

Nutrients and chlorophyll-*a* concentrations in tropical rivers of Ribeira de Iguape Basin, SP, Brazil

Concentrações de nutrientes e clorofila-*a* em rios tropicais da Bacia do rio Ribeira de Iguape, SP, Brasil

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Abstract: Artificial eutrophication is an environmental problem of great concern for many countries. For the characterization of lakes and reservoirs, trophic state assessment has been producing satisfactory results for water resources management. Nonetheless, little information is available about the main factors governing nutrient inputs and the associated biological responses on tropical lotic environments. In this case, not even the term eutrophication is unanimity among researchers, since many of them state that low residence time and high turbulence, for instance, are able to restrict any potential algal responses to nutrient enrichment in rivers. Within this context, the goal of this research was to assess the concentrations of total phosphorus, orthophosphate and chlorophyll-*a*, which are the variables traditionally related to biomass growth as a result of increasing in nutrients concentration, in two tropical ecosystems, Jacupiranguinha and Pariquera-Açu Rivers, both located in Ribeira de Iguape River Basin (São Paulo state, Southeast Brazil). The results reflected distinct levels of anthropogenic interference on each river. For Jacupiranguinha River, the total phosphorus and orthophosphate concentrations, for instance, reached 33,886.7 $\mu\text{g.L}^{-1}$ and 24,090.0 $\mu\text{g.L}^{-1}$, respectively, in Station 7, where there's a fertilizer factory discharge. On the other hand, Pariquera-Açu River presented a less critic situation. The impact of WTP (Wastewater Treatment Plant) effluent on this river caused an increase in chlorophyll-*a* concentrations, which ranged between 4.6 $\mu\text{g.L}^{-1}$ and 12.0 $\mu\text{g.L}^{-1}$. No consistent relationship was found between phosphorus species and chlorophyll-*a*, pointing that other factors, like light limitation and short hydraulic resident time, restricted the increase in the photosynthetic pigment concentrations. Statistical procedures were performed through cluster analysis, which assembled the sampling stations considering the influence of the industrial discharge in Jacupiranguinha River (Stations 7 and 8), and other factors in Pariquera-Açu River, like the proximity to its spring (Stations 1, 2 and 3) and to Pariquera-Açu city (Stations 4, 5, 6 and 7) and also the lentic behavior in the last sampling station (Station 9).

Keywords: total phosphorus, orthophosphate, chlorophyll-*a*, tropical rivers, hydrographic basins, Ribeira de Iguape Valley.

Resumo: A eutrofização artificial é um problema ambiental de grande preocupação em diversos países. Visando à caracterização de lagos e reservatórios, a avaliação do estado trófico tem produzido resultados satisfatórios para o manejo dos recursos hídricos. Entretanto, pouca informação está disponível acerca dos principais fatores que controlam o aporte de nutrientes e a resposta biológica associada em ambientes lóticos tropicais. Neste caso, nem mesmo o termo eutrofização é unanimidade entre os pesquisadores, já que muitos deles consideram que o baixo tempo de residência e a elevada turbulência da água, por exemplo, são capazes de restringir a resposta algal, em rios, ao incremento de nutrientes. Considerando este contexto, o objetivo desta pesquisa foi avaliar as concentrações de fósforo total, ortofosfato e clorofila-*a*, que são variáveis tradicionalmente relacionadas ao crescimento de biomassa como resultado do incremento na concentração de nutrientes, em dois ecossistemas tropicais, rios Jacupiranguinha e Pariquera-Açu, ambos localizados na Bacia Hidrográfica do rio Ribeira de Iguape (estado de São Paulo, Brasil). Os resultados refletiram níveis distintos de interferência antrópica em cada um dos rios. Para o rio Jacupiranguinha, as concentrações de fósforo total e ortofosfato, por exemplo, atingiram 33.886,7 $\mu\text{g.L}^{-1}$ e 24.090,0 $\mu\text{g.L}^{-1}$, respectivamente, na Estação 7, onde ocorre lançamento do efluente de uma indústria de fertilizantes. Por outro lado, o rio Pariquera-Açu apresentou situação menos crítica. O impacto da ETE (Estação de Tratamento de Esgotos) neste rio causou um aumento nas concentrações de clorofila-*a*, que saltaram de 4,6 $\mu\text{g.L}^{-1}$ para 12,0 $\mu\text{g.L}^{-1}$. Não foi encontrada relação significativa entre as formas fosfatadas e a clorofila-*a*, indicando que outros fatores, como limitação de luz e baixo tempo de residência da água, restringiram o aumento das concentrações do pigmento fotossintético. Procedimentos estatísticos foram desenvolvidos por meio de análise de cluster, que reuniu as estações amostrais considerando a influência do efluente industrial no rio Jacupiranguinha (Estações 7 e 8), e outros fatores no rio Pariquera-Açu, como a proximidade da nascente (Estações 1, 2 e 3) e da cidade (Estações 4, 5, 6 e 7) e também o comportamento lético do rio na última estação amostral (Estação 9).

Palavras-chave: fósforo total, ortofosfato, clorofila-*a*, rios tropicais, bacias hidrográficas, Vale do rio Ribeira de Iguape.

1. Introduction

World water resources do have a significant ecological, economic and social meaning. Therefore, the management, conservation and restoration of these aquatic ecosystems are extremely important subjects, influencing the economy and the whole society. The management of aquatic systems is very complex, since it depends on the conciliation of different, and frequently antagonistic, interests involved in multiple uses of water, like human consumption and irrigation and industrial uses.

Artificial eutrophication consists in an exaggerated nutrient enrichment process (mainly nitrogen and phosphorus) that occur in the water column, as a result of excessive nutrient loading, mainly from agriculture (i.e. rural runoff), urban areas (i.e. urban runoff, effluents from wastewater treatment plants) and industry (Wetzel, 1983; Raibe et al., 2003; Wood et al., 2005; Petzoldt and Uhlmann, 2006; Schindler et al., 2006). Artificial eutrophication studies are much more common for lentic ecosystems, like the ones conducted by Quiros (1990), Neto and Coelho (2002); Liou and Lo (2005) and Mariani (2006) for lakes and reservoirs.

For lotic environments, few researches about water quality, relating nutrients concentrations and algal growth (through chlorophyll-*a*), are available. In addition to that, not even the term eutrophication is a consensus. On one hand, Schmidt (1994), who assessed phytoplankton characteristics of the River Danube (Hungary), observed an inverse relationship between discharge and phytoplankton density, as a result of the high washout rate imposed on suspended algae by the river. On the other hand, some authors, like Smith et al. (1999), consider that the idea that flowing waters are usually nutrient-saturated and that, as a consequence, light limitation and short hydraulic residence time would avoid or restrict biomass responses to nutrient enrichments, no longer appear to be tenable.

For temperate rivers, the studies developed by Dodds et al. (1998), Young et al. (1999), Neal et al. (2005a), Dodds (2006), Jarvie et al. (2006), Neal et al. (2006), Billen et al. (2007) were important contributions. Dodds (2006) proposed two trophic states for rivers: heterotrophic, defined as the metabolic activity of the stream during dark periods, which is directly related to respiration; autotrophic, defined as the gross primary production during lighted periods. The author also stated that these two states are not mutually exclusive. Another important observation was that heterotrophic processes predominate in rivers, in comparison to lakes, given the contribution of organic carbon sources from terrestrial environment and the greater likelihood that light is intercepted by the vegetation.

High concentrations of nutrients in rivers may cause, in some cases, algal biomass growth and, as a consequence, some deleterious effects might happen, like increases of

ionic concentrations and of the water electric conductivity, threats to endangered aquatic species and decreases in water column transparency (Smith, 2003, Calijuri et al., 2006). Within this context, the aim of this research was to assess the concentrations of total phosphorus, orthophosphate and chlorophyll-*a* in water samples of two tropical lotic ecosystems located in Ribeira de Iguape River Basin, Southeast Brazil. These rivers were subordinated to different patterns of human interference and presented distinct land use and occupation schemes on their adjacencies.

1.1. Study area

The geographic coordinates of Ribeira de Iguape Basin are 23° 30' and 25° 30' S and 46° 50' and 50° 00' W. Despite of its localization, in two very developed states in Brazil, Sao Paulo and Parana, Ribeira de Iguape River Watershed owns a significant environmental patrimony, Mata Atlantica Tropical Forest. This environmental richness, however, contrasts with severe social and economical problems. Some characteristics include high illiteracy taxes of the population and low attendance levels of sanitary infrastructure (Table 1), both in Cajati city (Figure 1), which is crossed by Jacupiranguinha River, and in Pariquera-Au city, which is crossed by Pariquera-Au River.

Comparing the intensity of negative anthropogenic impacts in Jacupiranguinha and in Pariquera-Au Rivers, it was possible to observe that the former presented a higher level of human interferences. A characteristic of Jacupiranguinha River is the lack of original vegetation on the riversides, which was substituted by banana cultivation (Moccellin, 2006). Besides, there's an effluent of a fertilizer factory that is discharged in the river. On the other hand, Pariquera-Au River presents original vegetation on the riversides and does not receive industrial effluents. Wastewater Treatment Plants (WTPs), represented by stabilization ponds located in Cajati and Pariquera-Au cities, discharge treated sanitary wastewater effluents in both rivers. Stabilization ponds for wastewater treatment are a recurrent alternative for Ribeira de Iguape Basin cities, like Cajati, Pariquera-Au and also other cities, like Juquia,

Table 1. Some social and economic characteristics of Cajati and Pariquera-Au cities.

Social/Economic factor	Cajati city	Pariquera-Au city
Total population (in habitants)***	32,618	20,454
Illiteracy tax of the population – 15-year-old or more (%)*	13.9	8.9
Water supply - attendance level (%)*	96.7	93.8
Collected sanitary wastewater (%)*	69.2	63.3
Treated sanitary wastewater (%)**	62.3	63.3
Per capita income (US\$)*	201.00	279.00

References: *SEADE (2000), **SEADE (2003) and ***SEADE (2006).

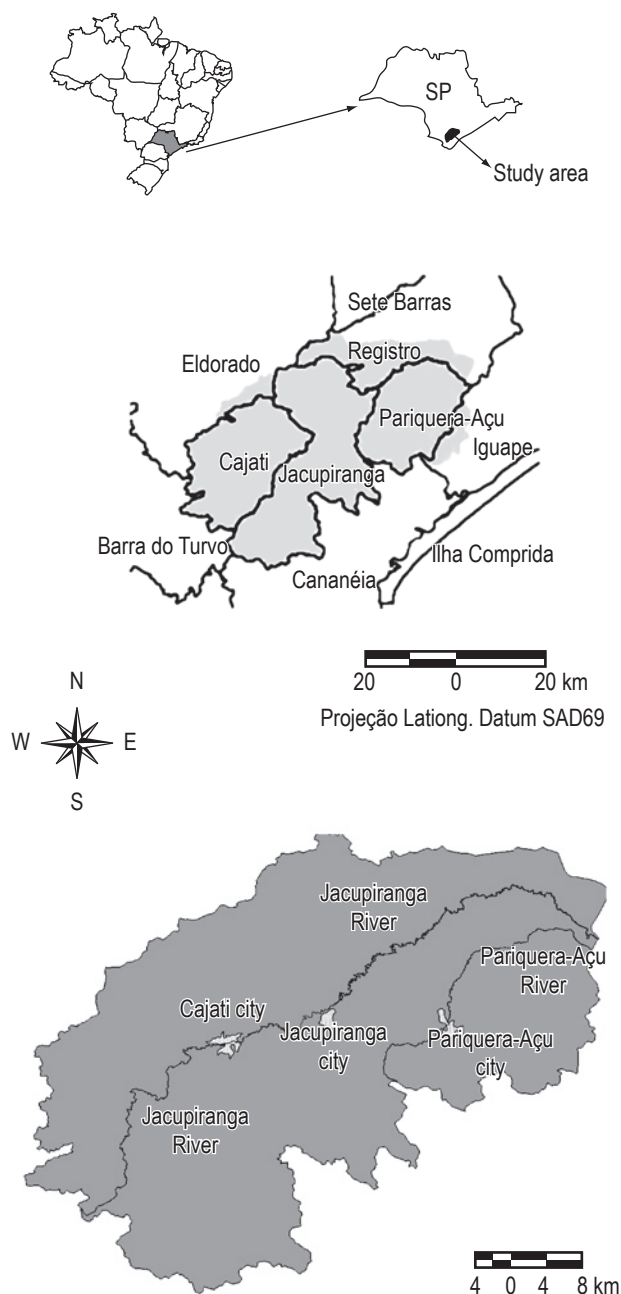


Figure 1. Study area map, showing São Paulo state (SP) in Brazil, Jacupiranguinha, Jacupiranga and Pariqueira-Açu Rivers and Cajati, Jacupiranga and Pariqueira-Açu cities. Reference: UFV (2007).

São Lourenço da Serra and Registro (Miwa et al., 2007). Nonetheless, effluents from WTPs may cause significant inputs of nutrients to rivers (Owens and Walling, 2002; Neal et al., 2005b). Brazilian WTPs, especially stabilization ponds, usually are not able to remove ions (tertiary treatment); so, their effluents commonly present high nitrogen and phosphorus concentrations.

Regarding the lack of limnological studies in Ribeira de Iguape Basin, the assessment of some water characteristics

of two tropical rivers, under different levels of anthropogenic impacts, will significantly help in the context of comprehending the dominant processes that occur in both systems, and also of evaluating the impacts of the human activities. The information achieved by this research will probably provide subsidies to the implementation of an integrated management plan for the watershed, considering the sustainability premises.

2. Material and Methods

Eight sampling stations were selected in each river (Table 2) and water samples were collected at about 10 cm below the surface, using 5 L plastic gallons. Chlorophyll-*a* analyses were performed following Nush (1980) method (modified by NEN, 1981), through ethanol extraction. Besides, total phosphorus and orthophosphate concentrations were determined according to APHA (2002). Statistical procedures were conducted, through analysis of variance (ANOVA), for all the water variables, in order to verify the differences between the rivers and also among the sampling stations and the sampling days, considering probability of 95% ($p < 0.05$).

All water variables were quantified in the three days of each sampling: January 26th to 28th, 2005, for Jacupiranguinha River, and January 17th to 19th, 2007, for Pariqueira-Açu River, under double-replica technique. Moreover, precipitation data were analyzed. For Jacupiranguinha River, the precipitation data were obtained from DAEE (2005), which owns a climatologic station in Jacupiranga city (Code F4-017, altitude: 90 m, 24° 43' S and 48° 01' W). For Pariqueira-Açu River, data were acquired through a climatologic station in Pariqueira-Açu city.

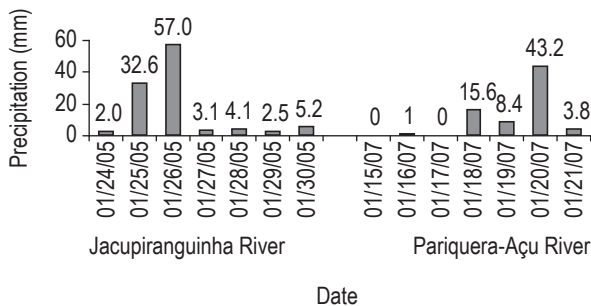
3. Results

The total amount of precipitation during January 2005 was 377 mm (106 mm just during the week when the sampling took place) in Jacupiranguinha River. During January 2007, the total precipitation was 236 mm (72 mm just during the sampling week) in Pariqueira-Açu River (Figure 2).

Total phosphorus concentrations in water were higher in Jacupiranguinha River (Table 3). Station 7, which corresponds to the effluent of a fertilizer factory, reached 33,886.7 $\mu\text{g}\cdot\text{L}^{-1}$ of total phosphorus. The concentration in the station before this effluent was 180.0 $\mu\text{g}\cdot\text{L}^{-1}$, so the impact accrued from it was prominent. The highest phosphorus concentration in Pariqueira-Açu River was detected in Station 8, which corresponds to the end of the river (474.1 $\mu\text{g}\cdot\text{L}^{-1}$). Both rivers presented a trend of increasing total phosphorus concentrations from their springs to their ends. For Jacupiranguinha River, this variation was from 120.0 $\mu\text{g}\cdot\text{L}^{-1}$ to 5,730.0 $\mu\text{g}\cdot\text{L}^{-1}$, and for Pariqueira-Açu River, it was from 36.2 $\mu\text{g}\cdot\text{L}^{-1}$ to 474.1 $\mu\text{g}\cdot\text{L}^{-1}$.

Table 2. Location references of sampling stations in Jacupiranguinha and in Pariquera-Açu Rivers.

Sampling station	Location [Reference/Latitude (S)/Longitude (W)]	
	Jacupiranguinha River	Pariquera-Açu River
1	Near Jacupiranguinha River spring (24° 43' 11" S and 48° 10' 26" W)	Near Pariquera-Açu River spring (24° 44' 54" S and 47° 56' 58" W)
2	Countryside, before Cajati city (24° 43' 56" S and 48° 08' 49" W)	Countryside, before Pariquera-Açu city (24° 43' 46" S and 47° 56' 28" W)
3	Station of water impounding for Cajati city population (24° 43' 51" S and 48° 07' 57" W)	Station of water impounding for Pariquera-Açu city population (24° 43' 00" S and 47° 53' 40" W)
4	Cajati city (24° 43' 47" S and 48° 06' 44" W)	Pariquera-Açu city (24° 43' 36" S and 47° 54' 26" W)
5	Before Cajati WTP (Wastewater Treatment Plant) (24° 43' 38" S and 48° 05' 55" W)	Before Pariquera-Açu WTP (Wastewater Treatment Plant) (24° 42' 07" S and 47° 52' 55" W)
6	After Cajati WTP effluent (24° 43' 22" S and 48° 05' 37" W)	After Pariquera-Açu WTP effluent (24° 42' 03" S and 47° 52' 55" W)
7	After Cajati city (24° 43' 05" S and 48° 05' 10" W)	After Pariquera-Açu city (24° 37' 57" S and 47° 50' 59" W)
8	End of Jacupiranguinha River (24° 43' 02" S and 48° 03' 00" W)	End of Pariquera-Açu River (24° 37' 56" S and 47° 44' 12" W)

**Figure 2.** Diary precipitation (mm) from 01/24/2005 to 01/30/2005 (the sampling period in Jacupiranguinha River was from 01/26/2005 to 01/28/2005) and from 01/15/2007 to 01/21/2007 (the sampling period in Pariquera-Açu River was from 01/17/2007 to 01/19/2007). Reference: DAEE (2005).**Table 3.** Mean (3 days of sampling) total phosphorus concentrations ($\mu\text{g.L}^{-1}$) in the water of Jacupiranguinha and Pariquera-Açu Rivers.

Station	Jacupiranguinha River	Pariquera-Açu River
1	120.0	36.2
2	193.3	42.1
3	163.3	62.6
4	216.7	62.5
5	1,726.7	160.3
6	180.0	162.2
7	33,886.7	113.1
8	5,730.0	474.1

The patterns for orthophosphate concentrations' spatial distribution (Table 4) were analog to the total phosphorus ones. The fertilizer factory discharge in Jacupiranguinha River caused an acute impact on orthophosphate concentrations, from $30.0 \mu\text{g.L}^{-1}$ (Station 6) to $24,090.0 \mu\text{g.L}^{-1}$ (Station 7). For Pariquera-Açu River, the WTP effluent also

Table 4. Mean (3 days of sampling) orthophosphate concentrations ($\mu\text{g.L}^{-1}$) in the water of Jacupiranguinha and Pariquera-Açu Rivers.

Station	Jacupiranguinha River	Pariquera-Açu River
1	130.0	20.7
2	20.0	15.1
3	20.0	14.6
4	13.3	27.2
5	33.3	32.3
6	30.0	52.1
7	24,090.0	42.2
8	14,816.7	303.7

caused an increment on orthophosphate concentrations, reaching $52.1 \mu\text{g.L}^{-1}$ (Station 6).

The highest chlorophyll-*a* concentration in Jacupiranguinha River was $3.7 \mu\text{g.L}^{-1}$ and, in Pariquera-Açu River, $12.0 \mu\text{g.L}^{-1}$ (Table 5). For Jacupiranguinha and Pariquera-Açu rivers, the increment in chlorophyll-*a* concentrations in Station 6, after the WTPs effluents, was evident: from $1.4 \mu\text{g.L}^{-1}$ to $3.7 \mu\text{g.L}^{-1}$, in Jacupiranguinha River, and from $4.6 \mu\text{g.L}^{-1}$ to $12.0 \mu\text{g.L}^{-1}$, in Pariquera-Açu River.

ANOVA revealed that both rivers are similar considering the variable chlorophyll-*a* ($p = 0.88$), but statistically and significantly different in respect to total phosphorus ($p < 0.05$) and orthophosphate ($p < 0.05$). Regarding this difference verified for phosphorus species, the statistical procedures were conducted for each river separately. The sampling stations were considered different with respect to total phosphorus and orthophosphate ($p < 0.05$) in Jacupiranguinha River, and with respect to total phosphorus, orthophosphate and chlorophyll-*a* ($p < 0.05$) for Pariquera-Açu River (Table 6).

Table 5. Mean (3 days of sampling) chlorophyll-*a* concentrations ($\mu\text{g.L}^{-1}$) in the water of Jacupiranguinha and Pariquera-Açu Rivers.

Station	Jacupiranguinha River	Pariquera-Açu River
1	1.2	0.6
2	1.4	0.3
3	1.4	0.3
4	1.4	1.5
5	1.4	4.6
6	3.7	12.0
7	3.0	1.0
8	1.2	4.0

Table 6. Analysis of variance (ANOVA) for Jacupiranguinha and Pariquera-Açu Rivers considering the sampling days and the sampling stations evaluated.

	Jacupiranguinha River			Pariquera-Açu River		
	TP	P-PO ₄	CHL- <i>a</i>	TP	P-PO ₄	CHL- <i>a</i>
Sampling days	0.90	0.87	<0.05	0.60	0.41	0.96
Sampling stations	<0.05	<0.05	0.46	<0.05	<0.05	<0.05

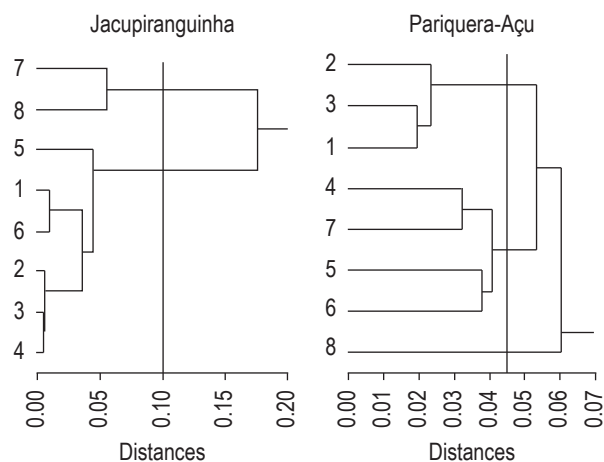
TP: Total Phosphorus; P-PO₄: Orthophosphate; CHL-*a*: Chlorophyll-*a*.

Since ANOVA analysis revealed that, in general, there was not statistically significant difference among the consecutive days of the samplings (Table 6), total phosphorus, orthophosphate and chlorophyll-*a* concentrations, determined for the three days of each sampling, were submitted to arithmetic mean for the clustering analysis, verifying the distance or similarity among the stations. Then, hierarchical clustering analysis was carried out using UPGMA (Unweighted Pair Group Method with Arithmetic Mean), considering cophenetic correlation coefficients superior to 0.8 (Legendre and Legendre, 1983).

Cluster analysis for Jacupiranguinha River (Figure 3) highlighted the impact of the industrial discharge in the water body (Station 7) and its influence on Station 8, considering phosphorus species and chlorophyll-*a*. For Pariquera-Açu River, Stations 1, 2 and 3 were isolated from the others since these three stations are not submitted to the city influence. Stations 4, 5, 6 and 7 and Station 8 were allocated in two separated groups.

4. Discussion

The high total phosphorus concentrations in Jacupiranguinha River were associated with the industrial effluent discharge in Station 7, as already observed by Moccellini (2006), who stated the harmful effect of the fertilizer factory discharge in the river, verified by the high electric conductivity verified in this station (maximum of $1,823 \mu\text{S.cm}^{-1}$), for instance. For Pariquera-Açu River, the high phosphorus concentrations verified in Station 8 may be explained by the lentic behavior presented by the river in this station, which promotes an intensive growth

**Figure 3.** Hierarchical clustering analysis for all sampling stations in Jacupiranguinha and Pariquera-Açu Rivers

of macrophytes and also the accentuation of decomposition processes in the water column, as verified by Demars and Harper (1998) for English rivers. Furthermore, the phosphorus release from the sediment may be considered in Station 8 of Pariquera-Açu River, whose lentic behavior facilitates stratification and low dissolved oxygen concentrations on the interface water-sediment, promoting the nutrient's release, as verified by Caraco et al. (1990) for freshwater systems.

Phosphorus is extensively used in fertilizers and other chemicals, and high phosphorus concentrations in streams may be associated with poor agricultural practices, urban runoff, or point-source discharges, like the effluents from wastewater treatment plants, for instance (EPA, 2006; Khan and Ansari, 2005). Brasil (2005) classifies Brazilian rivers based on many water variables, like total phosphorus and chlorophyll-*a* concentrations (special class, class 1, 2, 3 and 4). Both Jacupiranguinha and Pariquera-Açu Rivers are originally considered class 2. However, according to total phosphorus concentrations obtained in some of their sampling stations, these ecosystems could be considered class 4, since all stations in Jacupiranguinha River and Stations 5, 6, 7 and 8 in Pariquera-Açu River presented total phosphorus concentrations in water samples higher than $100.0 \mu\text{g.L}^{-1}$, which is the superior limit for class 3 and the inferior one for class 4.

The relationship between phosphorus concentrations and phytoplankton biomass (chlorophyll-*a*) in aquatic systems has yielded insights on nutrient limitation and it is an important management tool in experimental works and even in monitoring programs (Peters, 1986, Dos-Santos et al., 2003). Petrucio et al. (2005) obtained higher chlorophyll-*a* concentrations in a tropical river in Minas Gerais state, Brazil (Severo River), reaching $53.5 \mu\text{g.L}^{-1}$. The authors were expecting lower chlorophyll-*a* concentrations, since the study was performed in tropical lotic systems, but some sites presented high concentrations and the values fluctuated between $1.6 \mu\text{g.L}^{-1}$ and $53.5 \mu\text{g.L}^{-1}$. It was pos-

sible to observe that the biological response measured by chlorophyll-*a* concentrations, in both Jacupiranguinha and Pariquera-Açu Rivers, was not proportional to the phosphorus species concentrations, since non-significant relationship was found between these variables (Figure 4). Cunha et al. (2008) verified weak relationships between total phosphorus concentrations and phytoplankton total density in water of tropical rivers in Southeast Brazil. Chlorophyll-*a* responses to nutrient enrichment in Jacupiranguinha and Pariquera-Açu Rivers were probably restricted by physical factors such as light limitation, water turbulence and short hydraulic residence times.

An important factor for lotic systems, stated by Dodds et al. (2002) and Van Nieuwenhuysse and Jones (1996), is that there is an apparent decrease in planktonic chlorophyll yield per unit phosphorus when total phosphorus is in excess of approximately 300 $\mu\text{g.L}^{-1}$. It indicates that nutrient limitation is overcome when there are high nutrient concentrations in the water column. Positive correlations between chlorophyll-*a* and phosphorus concentrations are more common for lentic systems. Huszar et al. (2006) concluded that the high chlorophyll-*a* concentrations were related to high nitrogen and phosphorus concentrations in tropical and temperate lentic systems. This article also provided a detailed discussion about the differences found between total phosphorus and chlorophyll-*a* concentrations in tropical and temperate systems.

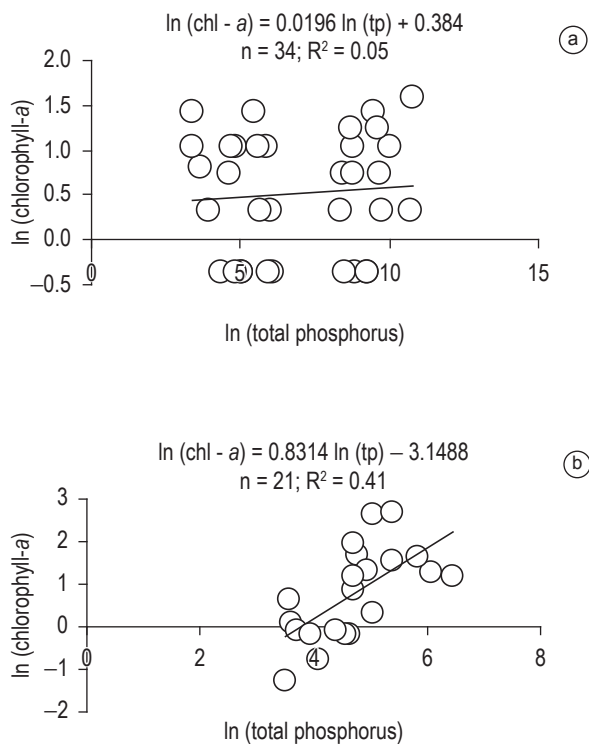


Figure 4. Relationships between \ln -total phosphorus ($\mu\text{g.L}^{-1}$) versus \ln -chlorophyll-*a* ($\mu\text{g.L}^{-1}$) for: a) Jacupiranguinha River ($n = 34$); and b) Pariquera-Açu River ($n = 21$).

Comparing the water quality of both rivers, it was possible to realize that Jacupiranguinha River severely depends on revitalizing actions. Its sediment is even polluted by heavy metals, notably by mercury, whose concentrations reached 0.8 mg.Kg^{-1} in January, 2005 (Cunha et al., 2007a; 2007b). The fact that some water variables may influence the bio-availability and the mobility (cycling) of many contaminants (Gunnarsson et al., 1996, Schaaning et al., 1996, Brown et al., 2000, Skei et al., 2000), like the heavy metals, for instance, is worrying in this case. Moreover, the high total phosphorus concentrations in the water, which reached almost $34,000.0 \mu\text{g.L}^{-1}$, are concerning, since the ecosystem might be conducted to a severe disequilibrium state.

Bringing to a conclusion, the assessment of total phosphorus, orthophosphate and chlorophyll-*a* concentrations in water of two tropical lotic ecosystems, Jacupiranguinha and Pariquera-Açu Rivers, located in Ribeira de Iguape Basin, Southeast Brazil, enabled to conclude that:

- Jacupiranguinha River presented a higher level of water quality deterioration, reflecting the different degree of anthropogenic activities, which were represented by banana cultivation and by an industrial plant located on its adjacencies. This deterioration was evinced by the high total phosphorus and orthophosphate concentrations, which were particularly high after Station 7, where there's a fertilizer's factory effluent discharge. Although Jacupiranguinha and Pariquera-Açu Rivers are considered class 2 by Brasil (2005), many total phosphorus concentrations found were characteristic of class 4 water bodies;
- Non-significant relationship was found between total phosphorus and chlorophyll-*a* in Jacupiranguinha and Pariquera-Açu Rivers. It indicated that other factors affected the biological response measured by the photosynthetic pigment concentration, like light limitation, low water residence time and high turbulence;
- For both rivers, hierarchical clustering analysis presented coherent results. For Jacupiranguinha River, the analysis assembled the sampling stations considering the influence of the industrial discharge on Stations 7 and 8. For Pariquera-Açu, factors like proximity to the spring (Stations 1, 2 and 3), influence of the Pariquera-Açu city (Stations 4, 5, 6 and 7) and lentic behavior (Station 8) determined three different groups.

Acknowledgements

The authors wish to express their sincere thanks and grateful to FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for the scholarship (Process 06/53550-4) and financial support (Process 02/13449-1), to CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for the scholarships.

References

- APHA – American Public Health Association. *Standard Methods for the examination of water and wastewater*. 20 ed. Washington: APHA, 2002.
- BILLEN, G., GARNIER, J., NÉMERY, J., SEBILO, M., SFERRATORE, A., BARLES, S., BENOIT, P. and BENOIT, M. A long-term view of nutrient transfers through the Seine River continuum. *Sci. Total Environ.* 2007, vol. 375, no. 1-3, p. 80-97.
- BRASIL. *Resolução nº 357*, de 17 de março de 2005. CONAMA – Conselho Nacional de Meio Ambiente, 2005. Available from: <<http://www.mma.gov.br>>.
- BROWN, SS., GASTON, GR., RAKOCINSKI, CF. and HEARD, RW. Effects of sediment contaminants and environmental gradients on macrobenthic community trophic structure in Gulf of Mexico Estuaries. *Estuaries* 2000, vol. 23, no. 3, p. 411-424.
- CALIJURI, MC., ALVES, MSA. and Dos-SANTOS, ACA. *Cianobactérias e cianotoxinas em água continentais*. São Carlos - SP: RiMa, 2006. 109 p.
- CARACO, N., COLE, J. and LIKENS, GE. A comparison of phosphorus immobilization in sediments of freshwater and coastal marine systems. *Biogeochemistry* 1990, vol. 9, no. 3, p. 277-290.
- COELHO, S., GAMITO, S. and PEREZ-RUZAFÁ, A. Trophic state of Foz de Almagem coastal lagoon (Algarve, South Portugal) based on the water quality and the phytoplankton community. *Estuar. Coast. Shelf Sci.* 2006, vol. 71, no. 1-2, p. 218-231.
- CUNHA, DGF., CAPPARELLI, H., CALIJURI, MC., MIWA, ACP. and BENASSI, RF. Comparison between some trace and heavy metals concentrations in sediments of a river and a natural wetland system in Ribeira de Iguape Basin, São Paulo state, Brazil. *Engenharia Ambiental (UNIPINHAL)* 2007a, vol. 4, no. 1, p. 32-53.
- CUNHA, DGF., CALIJURI, MC. and MIWA, ACP. A precipitação pluviométrica como agente indutor de modificações nas características químicas do sedimento do rio Jacupiranguinha, Vale do Ribeira de Iguape, SP. *Revista Minerva*, 2007b, vol. 4, no. 1, p. 41-49.
- CUNHA, DGF., FALCO, PB. and CALIJURI, MC. Densidade fitoplanctônica e estado trófico dos rios Canha e Pariquera-Açu, bacia hidrográfica do rio Ribeira de Iguape, SP, Brasil. *Revista Ambiente e Água* 2008. in press.
- DAEE – Departamento de Águas e Energia Elétrica. *Banco de Dados Pluviométricos do Estado de São Paulo*, 2005. Available from: www.daece.sp.gov.br.
- DEMARS, BOL. and HARPER, DM. The aquatic macrophytes of an English lowland river system: assessing response to nutrient enrichment. *Hydrobiol.* 1998, vol. 384, no. 1-3, p. 75-88.
- DODDS, WK. Eutrophication and trophic state in rivers and streams. *Limnol. Oceanogr.* 2006, vol. 51, no. 1-2, p. 671-680.
- DODDS, WK., JONES, JR. and WELCH, EB. Suggested classification of stream trophic state: distributions of temperate stream types by chlorophyll, total nitrogen and phosphorus. *Water Res.* 1998, vol. 32, no. 5, p. 1455-1462.
- DODDS, WK., SMITH, VH. and LOHMAN, K. Nitrogen and phosphorus relationships to benthic algal biomass in temperate streams. *Can. J. Fish. Aquat. Sci.* 2002, vol. 59, no. 1, p. 865-874.
- Dos-SANTOS, ACA., CALIJURI, MC., MORAES, EM., ADORNO, MAT., FALCO, PB., CARVALHO, DP., DEBERDT, GLB. and BENASSI, SF. Comparison of three methods for chlorophyll determination: spectrophotometry and fluorimetry in samples containing pigment mixtures and spectrophotometry in samples with separate pigments through High Performance Liquid Chromatography. *Acta Limnologica Brasiliensia* 2003, vol. 15, no.3, p. 7-18.
- EPA 2006. *The Wadeable Streams Assessment: A Collaborative Survey of the Nation's Streams*. Available from: <<http://www.epa.gov/owow/streamsurvey>>.
- GUNNARSSON, JS., SCHANNING, MT., HYLLAND, K., SKÖLD, M., ERIKSEN, DO., BERGE, JA. and SKEI, JM. Interaction between eutrophication and contaminants III. Mobilization and bioaccumulation of benzo(a)pyren from marine sediments. *Mar. Pollut. Bull.* 1996, vol. 33, no. 1-6, p. 80-90.
- HUSZAR, VLM., CARACO, NE., ROLAND, F. and COLE, J. Nutrient-chlorophyll relationships in tropical-subtropical lakes: do temperate models fit? *Biogeochemistry* 2006, vol. 79, no. 1-2, p. 239-250.
- JARVIE, HP., NEAL, C. and WITHERS, PJA. Sewage-effluent phosphorus: a greater risk to river eutrophication than agricultural phosphorus? *Sci. Total Environ.* 2006, vol. 360, no. 1-3, p. 246-253.
- KHAN, FA., ANSARI, AA. Eutrophication: an ecological vision. *The Botanical Review* 2005, vol. 71, no. 4, p. 449-482.
- LEGENDRE, L. and LEGENDRE, P. *Numerical Ecology: Developments in Environmental Modeling*, 3. Amsterdam: Elsevier Scient. Publ. Co., 1983. 435 p.
- LIOU, YT., LO, SL. A fuzzy index model for trophic status evaluation of reservoir waters. *Water Res.* 2005, vol. 39, no. 7, p. 1415-1423.
- MAINSTONE, CP. and PARR, W. Phosphorus in rivers: ecology and management. *Sci. Total Environ.* 2002, vol. 282, no. 1, p. 25-47.
- MARIANI, CF. 2006. *Reservatório Rio Grande: caracterização limnológica da água e biodisponibilidade de metais-traço no sedimento*. São Paulo: Instituto de Biociências – IB, Universidade de São Paulo – USP, 124 p. [Master Thesis].
- MARQUES, JC., NIELSEN, SN., PARDAL, MA. and JORGENSEN, S. Impact of eutrophication and river management within a framework of ecosystem theories. *Ecol. Model.* 2003, vol. 166, no. 1-2, p. 147-168.
- MIWA, ACP., FREIRE, RH. and CALIJURI, MC. Dinâmica de nitrogênio em um sistema de lagoas de estabilização na região do Vale do Ribeira (São Paulo – Brasil). *Eng. Sanit. Ambient.* 2007, vol. 12, no. 2, p. 169-180.
- MOCCELLIN, J. *A microbacia do rio Jacupiranguinha como unidade de estudo para a sustentabilidade dos recursos hídricos*

- no Baixo Ribeira de Iguape, SP. São Carlos – SP: Escola de Engenharia de São Carlos – EESC, USP, 2006. 151 p. [Master Thesis].
- NEAL, C., HOUSE, WA., JARVIE, HP., NEAL, M., HILL, L. and WICKHAM, H. Phosphorus concentrations in the River Dun, the Kennet and Avon Canal and the River Kennet, southern England. *Sci. Total Environ.*, 2005a, vol. 344, no. 1-3, p. 107-128.
- NEAL, C., JARVIE, HP., NEAL, M., LOVE, AJ., HILL, L. and WICKHAM, H. Water quality of treated sewage effluent in a rural area of the upper Thames Basin, southern England, and the impacts of such effluents on riverine phosphorus concentrations. *J. Hydrol.* 2005b, vol. 304, no. 1-4, p. 103-117.
- NEAL, C., HILTON, J., WADE, AJ., NEAL, M. and WICKHAM, H. Chlorophyll-*a* in the rivers of eastern England. *Sci. Total Environ.* 2006, vol. 365, no. 1-3, p. 84-104.
- NEN. *Nederlandse Norm 6520*. Netherlands, 1981.
- NETO, JFB., COELHO, RMP. A morfometria e o estado trófico de um reservatório urbano: lagoa do Nado, Belo Horizonte, Estado de Minas Gerais. *Acta Scientiarum* 2002, vol. 24, no. 1, p. 285-290.
- NUSH, EA. Comparison of different methods for chlorophyll and pheopigment determination. *Arch. Hydrobiol.* 1980, vol. 14, no. 1, p. 14-36.
- OWENS, PN. and WALLING, DE. The phosphorus content of fluvial sediment in rural and industrialized river basins. *Water Res.* 2002, vol. 36, no. 3, p. 685-701.
- PETERS, RH. The role of prediction in limnology. *Limnol. Oceanogr.* 1986, vol. 31, no. 1, p. 1143-1159.
- PETRUCIO, MM., BARBOSA, FAR. and THOMAZ, SM. Bacteria and phytoplankton production rates in eight river stretches of the Middle Rio Doce hydrographic basin (Southeast Brazil). *Braz. Arch. Biol. Technol.* 2005, vol. 38, no. 1, p. 487-496.
- PETZOLDT, T. and UHLMANN, D. Nitrogen emissions into freshwater ecosystems: is there a need for nitrate elimination in all wastewater treatment plants? *Acta Hydrochimica et Hydrobiologica* 2006, vol. 34, no. 1, p. 305-324.
- QUIRÓS, R. Factors related to variance of residuals in chlorophyll-total phosphorus regressions in lakes and reservoirs of Argentina. *Hydrobiol.* 1990. vol. 200, no. 1, p. 343-355.
- RÄIKE, A., PIETILÄINEN, OP., REKOLAINEN, S., KAUPPILA, P., PITKÄNEN, H., NIEMI, J., RAATELAND, A. and VUORENMAA, J. Trends of phosphorus, nitrogen and chlorophyll *a* concentrations in Finnish rivers and lakes in 1975-2000. *Sci. Total Environ.* 2003, vol. 310, no. 1, p. 47-59.
- SCHAANING, MT., HYLLAND, K., ERIKSEN, GO., BERGAN, TD., GUNNARSSON, JS. and SKEI, JM. Interaction between eutrophication and contaminants. II. Mobilization and bioaccumulation of Hg and Cd from marine sediments. *Mar. Pollut. Bull.* 1996, vol. 33, no. 1-6, p. 71-80.
- SCHMIDT, A. Main characteristics of the phytoplankton of the Southern Hungarian section of the River Danube. *Hydrobiol.* 1994, vol. 289, no. 1-3, p. 97-108.
- SCHINDLER, DW., DILLON, PJ. and SCHREIER, H. A review of anthropogenic sources of nitrogen and their effects on Canadian aquatic ecosystems. *Biogeochemistry* 2006, vol. 79, no. 1-2, p. 25-44.
- SEADE. Fundação Sistema Estadual de Análise de Dados. Secretaria de Economia e Planejamento, Governo do estado de São Paulo. Indicadores de desenvolvimento e inclusão social, 2007. *População. e Estatísticas Vitais*. Available at: <http://www.seade.gov.br>.
- SKEI, J., LARSSON, P., ROSENBERG, R., JONSSON, P., OLSSON, M. and BROMAN, D. Eutrophication and contaminants in aquatic ecosystems. *Ambio* 2000, vol. 29, no. 4, p. 184-194.
- SMITH, VH., TILMAN, GD. and NEKOLA, JC. Eutrophication: impacts of excess nutrients inputs on freshwater, marine, and terrestrial ecosystems. *Environ. Pollut.* 1999, vol. 100, no. 4, p. 179-196.
- SMITH, VH. Eutrophication of Freshwater and Coastal Marine Ecosystems: A Global Problem. *Environmental Science & Pollution Research* 2003, vol. 10, no. 2, 126-139.
- UFV. Universidade Federal de Viçosa. *Estudo dos sistemas naturais e artificiais redutores de cargas poluidoras para a sustentabilidade dos recursos hídricos do Baixo Ribeira de Iguape – SP*. São Paulo: FAPESP, 2007. (Mapa elaborado pela Universidade Federal de Viçosa, para o Projeto Temático FAPESP 02/13449-1:)
- Van-NIEUWENHUYSE, EE. and JONES, JR. Phosphorus-chlorophyll relationship in temperate streams and its variation with stream catchment area. *Can. J. Fish. Aquat. Sci.*, 1996, vol. 53, no. 1, p. 99-105.
- WETZEL, RG. *Limnology*. 2 ed. New York: Saunders College Publishing, 1983. 76 7p.
- WOOD, FL., HEATHWAITE, AL. and HAYGARTH, PM. Evaluating diffuse and point phosphorus contributions to river transfers at different scales in the Taw catchment, Devon, UK. *J. Hydrol.* 2005, vol. 304, no. 1-4, p. 118-138.
- YOUNG, K., MORSE, GK., SCRIMSHAW, MD., KINNIBURGH, JH., MACLEOD, CL. and LESTER, JN. The relation between phosphorus and eutrophication in the Thames catchment, UK. *Sci. Total Environ.* 1999, vol. 228, no. 2-3, p. 157-183.

Received: 21 January 2008

Accepted: 16 July 2008