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Dissolved Nitrogen and Phosphorus Dynamics in the Lower Portion of the Paraiba do Sul River, Campos dos Goytacazes, RJ, Brazil

Mônica Aparecida Leite Silva[*]**; Claudia Ferreira Calasans; Alvaro Ramon Coelho Ovalle and Carlos Eduardo Rezende**
Universidade Estadual do Norte Fluminense, Centro de Biociências e Biotecnologia, Laboratório de Ciências Ambientais, Av. Alberto Lamego, 2.000, Campos dos Goytacazes - RJ, Brasil

ABSTRACT

The Paraíba do Sul river lower reach was monitored monthly between August 1995 and July 1996. This study was aimed at evaluating the temporal dynamics of dissolved nitrogen and phosphorus and its main controlling factors. Minimum and maximum observed values were as follows: N-NO_2^- - 0.08/0.51; N-NO_3^- - 21/57; N-NH_4^+ - 1.4/6.7; DON - 4.9/86.0; DIN -24.5/60.9; P-PO_4^{3-} - 0.43/1.66; DOP - 0.05/0.92; pH - 6.2/7.8; Dissolved Oxygen - 6.4/10.1; Conductivity - 48/74; Temperature - 20.5/31.1 (Nutrients - µM; Dissolved Oxygen - mg/l; Conductivity - µS/cm; Temperature - °C). Discharge presented a characteristic seasonal variation, showing a peak in January. Increasing P-PO_4^{3-}, DOP, N-NH_4^+ and N-NO_2^- concentrations with increasing discharges could be associated to the partial flooding of inumerous fluvial islands and floodplains and to the agricultural practices of sugar cane crops that during the wet season could transfer nitrogen and phosphorus compounds to the fluvial channel.

Key-words: Dissolved nutrients, Paraíba do Sul River, Temporal dynamics, Nitrogen, Phosphorus, Discharge

INTRODUCTION

Rivers are landscape integrating components and receive the whole load of transported material from the drainage basin in which they are inserted. Variations observed in river flows depend on the rainwater that precipitates in its reception areas. After its entrance in the drainage basin, the part of the water that doesn't come back to the atmosphere by evapotranspiration can reach the fluvial system by overland flow, throughflow and groundwater baseflow. In its pathway through the soil-rock complex until reaching the fluvial channel, the water carries everything that can be mobilized by its physical or chemical action, including the soluble and particulate products that result of its interaction with the biota (Sioli, 1975). Among these products are nitrogen and phosphorus compounds.

The main natural sources of nitrogen for the aquatic ecosystems are: rain, organic and inorganic material of allochthonous origin and fixation of molecular nitrogen (Esteves, 1998). The human intervention in the nitrogen biogeochemical cycle occurs through three main paths: (i) atmospheric emissions, mainly through the burning of fossil fuels, that come back to the ecosystems by precipitation; (ii) agricultural practices, with the use of nitrogen fertilizers, whose portion not assimilated by the cultures is leached for the

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[*] Author for correspondence

groundwater, notably in the form of nitrate; (iii) release of domestic sewers and industrial effluents in the water-bodies, without previous treatment (Odum, 1988). From the aquatic ecosystems point of view, the first two paths act as diffuse sources of nitrogen, while the last is characterized as a punctual source.

The dissolved phosphorus present in continental aquatic ecosystems has origin in natural and artificial sources. Among the natural sources, rocks of the drainage basin constitute the main phosphate source. After the phosphate release, by the weathering of primary minerals of the rock, its distribution in the aquatic ecosystems occurs in the dissolved and particulate forms.

Other natural factors that allow the phosphate input can be pointed, such as the particulate material present in the atmosphere and the phosphate resulting of the decomposition of allochthonous organisms. The more important artificial sources of phosphate are domestic and industrial sewers, detergents, agricultural fertilizers and particulate material of industrial origin, contained in the atmosphere. Especially in industrialized and densely populated areas, the artificial sources of phosphate are more important than the natural ones (Esteves, 1998). The mining and processing of phosphate for fertilizers production create serious problems of local pollution. Therefore, the excess of dissolved phosphate in freshwaters, resulting from the increasing volume of urban-industrial and agricultural effluents is, today, of a great concern (Odum, 1988).

This study was aimed at studying the temporal dynamics of dissolved nitrogen and phosphorus in the Paraíba do Sul river lower reach, evaluating its main controlling factors.

MATERIALS AND METHODS

The Paraíba do Sul River (PSR) has 1.145 km of extension and drains a 55.400 km^2 area (DNAEE, 1983; Rosso et. al., 1991). This river crosses one of the most industrialized and inhabited Brazilian regions, São Paulo and Rio de Janeiro states, flowing into the Atlantic Ocean. Along the course of PSR, its waters are used to irrigate and supply several cities, among them are Rio de Janeiro and Campos dos Goytacazes, receiving different types of industrial and urban effluents, rich in nitrogen and phosphorus. The PSR lower reach (100 km of extension) is a wide alluvial plain located in the north of Rio de Janeiro State and it is characterized by almost 200,000 ha of sugar-cane crops and pastures, associated to the alcohol and sugar industries. The main PSR tributaries are the rivers Pomba, Muriaé and Dois Rios (Figure 1).

The sampling station, located at the end of PSR watershed (Campos dos Goytacazes municipality), was monitored monthly between August 1995 and July 1996. The transversal section of the river was subdivided in three subsections, where the depths were determined. To measure the water speed in different depths (one m below the surface, in the middle and one m above the bottom), flowmeters (General Oceanic model 2030) were used and the instantaneous discharge calculated. Samples were collected in each subsection with a Van Dorn bottle at a depth of approximately one meter. Samples were transferred to polyethylene flasks and transported to the laboratory in an icebox. In the laboratory aliquots were filtered in GF/F membranes with a porosity of approximately 0.70 µm. The dissolved material (<0.70 µm) was stored in clean polyethylene flasks and maintained frozen until the determinations were performed.

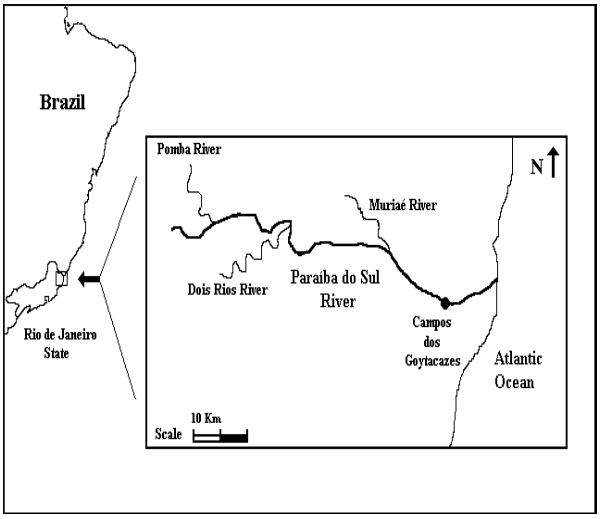

Figure 1 - Study area and sampling station.

Physico-chemical parameters such as pH, conductivity and temperature were measured *in situ*. pH was determined by a portable potentiometer with a glass electrode (Digimed model DM-PV). Conductivity was determined by a portable conductivimeter (WTW model LF 96) and temperature measured with a thermometer. Aliquots collected for determination of dissolved oxygen were preserved in the field and analyzed following the method of Winkler.

The determinations of $N\text{-}NO_2^-$ and $N\text{-}NO_3^-$ were performed by Flow Injection Analysis System (ASIA-ISMATEC). Concentrations of dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) were determined by digestion with potassium persulfate, in alkaline conditions for DON and acid conditions for DOP. Determinations of $N\text{-}NH_4^+$ and $P\text{-}PO_4^{3-}$ concentrations were performed, respectively, by the indophenol and molybidic acid methods. The methodologies used are described in details in Carmouze (1994).

The results presented in this study are average values of the samples of sub-superficial water collected in each subsection. The detection limits for the determined nutrients were: $N\text{-}NO_2^- = 0.05$ µM; $N\text{-}NO_3^- = 0.1$ µM; DON = 0.8 µM; DOP = 0.05 µM; $P\text{-}PO_4^{3-} = 0.05$ µM; $N\text{-}NH_4^+ = 0.5$ µM.

RESULTS AND DISCUSSION

Instantaneous discharges in the studied hydrological year are presented in the Figure 2, where it can be observed that the discharge presented a characteristic seasonal variation, with peaks in January. Minimum and maximum values found for this parameter were 200 m^3/s and 2600 m^3/s, respectively.

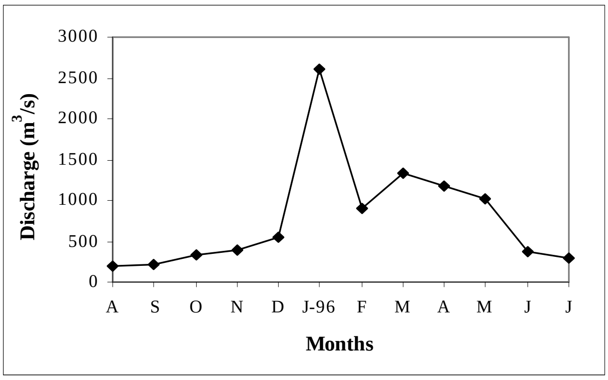

Figure 2 - Discharge variation in the lower portion of the PSR.

Costa (1994) analyzed PSR discharge data from 1934 to 1992 collected by National Department of Water and Electric Energy (DNAEE) in a station located at Campos dos Goytacazes. According to him, the highest discharges, ranging from 2,000 to 5,000 m^3/s, occurred between December and March, while the lowest discharge values, from 200 to 500 m^3/s, were found between July and September. Compared to the discharge data obtained by Costa (1994), the studied year was considered to be dry.

Physico-chemical parameters are shown in Table 1. Water temperature presented a defined pattern of annual variation, with a minimum value of 20.5 °C in the winter and maximum of 31.1 °C in the summer, coincident with discharge variation. pH was lightly basic, with an average value around 7.2. The highest concentrations of dissolved oxygen were observed in the dry period. This trend was probably due to a decrease of suspended particulate material, leading to a larger transparency of the water column and, consequently, to an increase of primary productivity.

Table 1 - Temporal variation of physico-chemical parameters in the lower portion of the Paraíba does Sul River.

Months	Temperature (°C)	pH	Conductivity (µS/cm)	Dissolved Oxygen (mg/L)
A	25.9	7.8	74	10.1
S	24.3	7.6	70	8.3
O	25.0	7.5	66	8.0
N	22.4	7.8	67	7.4
D	28.6	7.4	62	7.0
J-96	27.1	7.0	48	7.4
F	31.1	7.4	53	6.4
M	29.0	7.1	55	7.0
A	25.8	7.3	51	8.4
M	21.0	6.6	55	8.3
J	22.4	6.9	62	8.4
J	20.5	6.2	61	8.7

Water conductivity had an inverse relationship with the discharge, probably associated to the dilution effect by the rainwater. This parameter can be used as an indicator of the ionic force of the environment, which is mainly controlled by the abundance of larger cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and anions (SO_4^{2-}, Cl^- and HCO_3^-). Consequently, the studied micronutrients should follow the dilution tendency observed for conductivity. On the other hand, as the PSR system is under intense human pressure, the dynamics of these elements can be significantly affected by anthropogenic sources.

The N-NO_3^- concentrations did not present a clear pattern of seasonal variation (Figure 3), although a lower value has been observed in the discharge peak. This presented an inverse behavior of that of pH, suggesting a possible participation of the local agricultural sources in the acidification of the fluvial waters. According to Ovalle (personal communication), the alkalinity in this period also presented a pronounced reduction, indicating a decline of the system's buffer capacity.

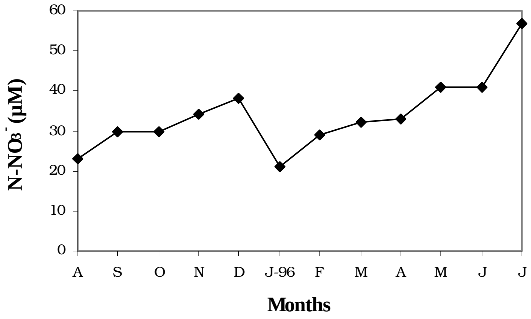

Figure 3 - Temporal variation of N-NO_3^- in the lower portion of the PSR.

Figures 4, 5, 6 and 7 show the temporal variations of N-NH_4^+, N-NO_2^-, DOP and P-PO_4^{3-}, respectively. The elevation of the concentration of these nutrients with the discharge increase can be associated to the partial flood of numerous fluvial islands and flooded marginal areas, where aquatic macrophyte detritus are accumulated during the dry season. The large oscillations of the water level and the consequent variation of flooded area lead to a dynamic interaction process between aquatic and terrestrial environments. Thus, the terrestrial environment can act as a source of nitrogen and phosphorus to the river water. Another source can be associated to the agricultural practices of the sugar-cane culture (burning, harvesting, fertilization and irrigation) which can transfer nitrogen and phosphorus compounds to the fluvial channel, especially during the rainy period. The burning of sugar-cane cultures before the harvest transfers large amounts of nitrogen from the soil-vegetation system to the atmosphere. Only a fraction of the nitrogen from the fertilizers applied to the cultivated lands is assimilated by the cultures, and a significant amount can reach the fluvial channel through the groundwater or superficial run-off. In addition, irrigation is made using a mixture of river water and sub-products of the alcohol and sugar industries, which are rich in nitrogen and phosphorus, and can potentially, reach the river. Also, the input of domestic sewage of several cities is a continuous source of nutrients that becomes particularly important during the months of low discharge.

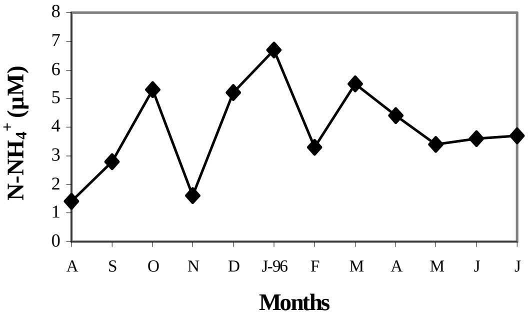

Figure 4 - Temporal variation of N-NH_4^+ in the lower portion of the PSR.

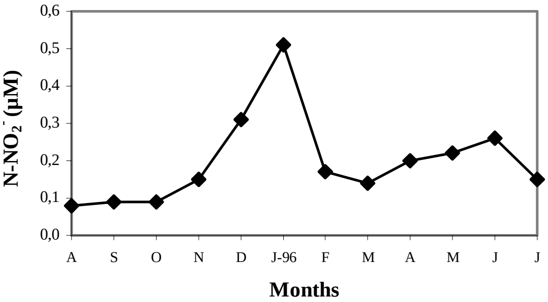

Figure 5 - Temporal variation of N-NO_2^- in the lower portion of the PSR.

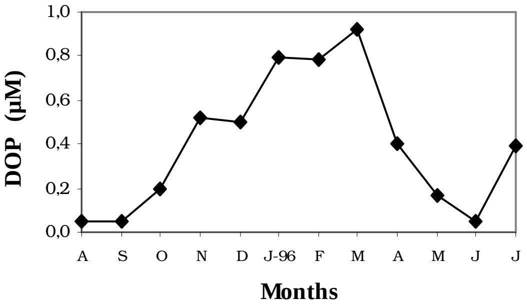

Figure 6 - Temporal variation of DOP in the lower portion of the PSR.

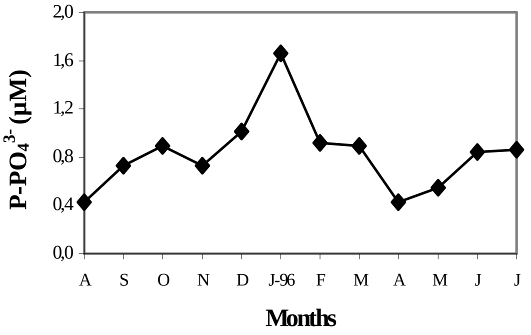

Figure 7 - Temporal variation of P-PO_4^{3-} in the lower portion of the PSR.

Temporal variation of dissolved organic nitrogen is presented in Figure 8. The decrease of the concentration of this nutrient in the period of higher discharges, as well as its increment during the periods of lower discharges, suggested that the input of untreated domestic sewers might be strongly influencing the dynamics of dissolved organic nitrogen in the fluvial system. According to Golterman (1975), among the sources of nitrogen to the aquatic environment, stand out those of human origin derived from agriculture, humans excretes and detergents.

Dissolved inorganic nitrogen forms are shown in Figure 9, which showed that NID was predominantly under the form of nitrate (about 89%). In the month of higher discharge, a slight decrease of N-NO_3^- and an increase of the relative contribution of N-NO_2^- and N-NH_4^+ occurred. The increase of DIN under nitrite and ammonium forms in the period of higher discharge possibly occurred due to the oxygen level reduction, decreasing the efficiency of nitrification process.

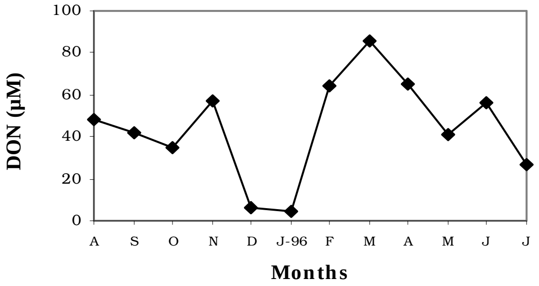

Figure 8 - Temporal variation of DON in the lower portion of the PSR.

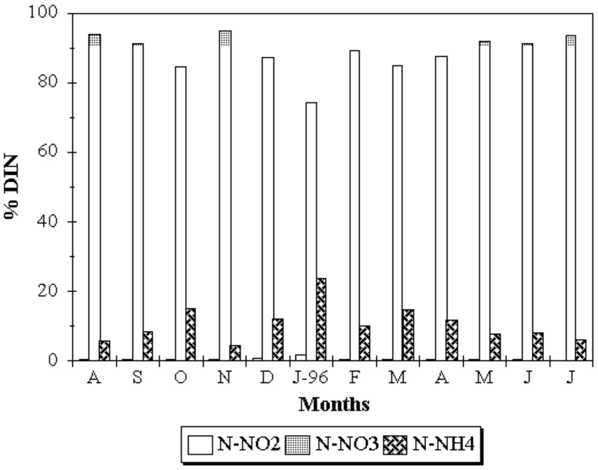

Figure 9 - Temporal variation of the percentage of NID forms in the lower portion of the PSR.

According to Odum (1988), the inorganic N:P ratio usually found in streams and rivers is about 28. However, the ratios found in Paraíba do Sul River were higher, except for the period of larger discharges (Figure 10). The fact that the lowest atomic N:P ratios have been found in the summer can be related to an acceleration in the process of phosphorus remineralization due to the temperature increase, which intensifies the metabolism of the microorganisms (Pomeroy, 1960; Ryther and Dustan, 1971; Nowichi and Nixon, 1985). The highest phosphorus values found in the summer can be associated to the bottom organic matter mineralization by bacteria and microzooplankton under high temperatures, resulting in fast mixture in the water column (Nixon, 1981).

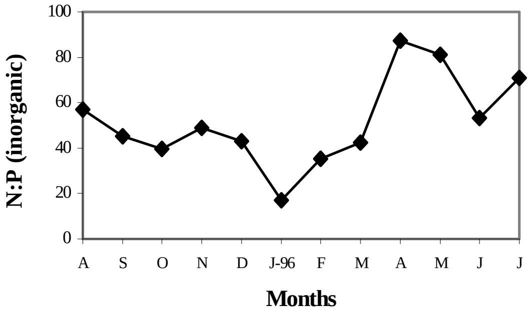

Figure 10 - Temporal variation of the atomic ratio of inorganic N:P in the lower portion of the PSR.

Table 2 presents the average values of nutrients concentrations found in the lower portion of PSR watershed and compares them with natural and impacted rivers in the Sepetiba Bay, RJ (Guandu River, Guarda River, São Francisco Channel and Cação River) and Maricá-Guarapina Lagoon system, RJ (Vigário, Ubatiba and Caranguejo Rivers). Nutrient concentrations in the present study were above the levels described for unpolluted rivers. On the other hand, when compared to rivers submitted to intense human pressures, one could observe that PSR had lower values for all parameters, except for nitrate that presented an average concentration within the range found for Sepetiba Bay and Maricá-Guarapina basin. Although these values were lower than those of impacted rivers, the atomic N:P ratios (inorganic) were within the range found for several watersheds under urban, industrial and agricultural influence (~ 10 to 100; Billen et al., 1991).

Nitrate results suggested the existence of intense nitrification processes during organic matter mineralization, and a pronounced contribution of the local agricultural sources to the PSR water. Rezende (1993), working in a system under strong industrial influence also observed the effect of nitrification processes in the studied annual cycle.

Table 2 - Comparison among the values found in this study with the one of natural and impacted rivers (µM).

Parameters	a	b	c	d	VR	UR	CR	PSR
$N\text{-}NH_4^+$	1.6	1.0	57.0	8.7	135	24.2	5.1	3.9
$N\text{-}NO_3^-$	8.9	7.1	32.2	28.9	49	15.1	4.5	34.1
DOP	—	—	—	—	—	—	—	0.4
$P\text{-}PO_4^{3-}$	0.4	0.3	1.5	0.5	6	3.2	1.4	0.8
$N\text{-}NO_2^-$	—	—	—	—	11	3.4	0.7	0.2
DON	37.5	18.6	—	—	—	—	—	44.4

(a) Average pondered by the discharge in 60 not polluted rivers (Meybeck and Helmer, 1989); (b) Global average for not polluted rivers (Meybeck and Helmer, 1989); (c) Annual average of the Guandu River and Guarda River (Rezende, 1993; Meybeck, 1993); (d) Annual average of the São Francisco Channel and Cação River (Rezende, 1993; Meybeck, 1993); (VR) Vigário River, (UR) Ubatiba River, (CR) Caranguejo River (Figueiredo, 1995).

RESUMO

O Rio Paraíba do Sul foi monitorado mensalmente na sua porção inferior, entre agosto de 1995 e julho de 1996, objetivando estudar a dinâmica temporal de nitrogênio e fósforo dissolvidos e avaliar seus principais fatores controladores. Os valores mínimos e máximos observados para os parâmetros analisados foram os seguintes: $N\text{-}NO_2^-$ - 0,08/0,51; $N\text{-}NO_3^-$ - 21/57; $N\text{-}NH_4^+$ - 1,4/6,7; Nitrogênio Orgânico Dissolvido (NOD) - 4,9/86,0; Nitrogênio Inorgânico Dissolvido (NID) - 24,5/60,9; $P\text{-}PO_4^{3-}$ - 0,43/1,66; Fósforo Orgânico Dissolvido (POD) - 0,05/0,92; pH - 6,2/7,8; Oxigênio Dissolvido - 6,4/10,1; Condutividade - 48/74; Temperatura - 20,5/31,1 (Nutrientes - µM; Oxigênio Dissolvido - mg/l; Condutividade - µS/cm; Temperatura - °C). A vazão apresentou uma variação sazonal característica, com pico de descarga em janeiro. A elevação das concentrações de $P\text{-}PO_4^{3-}$, POD, $N\text{-}NH_4^+$ e $N\text{-}NO_2^-$ com o aumento da vazão pode estar associada à inundação parcial de numerosas ilhas fluviais e áreas alagáveis e às práticas agrícolas da cultura de cana-de-açúcar que durante o período de chuva pode transferir compostos de nitrogênio e fósforo para o canal fluvial.

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