Brazil. The discharge of significant loads of waste-water rich in organic matter (which may also carry chemical substances of high toxicity) is the main cause of this degradation. The process consists of the enrichment of water with phosphorus and nitrogen, whose concentrations are both of great importance as indices of the degree of eutrophication of an aquatic environment, as they are essential elements for the growth of phytoplankton and aquatic macrophytes.

The present study focused on the River Tietê reservoirs (São Paulo State, SE Brazil) that, as a consequence of the relatively high local population density and the multiple industrial and agro-industrial activities widespread in the drainage basin, suffer from poor water quality, especially badly in the upper part of the Tietê basin (Billings reservoir in Metropolitan São Paulo), as well as its middle reaches (Barra Bonita and Bariri reservoirs) (Conselho Estadual de Recursos Hídricos, 1990; Calijuri, 1999). The lower Tietê (Promissão reservoir) has, in turn, been suffering great transformations, especially in the last few decades, firstly with extensive plantations of coffee, cotton, maize and orange, which have gradually given place to very extensive sugarcane plantations. Since 1975, when the Brazilian alcohol programme was launched, the effects of the development of an expanding agro-industrial park producing sugar, alcohol, citrus juices and fabrics must also be taken into account.

As pointed out by Straskraba & Tundisi (1999), the construction of reservoirs is a factor that must be considered on its own as a modifier of natural ecosystems, the greatest impact of which may be the rapid eutrophication that occurs, mainly in the first years after construction, as a result of flooding lateral areas. Moreover, climatic factors and the management of the dam itself for electric power production generate ecological effects that act in pulses. This phenomenon is observed as increasing concentrations of suspended particles and high nutrient loads in the water, mainly caused by turbulence generated by wind, rainfall and fluctuations of the water level created by changes in the flushing rates of the reservoir water (Tundisi & Matsumura-Tundisi, 1990; Tundisi et al, 1993; Calijuri, 1999). These events modify the ecological characteristics of the reservoirs, intervening in the dynamics of the biological communities (Calijuri, 1999; Güntzel, 2000).

In a study of the zooplankton composition and distribution over the last 20 years in 21 reservoirs of the São Paulo State, Matsumura-Tundisi & Tundisi (2003) show that the Barra Bonita reservoir fauna has undergone a complete change in composition, from species typical of waters of low conductivity and pH near 7.0 to those of much higher conductivity and a lower pH, and at least one new species has appeared. The authors point out that structural changes in the zooplankton community can be the first step towards large-scale functional changes in the reservoir, as a consequence of eutrophication and toxicity. In a recent paper Matsumura-Tundisi & Tundisi (2005), concluded that environmental gradients are strong selective factors that enhance phyto and zooplankton richness in eutrophic reservoirs exhibiting environmental instability, and that this could explain the presence of a large number of plankton species together with a high total population in Barra Bonita reservoir.

Barra Bonita reservoir is known to experience blooms of cyanobacteria almost

the whole year round (Sotero-Santos et al., 2006) and this may be a result of a combination of several factors such as: water column stability, low N:P ratio, moderate to high nutrient levels as the reservoir is highly eutrophic, according to total phosphorus and total nitrogen data, water temperatures in the range  $15\text{--}30\pm1^{\circ}\text{C}$ , pH between 6 and 9 or higher, mild or absent winds, low turbulence and water velocity, high insolation and a favorable morphometry of the aquatic system (Skulberg et al., 1984 and Mur et al., 1999, both in Sotero-Santos, 2006). While previous studies reported recurring blooms of cyanobacteria on Barra Bonita reservoir (e.g., Calijuri et al., 2002), there are no data regarding the effects of such cyanobacteria on other communities in that environment or their toxicological features. However, acute toxicity tests with crude bloom extract using cladocerans recently done by Sotero-Santos et al. (2006) indicate that toxins released from the cyanobacterial blooms on Barra Bonita reservoir are potentially capable of killing cladocerans and could therefore have

adverse effects on other aquatic invertebrates. These authors also postulate that these blooms of cyanobacteria may cause major disruption of the aquatic ecosystem, in addition to severe negative effects on wildlife and humans. Thus, the importance of cladocerans in aquatic food webs and their consumption of algae may contribute to a further deterioration in water quality and damage to other trophic levels (Sotero-Santos et al., 2006).

Considering a cascade of reservoirs as interdependent systems, some forecasts may be attempted about the sequence of physical, chemical and biological events along the course of the river (Barbosa et al., 1999; Guntzel, 2000). Since Barra Bonita and Bariri reservoirs are located practically in the middle of the Tietê River drainage basin, they are valuable objects for the study of the evolution of eutrophication from the highly-polluted upper Tietê (the metropolitan region of São Paulo that includes Billings reservoir) down to where it flows into the Paraná River (Promissão reservoir) (see Fig. 1).

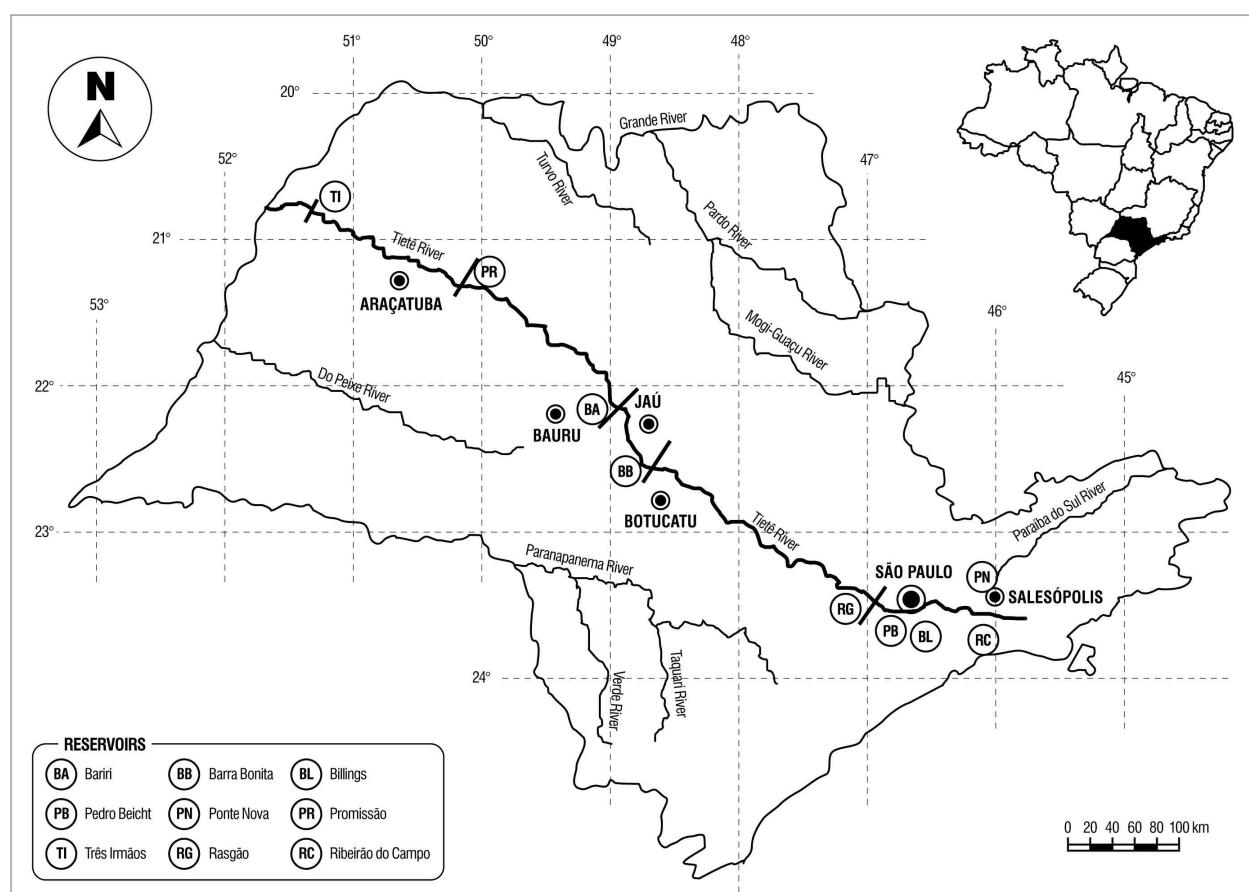


Figure 1: Map of the location of Billings, Barra Bonita, Bariri and Promissão reservoirs on the Tietê River, São Paulo State, SE Brazil (according to and modified from Nascimento & Mozeto, 2006).

With the above considerations in mind, the present study was carried out to gather new data on the quality of the water in the Tietê River reservoirs (Billings, Barra Bonita, Bariri and Promissão) which were assessed during 2001 and 2002 in a series of analyses of dissolved and particulate chemical constituents (nutrients), as well in situ measurements of physico-chemical variables and to compare these results with those from previous studies published elsewhere. Given the considerable accumulation of nutrients in the sediment and the potential release of these elements to the water column we specifically determined fluxes at the sediment-water column interface in Barra Bonita Reservoir. We thus present results on diffusive fluxes across the sediment-water column interface, calculated by Fick's first law. Apart from their intrinsic value as new data on these aquatic ecosystems, these data are particularly relevant because, as has been shown for water bodies around the world, the water quality may deteriorate, through time, even when external sources have been reduced or controlled, because sediment acts as an internal source of dissolved nutrients for the water column.

## **Study area**

**Billings reservoir:** The Billings reservoir, the largest water body in the Metropolitan São Paulo region (see Fig. 1), was built mainly to produce hydroelectric power at the Henry Borden Power Plant at Cubatão (SP) on the Atlantic coast, as this plant receives pumped water from the Tietê and Pinheiros rivers (Mozeto et al, 2003; EMAE, 2001). Since 1992, a much smaller amount of the contaminated water in those rivers has been pumped to Billings reservoir, following an environmental resolution (SMA/SES no. 03/1992) passed in an attempt to control flooding in São Paulo city. This measure has helped to improve water quality, according to the São Paulo State Environmental Agency (CETESB, 2001). See also (Tab. 1) for further characteristics of this reservoir and its drainage basin.

**Barra Bonita reservoir:** The Barra Bonita reservoir (see Fig. 1), is the first of the cascade series of six large reservoirs created along the entire Tietê River (São Paulo State, SE Brazil), which flows inland from the forested high watershed near the coast, across the whole State to the border of Mato Grosso do Sul State, where it joins

the Alto Paraná River. The water retention time in this reservoir varies from 30 to 180 days and the prevailing type of mixing is mainly affected by the wind, periods of turbulence alternating with short periods of stratification (Calijuri & dos Santos, 1996; Calijuri, 1999).

The tributaries of this reservoir, according to CETESB (2001), are used both by the public and for urban and industrial effluent discharges and industrial production. Besides the main land uses and other characteristics of this reservoir and its drainage basin, listed in Tab. I, highly populated and industrialized areas are also found here, with industries including paper and cellulose, food, textiles, leather tanning, chemicals and a petroleum refinery (CETESB, 2001). Quarrying and mining of material for civil construction are common activities, for example clay for ceramics, broken stone for road pavement, and carbonate rock (dolomite) for the treatment of acid soil.

**Bariri reservoir:** The water in the drainage basin of the Bariri reservoir (see Fig. 1) is mainly used for public (domestic) and industrial consumption, discharge of effluents (domestic and industrial) and crop irrigation (CETESB, 2001). See also Tab. I for further characteristics of this reservoir and its drainage basin.

**Promissão Reservoir:** The water in the Promissão reservoir (also known as Mario Lopes Leão) (see Fig. 1) as well as of its tributaries is mainly used for domestic and industrial activities, effluent discharge and crop irrigation (CETESB, 2001). See also Table I for further characteristics of this reservoir and its drainage basin.

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## **Materials and methods**

Water samples were collected in the deep zone of each reservoir, about 500 m from the dam itself. The collection was done at three depths in the water column (near the surface, mid-column and at the sediment-water interface) with an immersed pump connected to a hose. The samples were stored in polyethylene bottles, previously cleaned with 10% v/v HCl and rinsed with distilled and deionized water. The samples saved for the dissolved organic carbon (DOC) analysis were preserved with 10%  $H_3PO_4$  (5 mL of diluted the acid being added to 100 mL of sample). All the water samples were kept in a cooler

Table 1: Main characteristics of the studied reservoirs and their drainage basins.

	<b>Billings (1)</b>	<b>Barra Bonita (2)</b>	<b>Bariri (3)</b>	<b>Promissão (4)</b>
Construction (year)	1937	1957	1965	1975
Main objectives	Electricity at Henry Borden Power Plant at Cubatão (SP)	Electricity but also irrigation, fishery, water supply and recreation	Electricity	Electricity and navigation
Main tributaries	Rivers: Grande or Jurubatuba, Pires, Pequeno, Pedra Branca, Taquacetuba, Bororé, Cocais, Guaraci, Grota & Alvarenga (5)	Rivers: Sorocaba, Capivari, Jundiaí & Piracicaba (6)	Rivers: Tietê, Jaú, Lençóis e Bauru (7)	Rivers: Tietê, Dourado, São Lourenço, Batallha & Porcos (4)
Drainage basin area (km <sup>2</sup> )	560	32,330	35,430	12,930
Total volume (m <sup>3</sup> )	1,166 10 <sup>6</sup>	3,160 10 <sup>6</sup>	–	–
Inundation area (km <sup>2</sup> )	127.5	324.84	–	–
Main land use; soil cover	14.6% of catchment area is urbanized; 5.6 % small farms, condominium & scattered houses; 53% secondary Atlantic Forest; 0.69% planted forests (Eucalyptus and Pinus); 6.08% pasture, agriculture fields and wetlands. Note: 1999 data set (5)	Variety of industrial uses such as: textile, pulp and paper, slaughterhouses, sugarcane mills and sugar and alcohol mills; Sorocaba river: 25% of natural forests; 4.5% of 'cerrados/cerradões'; 7.5% planted forests; 32.5% pasture. Piracicaba, Capivari, Jundiaí rivers: 57% pasture + several types of agriculture.	Urban and industrial activities, cattle farming on large pastures and agricultural crops (sugarcane, coffee, corn and citrus fruits); industrial activities: sugar and alcohol mills, leather tanning, food industries and metalwork; Vegetation: savannah scrub and xerophytic forests, wetlands, shrubs and forests (7)	Urban and industrial (orange juice and sugar & alcohol mills), cattle farming activities and tanneries and food processing (7). Vegetation: semi-deciduous forests, shrubbery, xerophytic scrub, forests and wetlands (natural) and planted forests, horticulture, pastures, crops such as coffee, sugarcane, corn and oranges (4)
Climate	Tropical & subtropical. Average temperature: 19 °C Rainfall: 1,300 – 3,500 mm year <sup>-1</sup>	Rainfall: 1,270 – 1,383 mm year <sup>-1</sup>	Köppen classification: (i) Cwa – hot and humid summer, with dry winter season; (ii) Cwb – temperate and humid summer, with dry winter season. Precipitation: 1,500-2,000 mm year <sup>-1</sup>	Hot and humid summer and dry winter; temperature of 18-24°C in summer (tropical and subtropical). Rainfall: 1,323 mm year <sup>-1</sup> (4)

box with ice (approximately 4°C) during transport and then stored in a refrigerator until analysis.

For the evaluation of diffusive fluxes, sediment cores were collected using a cylindrical, gravity-type collector (acrylic pipes) (Ambühl & Bührer, 1975, modified by Esteves & Camargo, 1982). The cores were about 9 cm in diameter and 50 cm in length. They were sliced under a flow of nitrogen gas in a glove-box, enclosed in bags sealed by pressure ('zip-lock' type) and stored as the water samples.

Sediment samples used for the extraction of pore water (in seasonal variation studies) were collected with a Birge-Ekman grab and, with the aid of a plastic spatula, only the top 10 cm of the sediment was stored for analysis. These samples were packed as described above. Pore-water samples were extracted by centrifugation at 4°C, followed by vacuum filtration through a pre-washed (in distilled/deionized water) nitrate cellulose 0.45 mm membrane under a constant flow of gaseous nitrogen (Mozeto et al., 2001).

The physico-chemical variables (pH,  $E_{H^+}$ , dissolved oxygen, electric conductivity and temperature) were measured *in situ* using a Hydrolab Quanta multi-probe. The dissolved organic carbon (DOC) was determined in an total organic-carbon analyzer, TOC-5000 (Shimadzu, Japan).

The analytical procedures used for the chemical determination of the nutrients in the water samples are described in APHA (1985).

Monthly rainfall data (mm) over the study period in the Tietê River basin, collected by the agrometeorological monitoring station at Jau, SP (AC – CIAGRO, 2006) is shown in Fig. 2.

Two types of statistical analysis were performed on the data: principal components analysis (PCA) and hierarchical cluster analysis (HCA). The PCA is a mathematical manipulation of a data matrix where the goal is to represent most of the variation observed in many variables by that in a smaller number of "factors" that are mutually independent. A new space is constructed in which to plot the data by

using factors as axes rather than the original measurement variables. These new axes, referred to as principal components (PCs), allow the analyst to probe matrices with many variables and view the true multivariate nature of the data in a relatively small number of dimensions. With this new view, human pattern recognition can be used to identify structures in the data (Beebe et al., 1998). The HCA is an unsupervised technique that examines the distance in data space between pairs of samples and represents that information in the form of a two-dimensional tree-plot called a dendrogram. These dendograms present the data from high-dimensional spaces in a form that facilitates human pattern recognition. To generate the dendrogram, HCA methods form clusters of samples based on their nearness in data space. A common approach is to initially treat every sample as a cluster and join the closest clusters together. This process is repeated until only one cluster remains (Beebe et al., 1998).

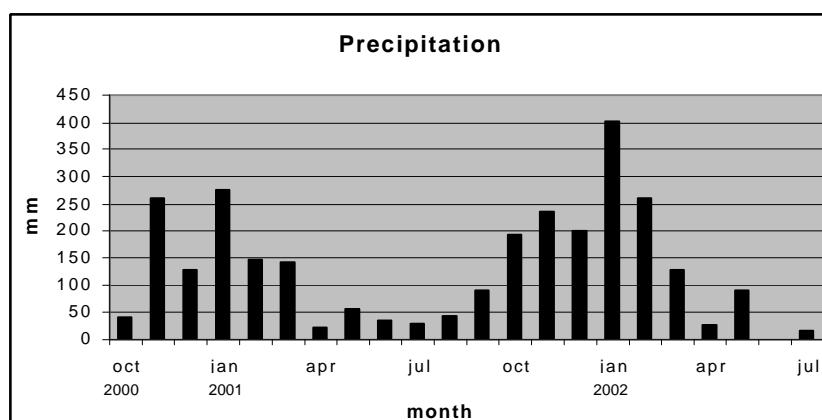


Figure 2: Monthly rainfall data over the study period, recorded by the agrometeorological monitoring station at Jau, SP (IAC – CIAGRO, 2006). Geographical coordinates: height above sea level: 495m; longitude: -48.62°; latitude: -22.19°.

## Results and discussions

### Preamble

The results of this study are presented as a special case-study of Barra Bonita reservoir. Seasonal variation in the water-column data and sediment fluxes calculated from Fick's 1<sup>st</sup> law are presented. These sections are followed by a time-series comparison of the data gathered for Barra Bonita reservoir with those for Billings, Bariri and Promissão reservoirs (for which new data sets are shown) and from the literature.

Water and sediment samples were collected in field trips conducted in the

years of 2001 and 2002 under the QualiSed Project (1999-2003), a cooperative research project involving two universities (UFSCar and UNICAMP) and a water authority (CETESB), which was funded by the São Paulo Foundation for Research (FAPESP).

### Seasonal variations of nutrients in the water column and sediment pore water of Barra Bonita reservoir.

Understanding the temporal variations in chemical element concentrations and physico-chemical variables in the water column of freshwater bodies, such as

hydroelectric reservoirs, is not an easy task. In the case of Barra Bonita reservoir, an extensive body of limnological research can be found in the literature that consistently shows how complex this system is (eg.; Matsumura-Tundisi & Tundisi, 2005; Matsumura-Tundisi & Tundisi, 2003; Calijuri and dos Santos, 2002; Güntzel, 2000; Barbosa et al., 1999; Calijuri, 1999; Straskraba & Tundisi, 1999; Tundisi & Matsumura-Tundisi, 1990; Tundisi et al., 1988). Among the principal reasons for this are natural driving forces represented mainly by climatic factors (wind and rain action) that, acting directly on the reservoir, may drastically alter limnological conditions in the water column and at the sediment-water interface. Evidently, human activities in the drainage basin (including various large-scale forms of land use) is equally important, potentially leading to rapid eutrophication due to the discharge of untreated urban and industrial sewage. Superimposed on these factors is one that may be the main cause of water-body degradation: changes in the water residence time as a direct consequence of measures adopted to optimize energy production (Tundisi & Matsumura-Tundisi, 1990). As proposed by these authors, in flow-through reservoirs rainfall and wind are the main factors in nutrient seasonal cycles and fluctuations, but in regulated reservoirs like Barra Bonita, the flushing rate and, consequently, the water residence time is the prime factor controlling this cycle (see also Straskraba & Tundisi, 1999). The data we present in this study corroborate these conclusions remarkably well. Therefore, the main approach in the interpretation of the data presented here is based on that of Tundisi & Matsumura-Tundisi (1990) and Straskraba & Tundisi (1999), focussing on the flushing rate and water-residence time in these man-made reservoirs.

The monthly rain distribution in the Tietê River drainage basin for the period from 2000 to 2002 is shown in Fig. 2, where the rainy and dry periods are clearly seen. The dry period coincides with the autumn-winter-spring (April-September) season of low precipitation, and the rainy season with the summer (November-March), with a significant increase in rainfall. Although the maximum (May) and minimum (September) amounts of stored water in Barra Bonita

Reservoir do not necessarily coincide with the times of maximum (November-March) and minimum (April-September) precipitation in the drainage basin (as a direct result of reservoir management to produce energy) (Dr. Odete Rocha - personal communication), some trends were observed in nutrient concentrations on a temporal or seasonal basis. The interpretations of our data with respect to flushing rate and water residence time are presented in these paper in a very conscious way as the authors are aware of the time and spatial variations that may exist in one particular reservoir as well among different reservoirs.

As far as water quality in the water column is concerned, all nutrient concentrations (see Figs. 3 and 4) except chloride and reactive silica concentrations (see Fig. 4) are significantly higher during the dry season than in the rainy season. Therefore, these fluctuating concentrations are inversely proportional to the rainfall (see Fig. 2). As already stated, Tundisi & Matsumura-Tundisi (1990) also found this type of variation in a previous study of the Barra Bonita reservoir and attributed it to temporal variations in its water residence time and flushing rate. According to those authors, water management is such that relatively high residence times are detected during the dry season. Consequently, as stated by Güntzel (2000), the influence of biological processes on the internal functioning of the water body increases relative to the external load (allochthonous sources); allochthonous contributions are maximized during the rainy season, due to surface runoff. The findings from previous studies described above for the reservoir corroborate or reinforce the interpretation of the data presented in this paper.

As chloride and reactive silica seasonal concentrations (the exceptions mentioned above) (Fig. 4) correlated directly with rainfall, they may be influenced by specific factors, such as soil erosion or leaching and domestic sewage discharge. The concentrations of those analytes usually increase with increasing surface runoff discharge during the rainy season, as silica is a common chemical species in soil erosion leachate (Tardy et al., 2004; Krusche & Mozeto, 1999; Gaillardet et al., 1999; Mozeto & Albuquerque, 1997; Mozeto et al., 1991) and chloride is a main chemical

species in urban and industrial sewage (Ibarra et al., 2005; Robson & Neal, 1997).

Fig. 3 shows increased concentrations of soluble reactive phosphorus (SRP) and total phosphorus detected in the dry season, a trend similar to that documented for nitrate, nitrite and ammonium in the water column of Barra Bonita Reservoir (Fig. 3). These trends are in agreement with the relatively high measured dissolved oxygen concentrations and redox potential values in the dry season (specially for the bottom waters) (see Fig. 5) that show that sediments are relatively more oxidized during this season, thus preventing dissolved phosphorus from being released from the sediment into the water column. During the rainy season, oxygen consumption increases, to oxidize the greater amount of organic matter that enters the water column from surface runoff.

Therefore dissolved oxygen and redox potential decrease in this season and phosphorus is kept in the sediment by precipitation (see also next section).

Fluoride and sulphate seasonal cycles in the water column, shown in Fig. 4, follow the same trend as the other nutrient species described above. The fluoride concentration peak was measured in December/2001, reaching  $0.56 \text{ mg L}^{-1}$ , while that for sulphate, a value of  $30 \text{ mg L}^{-1}$  was also measured in the dry season (Fig. 4). On the other hand, the concentration of dissolved organic carbon (DOC) shown in Fig. 5 remained practically constant throughout the period of study, although a slight increase was detected during the dry season months. However, a small increase was also observed in the rainy season, which may indicate a soil-leaching contribution.

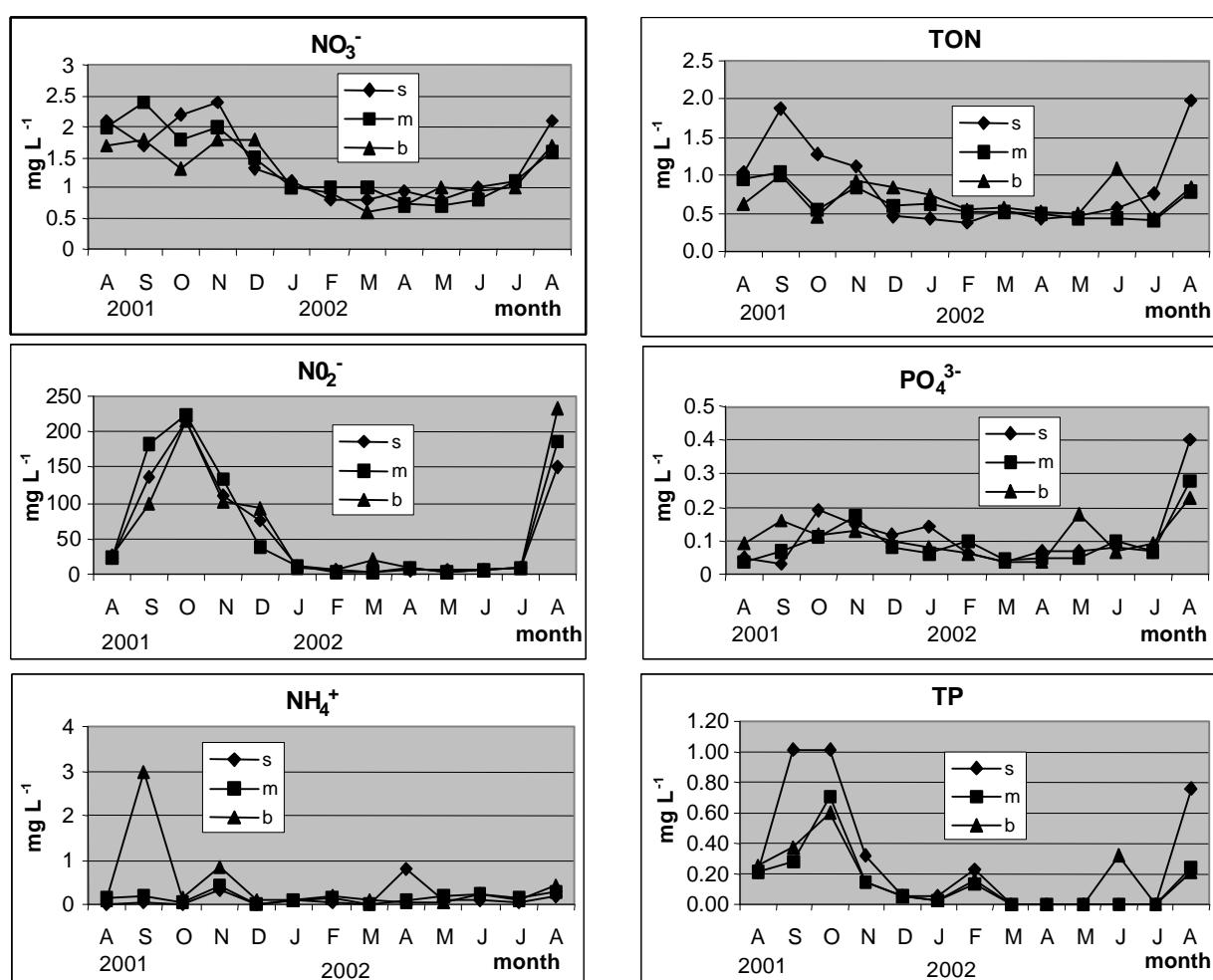


Figure 3: Monthly readings of concentrations of nitrate, nitrite, ammonium, total organic nitrogen, soluble reactive phosphorus and total phosphorus over a complete hydrological year for the water column in Barra Bonita reservoir (surface, middle and bottom).

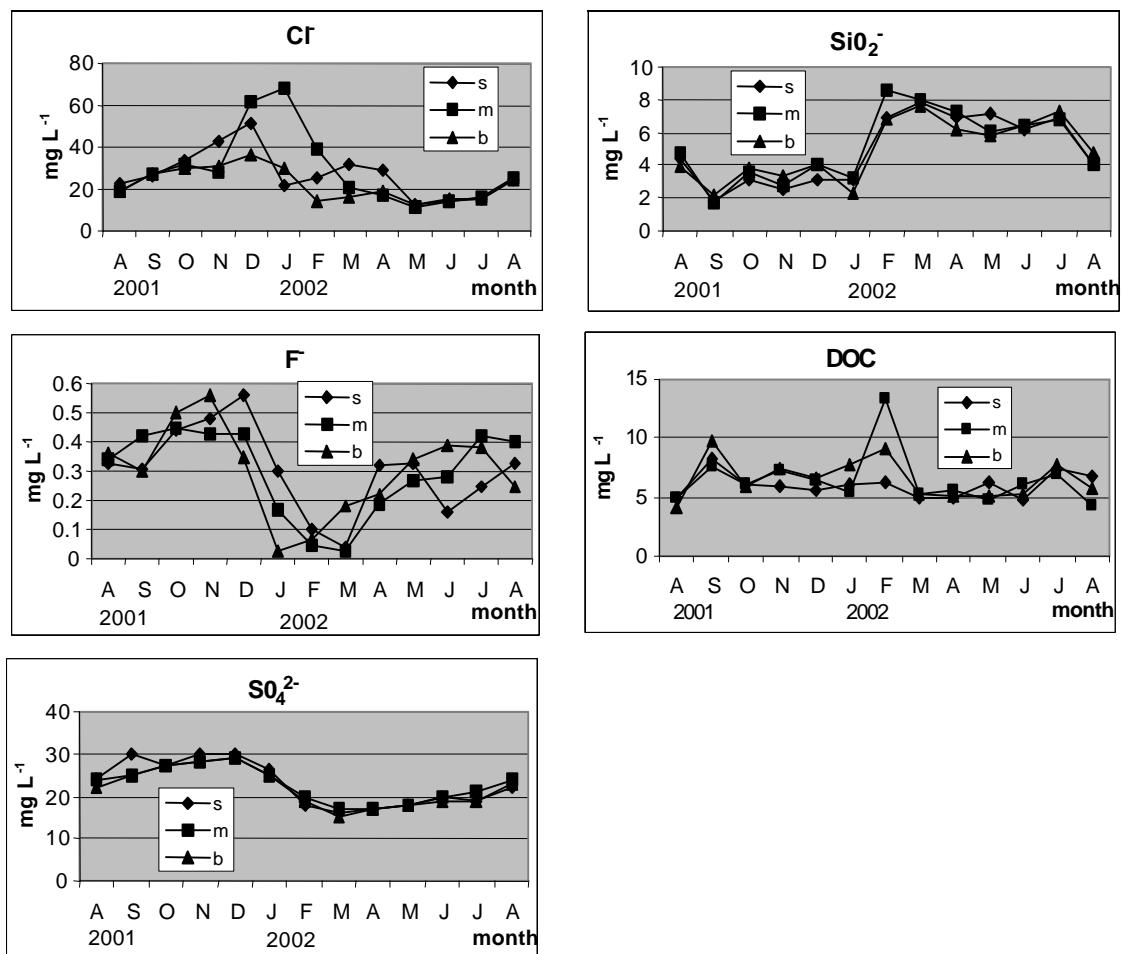


Figure 4: Monthly readings of concentrations of fluoride, chloride, sulphate, reactive silica and dissolved organic carbon over a complete hydrological year for the water column in Barra Bonita reservoir (surface, middle and bottom).

### **Physico-chemical variables in the water column**

The pH values in the water column remained practically unchanged during the entire period of study (Fig. 5). The peak of about 9.5, detected at the surface of the water column in the dry season of 2001 and 2002, is most certainly related to a high photosynthetic rate removing large quantities of  $\text{CO}_2$  from the water. In a similar study carried out by Costa (2001) at the same sampling station, a peak in pH was also detected during this season. pH values of bottom water were almost invariably lower and this may be attributed to anaerobic oxidation of organic matter in the hypolimnium.

Dissolved oxygen also has its highest degree of saturation at the surface in the dry season, reaching values as high as 122 % in September 2001 or even 150% in August 2002 (see Fig. 5). This tendency had also been previously observed by

Tundisi & Matsumura-Tundisi (1990) and Costa (2001). In the water column, the surface layers always contain more dissolved oxygen than deeper water, which is usually under anaerobic conditions at the sediment-water interface. The rather low redox potential values corroborate these trends (Fig. 5).

In the dry season, with its usually high water evaporation rates and relatively high water-residence time, the dissolved chemical species tend to become more concentrated in the water column, resulting in an increase in the electrical conductivity, which can be seen in Fig 5. A similar seasonal variation in this variable was also documented by Tundisi & Matsumura-Tundisi (1990). In the present study, a maximum value of  $0.306 \text{ mS cm}^{-1}$  was measured in this season, which is rather a high value, but even higher values of about  $0.400 \text{ mS cm}^{-1}$  were observed by those authors, back in the autumn-winter of 1984. A study of these seasonal variations was

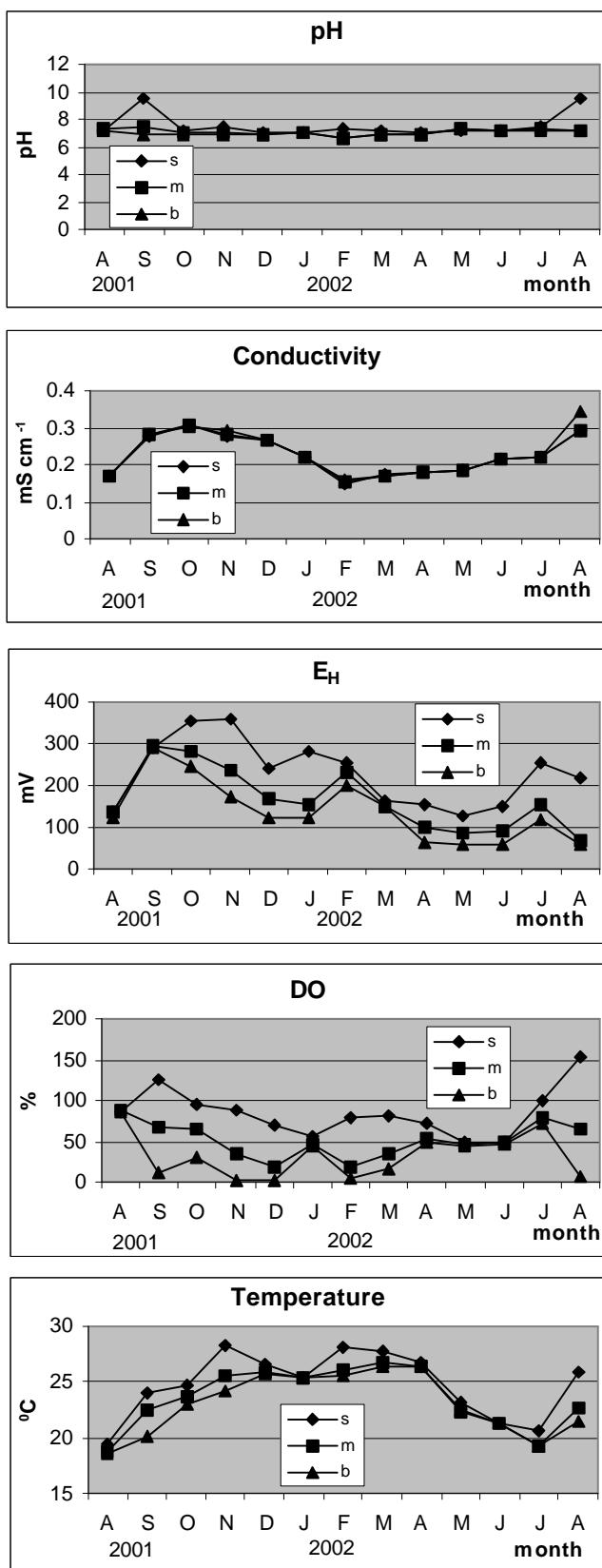


Figure 5: Temporal variations in physico-chemical variables measured over a hydrological year in the water column of Barra Bonita reservoir (surface, middle and bottom).

carried out by Mozeto et al. (1991) in the oxbow lakes of the Mogi-Guaçu River wetlands in a nearby region, in which the stable isotopes  $^{18}\text{O}$  and  $^2\text{H}$  were measured in the water. It was shown that the oxbow lakes and the river itself exhibit an increase in the concentration of chemical dissolved species in the period of drought, responsible for the increase in conductivity, as documented by the isotopic enrichments of those stable isotopes in the water.

The temperature variations in the water column follow the annual climatic fluctuations that prevail in the study area. Higher values were seen in the summer months (November-March) while in the autumn-winter-spring months (April-September), lower temperatures were measured (Fig. 5).

It can be concluded that the trends in physico-chemical variables shown in Fig. 5 are indeed a confirmation of factors or phenomena postulated to explain the observed temporal nutrient variations discussed in the previous section of this study.

### **Diffusive Fluxes**

Trace element concentrations in sediments have been widely used to interpret the history of a water body in water quality assessment studies (Hallberg, 1991; Owens & Cornwell, 1995). However, soon after sediments are deposited, processes such as bioturbation and diagenesis may cause significant changes in the redox potential ( $E_{\text{h}}$ ) and other biogeochemical properties of this compartment that can significantly alter the mobility and bioavailability of such elements (Aller, 1984; Kramer et al., 1991).

Pore water is, perhaps, the most important compartment in sediments, as it is the medium or route by which the transport of nutrients and contaminants occurs, and through which these chemical species may become available to the biota. Therefore, extraction and chemical analyses of pore water are of great importance, helping to determine the routes of exposure, partition, bioavailability and toxicity in nutrient and contaminant-associated sediment. The pool of these chemical species present in the sediment is usually adsorbed on particle surfaces in an 'apparent chemical equilibrium' (under steady-state conditions indeed), with the truly dissolved phase (i.e., not complexed

by DOC molecules) in the pore water (see for example, Mozeto et al., 2003a).

At the sediment-water interface, particularly within the oxidic layer, a faster rate of mineralization occurs (early diagenesis). These reactions can change not only the minerals on which the trace elements are adsorbed but also the entire speciation of the elements and, therefore, the mobility, bioavailability and toxicity of these chemical species. Thus, these diagenetic processes are often considered responsible for the establishment, through diffusion, of chemical gradients across the sediment-pore water-water column interface. Hence, dissolved nutrients and contaminants may be transported (upwards or downwards) across this interface (Lyons & Fitzgerald, 1980; Ciceri et al., 1992). Sediments, therefore, may act as a source or sink for chemical elements, as many studies have documented (e.g.: Petersen et al., 1995; Riedel et al., 1997; Mozeto et al., 2001). This process may vary from element to element and water body to water body.

Taking into account these processes that cause nutrient and contaminant accumulation in the sediment and/or their release to the water column, fluxes of soluble species across the sediment-water column interface can be calculated by determining the concentration gradient  $(dC/dZ)_{z=0}$  across that interface and applying Fick's 1<sup>st</sup> Law in one dimension (Azcue et al., 1996; Mozeto et al., 2001). This model is represented by the equation  $F = -F D_s (dC/dZ)$ , where  $F$  is the diffusive flux of the species ( $\text{mg cm}^{-2} \text{ year}^{-1}$ ),  $F$  the porosity of the layer where the concentration peak is detected,  $D_s$  is the diffusion coefficient in the pore water ( $\text{cm}^2 \text{ year}^{-1}$ ) and  $dC/dZ$  is the concentration gradient ( $\text{mg cm}^{-4}$ ). For the calculation of  $F$ , some considerations and assumptions must be made: a) the position of the sediment-water interface must be known; b) viscosity and effect of load junction can be neglected; c) neither precipitation nor biogenic release of dissolved species occur next to the sediment-water interface; d) the concentration gradient is linear, so that  $(dC/dZ)_{z=0}$  is equivalent to  $C/Z$  (Lerman, 1979). The diffusion coefficient ( $D_s$ ) is estimated by the empirical relationship  $D_s = F^n D$ , where  $n$  is a constant ( $n=2$ ; Lerman, 1979) and  $D$  is the diffusion coefficient at infinite dilution, corrected by

the Stokes-Einstein equation (Li & Gregori, 1974) for the in situ temperature of the water at 25°C.

Tab. II shows the calculated diffusive fluxes between sediment and water column in the Barra Bonita reservoir, according to the equation above.

The concentration profiles of the various chemical species under study demonstrate that the fluxes are bi-directional, that is, the sediment can either be a source or sink of dissolved elements. The extent and sign of the concentration gradient between the water column and the sediment (in fact, the pore water) determi-

ne the rate and direction of species transport across deeper layers in the sediment as well as at the sediment-water column interface (upwards or downwards). It must be pointed out, however, that fluxes calculated by invoking diffusional processes are in reality conservative, and that the total fluxes in many cases are much larger (Azcue et al., 1996; Mozeto et al., 2001).

The concentration profiles determined in the present study clearly reflect the strong influence of the redox status of the sediment-water column interface and the sediment layers themselves (Fig. 6).

Table II: Fluxes (sediment to water column) of dissolved species of nutrients across the sediment-water interface in Barra Bonita reservoir.

Ion	Depth of the concentration peak (cm)	Porosity	$\Delta C/\Delta Z$	Ds	Diffusive Fluxes
				(cm <sup>2</sup> year <sup>-1</sup> )	(mg cm <sup>-2</sup> year <sup>-1</sup> )
NO <sub>3</sub> <sup>-</sup>	1.5	0.84	0.182	364	- 55.6
NO <sub>2</sub> <sup>-</sup>	1.5	0.84	0.003	366	- 0.92
NH <sub>4</sub> <sup>+</sup>	1.5	0.84	0.89	379	- 284
PO <sub>4</sub> <sup>3-</sup>	10.5	0.84	0.035	162	- 4.76

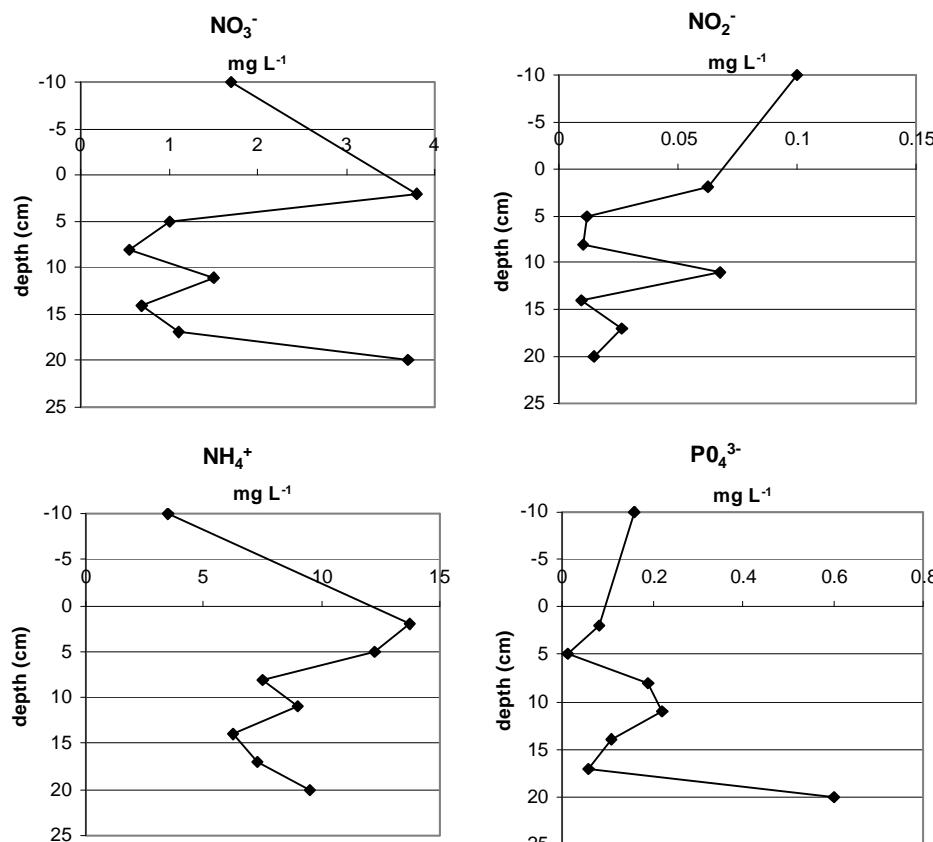


Figure 6: Profiles of nutrient concentrations (nitrate, nitrite, ammonium and soluble reactive phosphorus) in deep water column (sediment-water column interface) and sediment pore water.

Nitrate concentrations, for example, tend to diminish with depth in response to denitrification processes operating in the deeper strata (hypolimnium). The high value detected at the deepest sediment stratum analyzed (at a depth of 20.5 cm) was considered an outlier and therefore was neglected (indeed, the depth of the concentration peak used in the Fick's Law model was taken as 1.5 cm). Ammonium concentration profiles, consequently, tend to increase with depth in the pore water. A similar trend (but not shown in Fig. 6) was observed for silica, explained by the dissolution of amorphous silica (Van Eck & Smits, 1986).

Nitrification processes are very likely to occur as this sediment is a significant source of  $\text{NH}_4^+$  coming from the decomposition of the organic matter, subsequently transformed into  $\text{NO}_3^-$  (nitrification) and set free into the water column. Therefore, the sediment is an important source of ammonium ions in the water column ( $284 \text{ mg cm}^{-2} \text{ year}^{-1}$ ) (see Tab. II).

Orthophosphate fluxes are in the order of  $4.76 \text{ mg cm}^{-2} \text{ year}^{-1}$  (depth of concentration peak was taken as 10.5 cm; therefore the outlying value at 20.5 cm depth was also neglected as it may represent an analysis error) (see Fig. 6 and Tab. II).

Conservative benthic fluxes of nutrients across the sediment-water column interface were also calculated for the sediments of the Billings and Bariri reservoirs (but the data are not shown in Tab. II). Nitrate flux is about 3 times higher in Billings and Bariri reservoirs ( $178$  and  $170 \text{ mg cm}^{-2} \text{ year}^{-1}$ , respectively) than in Barra Bonita, while the flux for ammonium ions is about 6 and 2 times higher, respectively ( $1,782$  and  $520 \text{ mg cm}^{-2} \text{ year}^{-1}$ , respectively). In Barra Bonita and Billings, the orthophosphate ion fluxes are practically equivalent ( $4.18$  versus  $4.76 \text{ mg cm}^{-2} \text{ year}^{-1}$ ), while Bariri has a flux 1.6 times larger than that of Barra Bonita.

Fluxes for ammonium and orthophosphate ions are in the same order of magnitude as those calculated for Guarapiranga reservoir (São Paulo Metropolitan area), according to Mozeto et al. (2001); however, for nitrate in the present case, sediment was a source ( $55.6 \text{ mg cm}^{-2} \text{ year}^{-1}$ ), whereas in Gurapiranga reservoir, sediment was a sink ( $134.5$ - $140.6 \text{ mg cm}^{-2} \text{ year}^{-1}$ ).

Barra Bonita reservoir is a highly dynamic water body, not only as a consequence of its management for hydroelectric generation, but also due to the climatic conditions (e.g., wind variation) (Tundisi & Matsumura-Tundisi, 1990; Barboza et al., 1999; Calijuri, 1999; Güntzel, 2000). Therefore, sediment resuspension, which provokes sediment oxidation and alters the partition, availability and toxicity of chemical species, should also be considered in studies of this kind. Evidently, these phenomena introduce significant variations into the normal rates of element oxidation and reduction, as can be seen in the graphs for sulfate and other redox-sensitive species in our study.

The majority of the concentration profiles obtained in the present study shows the chemical species concentration peak in the first centimeters of the sediment, demonstrating the importance of redox processes in this region, and promoting nutrient mobilization and/or retention. Although yielding conservative estimates, diffusion is the main vector of transport of species, not only at the sediment-water interface, but also through the layers of the sediment column going down from this interface. These calculated fluxes only take into consideration the steady-state conditions of the diffusional process, but bioturbation events that also occur in the deeper layers of the sediment may also remobilize these elements to the water column.

Finally, it is important to point out that diffusional fluxes of nutrients (or of any other chemical species), whether computed by Fick's 1<sup>st</sup> Law or directly measured in bottom chambers, to determine the internal load in a water body, would be more meaningful in cases where and when pollution sources are under control than in cases like the Tietê River reservoirs. Unfortunately, nowadays, when the external load of nutrients and contaminants is extremely high in our water bodies, to talk about internal load does not make so much sense. However, such data will become important information where and when the external load diminishes and is to some extent under control.

Notwithstanding these remarks, it should be emphasized that the data presented in this study are rather critical findings, because even if nutrient sources were controlled at Barra Bonita reservoir (or

at the other reservoirs), water quality would not necessarily improve immediately, as sediment would continue to be an important internal source of nutrients (and of contaminants) to the water column for a long time.

### **Comparative analysis of Barra Bonita, Billings, Bariri and Promissão reservoirs**

Physico-chemical parameters and nutrient concentration data obtained in the present study and collected from the literature are shown in Tab. III (Billings Reservoir), Tab. IV (Barra Bonita Reservoir), Tab. V (Bariri Reservoir) and Tab. VI (Promissão Reservoir). The objective here is to compare our data with those from reports on inland water quality in the State of São Paulo, surveyed by CETESB (State of São Paulo Environmental Agency) (CETESB,

1992; 1995; 1996; 1998; 2000; 2001), and from a relatively recent doctoral thesis (Güntzel, 2000), for Barra Bonita, Bariri and Promissão reservoirs. We have also compared these sets of data with permissible concentration values for Class 2 waters, according to the Brazilian Federal environmental resolution, CONAMA 357/2005.

Examination of the time-series data found in Tabs. III to VI reveals that the concentrations of the main nutrients associated with eutrophication processes (dissolved inorganic nitrogen species and total phosphorus) tended to rise over time. Some deviation from this trend could be expected, owing to the natural dynamics of these water bodies and additional perturbations of the natural processes by the management strategy adopted to produce electric power.

Table III: Time-series of physico-chemical variables and nutrient concentrations in Billings reservoir waters.

<b>Variables</b>		<b>CONAMA</b>	<b>1992</b>	<b>1995</b>	<b>1996</b>	<b>1998</b>	<b>1999</b>	<b>2000</b>	<b>2000</b>	<b>2001</b>	<b>2001</b>
		<b>20/86</b>	*	*	*	*	*	**	*	**	*
Temperature	°C		22	24	21	22	27	24	23	25	21
Secchi disc depth	m		nd	nd	nd	nd	nd	0.4	nd	0.4	nd
Diss. Oxygen	mg L <sup>-1</sup>		7.1	7.8	5.0	11.3	9.7	9.8	9.4	3.1	13.2
pH		6.0 a 9.0	9.5	8.4	6.6	9.7	9.2	8.7	9.2	7.0	9.1
Conductivity	mS m <sup>-1</sup>		0.290	0.176	0.154	0.164	0.157	0.161	0.157	0.218	0.176
Redox Potential	mV		nd	nd	nd	nd	nd	376	nd	358	nd
Chloride	mg L <sup>-1</sup>	250	36.0	20.5	100	16.2	15.7	19.5	16.7	23.3	16.9
Nitrate	mg L <sup>-1</sup>	10	2.8	0.32	0.34	0.27	< 0.20	1.0	0.29	0.95	0.63
Nitrite	mg L <sup>-1</sup>	1	0.020	< 0.01	< 0.01	0.010	0.008	0.17	0.01	0.072	0.02
Ammonium	mg L <sup>-1</sup>		0.03	0.03	0.03	0.05	0.02	0.70	0.06	8.5	< 0.02
Total nitrogen	mg L <sup>-1</sup>		2.5	5.3	7.25	2.88	4.98	nd	1.62	4.102	0.39
Orthophosphate	mg L <sup>-1</sup>		0.315	< 0.005	< 0.01	< 0.01	< 0.007	0.01	< 0.007	0.055	0.02
Total phosphorus	mg L <sup>-1</sup>	0.025	0.36	0.05	0.04	0.05	< 0.09		0.11	nd	< 0.03
Reactive silica	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	0.28	nd	3.4	nd
Sulfate	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	12	nd	18	nd
Fluoride	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	0.30	nd	0.33	nd
DOC	mg L <sup>-1</sup>		nd	nd	nd	nd	nd		nd	6.82	nd

\* CETESB (1992; 1995; 1996; 1998; 1999; 2000; 2001).

\*\* This study.

nd = not determined.

In Barra Bonita reservoir specifically, the increasing eutrophication is evident in

the nitrate, ammonium and total organic nitrogen concentrations. These variables are

Table IV: Time-series of physico-chemical variables and nutrient concentration in Barra Bonita reservoir waters.

<b>Variables</b>		<b>CONAMA 20/86</b>	<b>1978/ 1979*</b>	<b>1979/ 1980*</b>	<b>1995</b>	<b>1996</b>	<b>1998</b>	<b>1999</b>	<b>2000</b>	<b>2000</b>	<b>2001</b>	<b>2001</b>
Temperature	°C		27.7	24.7	18.0	26.0	25.0	26.0	26.2	28	28.3	29
Secchi disc depth	m		0.7	2.0	nd	1.3	nd	nd	0.6	nd	1.2	nd
Diss. Oxygen	mg L <sup>-1</sup>		7.20	7.20	6.60	9.00	9.80	12.8	13.3	8.6	6.77	21.5
pH		6.0 a 9.0	8.2	7.5	6.7	6.2	8.9	9.3	9.1	7.3	7.5	10
Conductivity	mS cm <sup>-1</sup>		0.113	0.118	0.157	0.223	0.206	0.247	0.308	0.261	0.277	0.261
Redox Potential	mV		nd	nd	nd	nd	nd	nd	278	nd	360	nd
Chloride	mg L <sup>-1</sup>	250	nd	nd	13.5	22.4	19.7	33.0	27.0	33.6	26.3	28.9
Nitrate	mg L <sup>-1</sup>	10	0.29	0.24	1.25	1.05	2.09	3.77	1.50	3.37	1.70	3.26
Nitrite	mg L <sup>-1</sup>	1	0.003	0.008	0.006	0.060	0.112	0.650	0.216	0.362	0.137	0.15
Ammonium	mg L <sup>-1</sup>		0.051	0.027	0.040	<0.08	0.140	0.090	0.450	0.09	0.055	<0.02
Total nitrogen	mg L <sup>-1</sup>		nd	0.271	3.300	1.710	3.09	6.05	nd	3.23	1.288	5.53
Ortophosphate	mg L <sup>-1</sup>		0.018	0.010	nd	nd	<0.006	<0.006	0.010	0.06	3.000	0.03
Total phosphorus	mg L <sup>-1</sup>	0.025	nd	nd	0.015	0.038	0.016	0.016		0.122	<0.004	<0.03
Reactive silica	mg L <sup>-1</sup>		3.3	4.0	nd	nd	nd	nd	4.7	nd	1.7	nd
Sulfate	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	nd	23	nd	30	nd
Fluoride	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	2.00	0.50	nd	0.32	nd
DOC	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	nd	nd	nd	8.2	nd

\* Guntzel (2000)

\*\* CETESB ( 1995; 1996; 1998; 1999; 2000; 2001).

\*\*\* This study.

nd = not determined.

commonly related to effluent discharge from domestic and industrial activities, and, as in the present case, also agricultural activities. Guntzel (2000) reported nitrate at 0.29 mg L<sup>-1</sup> in the years 1978-1979, while we measured concentrations as high as 1.50 mg L<sup>-1</sup> in 2000; ammonium ion levels increased from 0.027 mg L<sup>-1</sup> in 1979-1980 (Guntzel, 2000) to as high as 0.450 mg L<sup>-1</sup> in 2000, while CETESB had already detected relatively high values such as 0.140 mg L<sup>-1</sup> in 1998 (see Tab. IV). Total organic nitrogen concentrations had modest values such as 0.27 mg L<sup>-1</sup> in 1978-1979 (Guntzel, 2000) and reached 3.3 mg L<sup>-1</sup> in 1995 and 5.53 mg L<sup>-1</sup> in 2001, according to data from CETESB (see Tab. IV).

Data from Bariri reservoir followed the trend observed in Barra Bonita, as may be

noted in Tab. V. Nitrate concentrations, for instance, amounted to only 0.18 mg L<sup>-1</sup> in 1979-1980 (Guntzel, 2000), but reached 2.95 mg L<sup>-1</sup> in 1998 (CETESB, 1998), 2.79 mg L<sup>-1</sup> in 2000 (CETESB, 2000) and 2.25 mg L<sup>-1</sup> in 2001 (this study). Again, as stated above, there are fluctuations in the time-series data due to natural seasonal variations depending upon exactly when (ie., summer-autumn x winter-spring) samples were collected. The evolution of the ammonium concentration in time is a good example, as it varied from 0.031 (1978/1979) or 0.014 (1979/1980) mg L<sup>-1</sup> (Guntzel, 2000) to values as high as 0.27 mg L<sup>-1</sup>, already in 1995 (Guntzel, 2000), or to a concentration peak of 2.0 mg L<sup>-1</sup> detected in this study in 2000 (see Tab. V).

Table V: Time-series of physico-chemical variables and nutrient concentration in Bariri reservoir waters.

Variables		Conama	1978/	1979/	1995	1996	1998	2000	2000	2001	2001
		20/86	1979*	1980*	**	**	**	***	**	***	**
Temperature	°C		27,2	25.9	25.0	29.0	24.0	28.5	27	24.3	24
Secchi disc depth	m		0.7	2	nd	nd	nd	nd	nd	nd	nd
Diss. Oxygen	mg L <sup>-1</sup>		5.9	7.3	4.3	6.9	4.6	4.6	3.7	5.8	7.7
pH		6.0 a 9.0	7.7	7.5	7.2	7.1	7.1	7.3	6.9	7.3	7.9
Conductivity	mS cm <sup>-1</sup>		0.122	0.111	0.235	0.200	0.221	0.276	0.253	0.181	0.205
Redox Potential	mV		nd	nd	nd	nd	nd	340	nd	176	nd
Chloride	mg L <sup>-1</sup>	250	nd	nd	22.5	19.2	23.9	27.0	32.6	29.0	21
Nitrate	mg L <sup>-1</sup>	10	0.53	0.18	1.35	0.83	2.95	1.10	2.79	2.25	0.93
Nitrite	mg L <sup>-1</sup>	1	0.004	0.008	0.070	0.14	0.243	0.128	0.235	0.132	0.049
Ammonium	mg L <sup>-1</sup>		0.031	0.014	0.27	0.15	0.12	2.0	0.21	0.14	0.11
Total nitrogen	mg L <sup>-1</sup>		nd	nd	2.25	2.2	4.35	nd	4.12	0.686	1.94
Orthophosphate	mg L <sup>-1</sup>		0.014	0.007	<0.008	<0.0008	0.006	0.22	0.08	0.19	nd
Total phosphorus	mg L <sup>-1</sup>	0.025	nd	nd	0.044	0.014	<0.01	nd	0.119	<0.004	0.034
Reactive silica	mg L <sup>-1</sup>		4.2	2.1	nd	nd	nd	6.5	nd	7.0	nd
Sulfate	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	21	nd	24	nd
Fluoride	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	0.45	nd	0.50	nd
DOC	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	nd	nd	6.88	nd

\* Guntzel (2000)

\*\* CETESB ( 1995; 1996; 1998; 1999; 2000; 2001).

\*\*\* This study.

nd = not determined.

A relevant and rather alarming conclusion that can be drawn when we examine the data collected in the present study is that the water column in Barra Bonita and Bariri reservoirs at present have nitrate concentrations similar to if not larger than those found in the Billings reservoir (see Tabs. III, IV and V). This is true because it is well known that Billings is a highly degraded water body as it is located close to the most populated and industrialized urban area in the country (Metropolitan São Paulo). Nevertheless, Barra Bonita and Bariri reservoirs, although far from São Paulo, already show signs of severe degradation. A plausible explanation may be found in the fact that the highly polluted Piracicaba River discharges into Barra Bonita, and the

Jaú and Bauru rivers into Bariri reservoir, respectively.

Promissão reservoir, on the other hand, is still a fairly new water body (about 20 years old). Due to its location, as long way downstream of Metropolitan São Paulo, in a less populated and industrialized region, it shows much lower values of nutrient concentration than the other reservoirs under study (see Tab. VI), although very recently (2000-2001) some nutrients are exceeding past values, such as total phosphorus, orthophosphate, ammonium, total organic nitrogen and nitrate. This is probably a result of the extensive land use seen in this drainage basin in very recent years.

Table VI: Time-series of physico-chemical variables and nutrient concentration in Promissão reservoir waters.

Variables		Conama	1978/	1979/	1995	1996	1998	1999	2000	2000	2001	2001
		20/86	1979*	1980*	**	**	**	**	***	**	***	**
Temperature	°C		27.8	27.3	26.0	27.0	25.0	24.0	27.1	28	25.5	25
Secchi disc depth	m		3.2	2.5	nd	nd	nd	nd	nd	nd	3.5	nd
Diss. Oxygen	mg L <sup>-1</sup>		6.10	7.70	8.10	8.10	8.70	7.90	7.16	6.3	7.00	6.2
pH		6.0 a 9.0	7.7	8.1	7.3	7.4	8.7	8.3	8.2	7.4	7.8	7.6
Conductivity	mS cm <sup>-1</sup>		0.085	0.080	0.182	0.169	0.180	0.100	0.171	0.134	0.133	0.155
Redox Potential	mV		nd	nd	nd	nd	nd	nd	395	nd	307	nd
Chloride	mg L <sup>-1</sup>	250	nd	nd	17.1	19.2	19.4	9.80	9.10	12.3	11.25	11.1
Nitrate	mg L <sup>-1</sup>	10	0.043	0.033	1.1	0.98	0.048	0.79	0.20	<0.30	0.30	<0.3
Nitrite	mg L <sup>-1</sup>	1	0.0042	0.0012	0.010	0.010	0.0081	0.011	0.0050	0.004	0.0075	0.004
Ammonium	mg L <sup>-1</sup>		nd	nd	0.123	0.890	0.9000	1.11		0.95	0.56	1.56
Total nitrogen	mg L <sup>-1</sup>		0.030	0.0053	0.090	0.090	<0.08	<0.08	0.040	<0.08	0.030	0.22
Orthophosphate	mg L <sup>-1</sup>		0.007	0.005	nd	nd	<0.006	nd	0.06	nd	0.2	nd
Total phosphorus	mg L <sup>-1</sup>	0.025	nd	nd	0.123	<0.010	0.029	<0.01		0.046	<0.004	<0.019
Reactive silica	mg L <sup>-1</sup>		3.0	3.4	nd	nd	nd	nd	10	nd	9.8	nd
Sulfate	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	nd	12	nd	16	nd
Fluoride	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	nd	0.35	nd	0.26	nd
DOC	mg L <sup>-1</sup>		nd	nd	nd	nd	nd	nd	nd	nd	5.51	nd

\* Guntzel (2000)

\*\* CETESB ( 1995; 1996; 1998; 1999; 2000; 2001).

\*\*\* This study.

nd = not determined.

When the concentrations values shown in Tabs. III-VI are compared with those prescribed in CONAMA 357/2005, it is clear that these water-bodies still meet class 2 water quality standards. However, if pollution sources are not controlled in the near future, this situation may no longer hold, which would be a cause for great concern. We hope that this study acts as a warning (maybe an early warning) to environmental policy makers of the State of São Paulo, to redouble their efforts to control sources of pollution in the State more rigorously.

At this point it should be emphasized that, already back in 1999, Barbosa et al. (1999) called attention to this question, arguing that "a progressive downstream eutrophication of the Tietê River could be forecast and that there was an urgent need for restoration measures at the headwaters."

So as to understand these factors better, a principal components analysis (PCA) was applied to the data, using eight variables (nitrate, nitrite, ammonium, chloride, orthophosphate, sulfate, fluoride and reactive silica). This treatment revealed that two principal components explained 83% of the data variance. When these components were plotted against each other, the variables were associated with each of the reservoirs as follows: (a) nitrate with Billings; (b) nitrate and nitrite with Barra Bonita; (c) chloride, fluoride and sulfate with Bariri and (d) reactive silica only with Promissão.

In order to demonstrate further the use of the PCA analysis, this statistical technique was repeated, now including data surveyed by Mozeto et al. (2003b) from Rasgão (extremely degraded) and Pedro Beicht (well preserved) reservoirs (both lying close to

Metropolitan São Paulo) the following chemical species-reservoir associations were then added: orthophosphate, ammonium, sulfate and fluoride with Rasgão and only reactive silica with Pedro Beicht. It can be concluded that the chemical species-reservoir association should help to determine the degree and nature of the degradation in these water bodies, as degraded water bodies are linked to chemical species originating in various anthropogenic activities, mainly coming from untreated urban (domestic) and industrial sewage, whereas clean water bodies are exclusively associated with reactive silica that is leached from soil by surface runoff.

Finally, it has to be added that the unsupervised ordering of the data into a hierarchical tree by cluster analysis produced two separate groups of reservoirs: one made up of Pedro Beicht and Promissão, the other of Billings, Rasgão, Barra Bonita and Bariri. This result is consistent with the ordering produced by PCA.

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