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Dissolved Nutrient, Chlorophyll a and DOC Dynamic Under Distinct Riverine Discharges and Tidal Cycles Regimes at the Paraíba do Sul River Estuary, R.J.,

G.C.T. Krüger† , C.E.V de Carvalho† and M. S. Suzuki†

Universidade Estadual do Norte Fluminense,
Centro de Biociências e Biotecnologia,
Laboratório de Ciências Ambientais,
Campos dos Goytacazes, 28013-602, R.J, Brasil.
carvalho@uenf.br

ABSTRACT

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The aim of the present work is to evaluate the role of Paraíba do Sul River (PSR) in the nutrient, dissolved organic carbon and chlorophyll a input to the adjacent coastal area. In order to achieve this goal, four samplings were performed between 2000 and 2001, two in the dry season and two in the rainy season. Samples were collected every hour during a complete tidal cycle as well as physico-chemical parameters and currents direction and velocity with an acoustic Doppler profiler (ADP1500 ®). Inorganic (P-PO_4, N-NO_3, N-NO_2, N-NH_4 and Si) and organic (DON, DOP) nutrient as well as dissolved organic carbon (DOC) analysis was performed at the laboratory. Statistical difference between dry and rainy season were observed for the majority of the studied nutrients (Si, N-NO_3, N-NO_2, N-NH_4 and P-PO_4), COD and chlorophyll a. The average nutrient concentration observed at the present study were higher than other small and medium size rivers estuaries along the Brazilian south and southeastern coast, as the Camburiú (SC), except for NH_4 and PO_4, and the Mucuri (BA) and similar to the values observed for the Patos Lagoon estuary (RS).

INTRODUCTION

The high primary production and the position between the marine and the continental environment make the estuarine systems one of the most vulnerable ecosystems to the global changes and human activities (HASSEN, 2001).

Scientific studies in tropical estuaries began to be published at the literature between the sixties and the seventies and in the last years these areas are receiving special attention (BERNER and RAO, 1994; EYRE, 1995), mainly due to the riverine systems of these areas represent the main freshwater source to the world oceans (MILLIMAN and MEADE, 1983). The majority of the studies dealing with nutrient dynamic and flux to the coastal zones performed at the eastern South American Coast only considered the two large rivers of the region the Amazon and the São Francisco. Therefore there is a huge deficiency of data from the other medium and small sized rivers that also discharges their waters along this part of the Atlantic Ocean (CARNEIRO 1998; CARVALHO *et al.*, 2002).

Tropical estuaries present several differences from temperate and polar estuaries, the main are: the higher rainfall rates; the presence of perennial vegetation that reduces the soil erosion rates and a limited temperature variation. Besides that, the rivers from these regions present high water discharge; transport a smaller amount of suspended particulate matter (mainly due to the vegetation presents a higher density) and present a higher nutrient concentration (MEYBECK, 1984; NITTROUER *et al.*, 1995; ZHANG, 1999).

The world population growth has severely raised the demand on the aquatic and terrestrial systems. One third to half of the earth surface have already been changed due to the intense urbanization, agriculture, deforestation and reforestations processes that altered the hydrological cycle. Additional factors are the alteration of the natural biological communities and the introduction of exotic (non-native) species in the environments (VITOUSEK *et al.* 1997 apud SMITH *et al.*, 1999).

In Brazil the largest population densities were observed at coastal regions, being the PSR drainage basin entirely situated in an intense urbanized region. The main pollution sources to the PSR lower basin include the disposal of untreated domestic effluents and the sewage from the sugarcane and alcohol industries also disposed directly at the river or in it's affluent without any previous treatment (COSTA, 1998).

The present study objectives are to determinate the nutrient, chlorophyll a and DOC dynamic at the Paraíba do Sul River estuary during distinct riverine discharges (dry and rainy season) and tidal regime (spring and neap tides).

METHODS

The Paraíba do Sul River (Figure 1) is located between 20°26' and 23°38' S and 41° and 46°39' W, being entirely inserted at the southeastern region of Brazil. Its drainage basin is closely related to the most industrialized region of the country, the States of São Paulo, Minas Gerais and Rio de Janeiro.

The RPS river net discharge near its delta present a seasonal variation ranging from 300 to 1650 m^3s^{-1}, with the winter months (June-August) corresponding to the lower discharge and the summer months (December-February) to the higher discharge period. The annual average discharge is 672 m^3s^{-1} (COSTA, 1998).

Four tidal cycles, one during neap tide and another during spring tide at October 2000 (dry season) and February 2001 (rainy season) were analysed. In each survey water samples were taken (surface and bottom), physico-chemical parameters were measured (pH, conductivity, temperature, dissolved oxigen) every hour. Water samples were collected by a "Van Dorn" sampler and immediately filtered in cellulose acetate membranes (0.45µm) for nutrient analysis, and in glass fiber filters (GF/FV Millipore®) for DOC and chlorophyll a. For nutrients the filtered samples were than stored in plastic flasks and frozen until analysis. For DOC analysis the filtered samples were stored in amber glass flasks with 10 ml of H_3PO_4 10% and stored at a refrigerator until analysis (CALASANS *et al.*, 1995).

At the laboratory the DOC was analyzed by high temperature catalytic oxidation (680°C), in a carbon analyzer Shimadzu TOC-5000 (SUGIMURA and SUZUKI, 1988). The dissolved

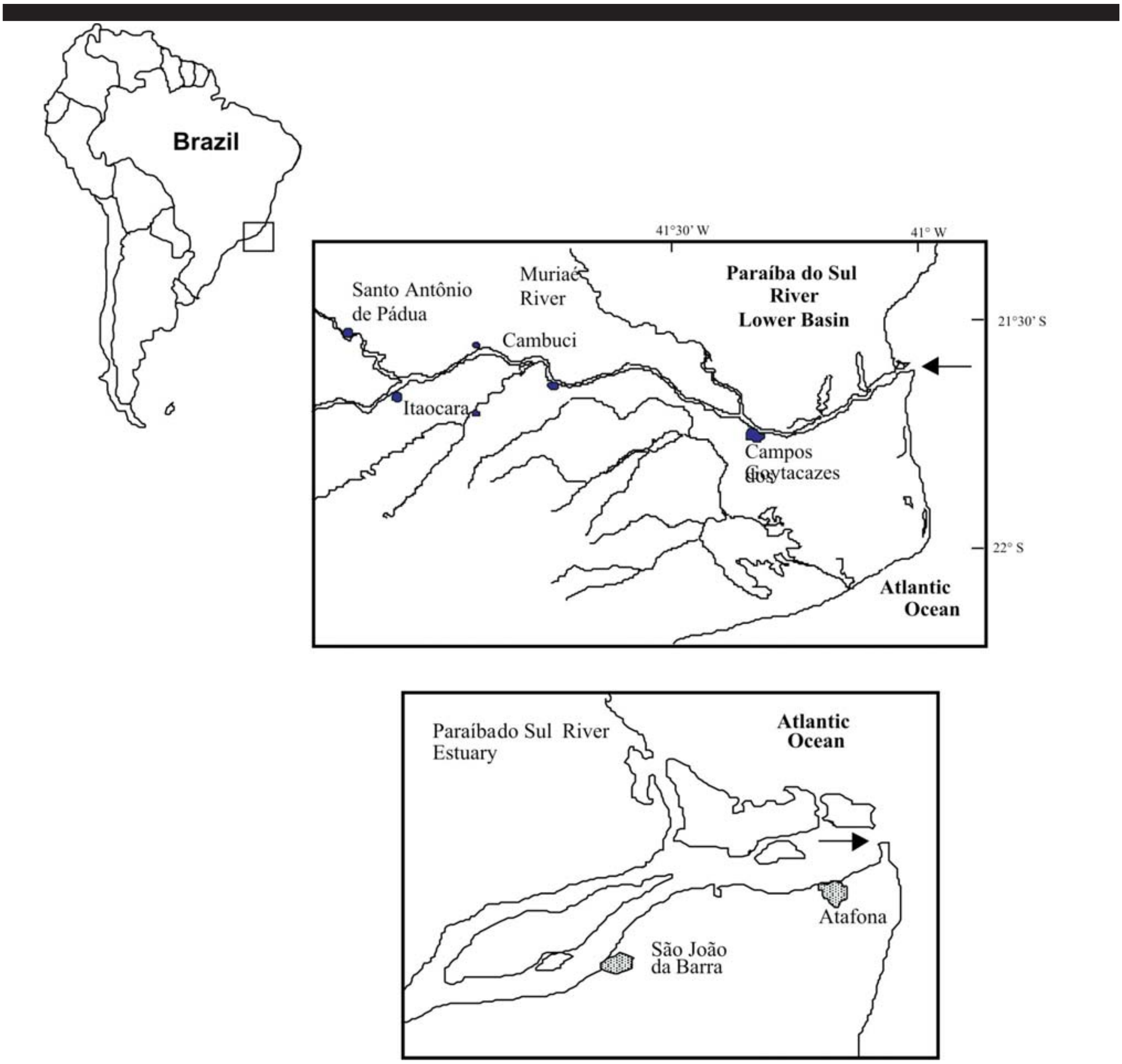

Figure 1. Map showing the geography of the Paraíba do Sul lower basin and the sampling site location (pointer).

nutrient species and the chlorophyll a were analyzed by colorimetric methods. The ions N-NO_3 and N-NO_2 were analyzed by flow injection analysis (ASIA Ismatec) and the ions P-PO_4, N-NH^4 and Si analyzed following the methodology described by GRASSHOFF et al. (1983). The DOP and the DON were obtained by the subtraction of the total concentration from the inorganic fraction. All the analysis was performed in triplicate.

In order to detect significant statistical differences between the surface and the bottom of the water column and between the dry and the rainy periods (á = 0,05), a T test for independent samples was used with the help of the software Statistica for Windows, version 5.5, 2000 (by StatSoft, inc.)

RESULTS

Hydrodynamic

D2°uring the dry period samplings (October) the average salinity was 6.36, ranging between 0.1 and 29.5 psu, with higher values at the bottom samples. In the rainy period (February) on the neap tide sampling, there was no penetration of the coastal waters inside the estuary and thus no salinity was observed. Although during the spring tide the salinity ranged from 0.04 to 30.37 psu (Figure 2). Concerning the tide amplitude, the neap tides presented smaller variations when compared with the studied spring tides. During the rainy season sampling the stream velocity ranged from 1.44 m s^{-1} to 1.28 m s^{-1}, although during the neap tide sampling all the measures velocities were negative indicating a seaward flow. In the dry period the variation was smaller, with stream velocity ranging from 0.76 to 0.78 m s^{-1} (Figure 3). The average pH values were 8.21 in the dry period and 7.22 in the rainy. The average dissolved oxygen was also higher during the dry period (6.38 mg l^{-1}) when compared to the rainy period (4.64 mg l^{-1}). The average temperature ranged from 23.8°C to 27.3 °C in October and from 26.0°C to 31ºC in February.

Nutrients and Chlorophyll a

Table 1 summarizes the obtained results during all the sampling periods. In general, a decrease in the nutrient concentration was always observed during the flood and at the high tide. The NO_3 correspond to 94% to 95% of the dissolved inorganic nitrogen (DIN). In the dry period the dissolved organic nitrogen (DON) was the dominant fraction, although in the rainy season the NO_3 concentrations were slightly higher. Both DON and NO3 values decreased their concentrations with the salinity increase. The ammonia concentrations were

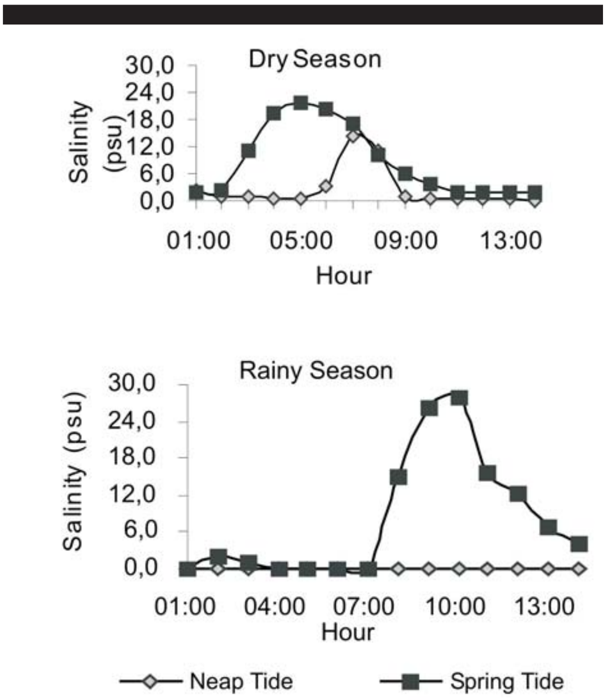

Figure 2. Salinity variations along time during neap and spring tides in the rainy and dry season.

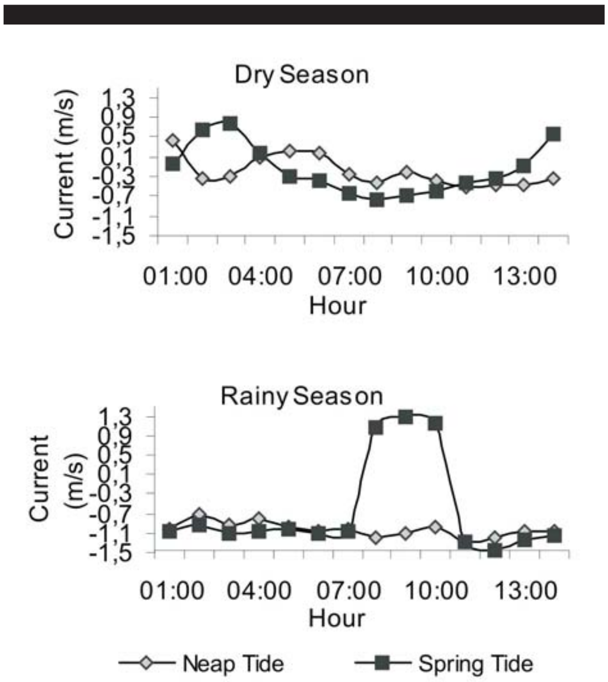

Figure 3. Average stream velocity along time during neap and spring tides in the rainy and dry season.

generally low in the estuary, and in the dry period (October), and during the high tide the concentrations were below the detection limit of the method. The NO_2 and the NH_4 presented an inverse trend when compared with NO_3 and DON, with situations of gain in relation to the salinity (Figure 4). The orthophosphate concentrations were always higher than the dissolved organic phosphate (DOP) in all the studied periods and tides, both elements presented higher concentrations during the ebb tide. In relation to Si, the rainy period presented higher concentrations when compared to the dry period, probably reflecting the fluvial input of this element to the estuarine system. The DOC variation was better understood during the spring tides where the concentrations tend to raise at the same time that the tide was ebbing. The DOC concentrations ranged from 1.5 mg l^{-1} to 5.6 mg l^{-1}. Orthophosphate presented the same trend observed for silica and nitrogen, higher concentrations observed in the rainy period with the predominance of the inorganic form.

The N:P ratio ranged from 16 to 39, with a relative enrichment of the inorganic nitrogen in relation to the orthophosphate.

Chlorophyll *a* presented its higher values when the river discharge was lower (dry period). During the dry period the chlorophyll a decrease its concentration with the penetration of the marine waters inside the estuary (flood tide). Although during the rainy season an opposite trend was observed, with increasing concentrations while the tide was flooding.

Statistical Analysis

The T-test showed significant statistical differences ($P<0,05$) between the surface and bottom samples for temperature in both studied periods (dry and rainy), with higher values observed at the surface (± 1ºC). Concerning the nutrients, only NO_3 presented significant statistical differences ($P<0,02$) between surface and bottom samples on the February sampling (rainy season, neap tide). Comparing the nutrient, Chl-a and DOC behavior between the two studied periods (dry x rainy, Table 2),

Table 1. *Average nutrient, chlorophyll a and DOC concentrations in the Paraíba do Sul River Estuary, in the rainy and dry seasons.*

	COD (mg l^{-1})	Chl-a (µg l^{-1})	P-PO_4 (µM)	POD (µM)	NO_3 (µM)	NO_2 (µM)	NH_4 (µM)	NOD (µM)	Si $(OH)_4$ (µM)	N:P
19 October 2000 (dry season, neap tide) (n=28)										
Mean	3,24	15,91	0,66	0,25	20,7	0,36	0,50	-	132,2	35
s.d.	0,4	4,26	0,18	0,17	6,2	0,09	0,43	-	26,8	17
Range	1,9 - 4,6	7,1- 33,7	0,25 - 1,15	0,08 -0,63	4,2 - 30,4	0,18 - 0,64	0,05 - 1,27	-	30,7 -214,7	19 -7
25 October 2000 (dry season, spring tide) (n=28)										
Mean	3,01	19,91	0,65	0,54	7,41	0,57	0,33	21,76	67,4	16
s.d.	0,6.5	7,19	0,31	0,15	5,64	0,30	0,39	6,23	33,2	14
Range	1,2 - 4,6	3,0 -37,3	0,25 -2,03	0,27 -1,15	0,46 -15,60	0,24 -1,14	0,05 - 1,33	40,7 -6,55	14,3 -103,0	3 -41
17 February 2001 (rainy season, neap tide) (n=28)										
Mean	3,19	2,91	1,19	0,57	32,8	0,20	1,25	11,85	174,0	39
s.d.	0,79	0,98	0,3	0,51	4,2	0,19	0,74	7,48	26,38	24
Range	2,3 -6,7	0,92 -5,55	0,56 -1,98	0,1 -2,9	24,2 -37,8	0,10 -0,84	0,31-3,94	2,1 -44,9	62,6 -205,5	20 -89
24 February 2001 (rainy season, spring tide) (n=28)										
Mean	2,19	8,41	0,69	0,35	17,56	0,32	0,58	19,90	123,6	29
s.d.	0,38	2,58	0,29	0,29	11,49	0,22	0,38	16,23	53,15	15
Range	1,4 - 3,7	1,9 -23,4	0,16 -1,48	0,04 -1,02	2,71 -33,75	0,08 -0,86	0,08 - 2,45	1,8 -57,4	21,2 -203,9	5 - 46

s.d.: standard deviation, n: number of samples.

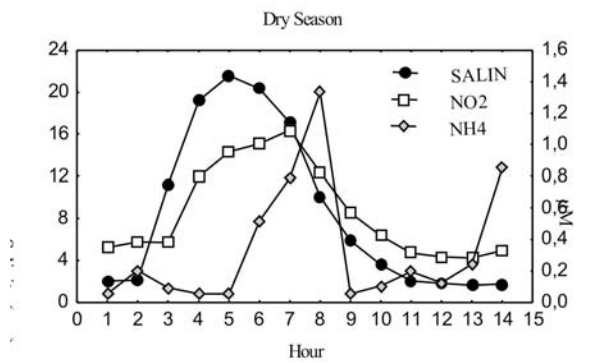

Figure 4. NH_4 and NO_2 variation during the spring tides (25/10/00).

the test was statistically significant for all the studied elements; the only exception was the DOP (P=0,13) and the DON (P=0,10). Concerning the physico-chemical parameters, it was observed seasonal variation for pH and temperature. The average pH was 8.21 and 7.22 in the dry and rainy periods respectively, and the average temperature was 26.3ºC in October/2000 and 29.5ºC in February/2001. All the data was statistically correlated using the Pearson coefficient ($P<0.05$). Based on this data it was possible to show that in the dry period the penetration of the marine waters inside the estuary is probably promoting the decrease of PO_4 (-0,44), NO_3 (-0,74) and Si (-0,75). During the rainy period the salinity presented a significant correlation with NO_3 (-0,62), Si (-0,71) and with DOC (-0,54).

DISCUSSION

The hydrographic conditions of the Paraíba do Sul River estuary are closely related with the seasonal variations. As well as in other Brazilian and world rivers and bays, it's accepted that nutrient concentrations have risen over the last 50 years as a consequence of agricultural practices (excess of fertilizers) and the discharges of urban wastewaters (SIERRA *et al.*, 2002; VALIELA and BOWEN, 2002). As already observed in other tropical estuaries, there is a general trend showing an increase in the nutrient concentration in the rainy season mainly due to the riverine input that also raises during this time of the year (EYRE, 1994). Once mixed with marine waters, inorganic nutrients are progressively transformed along the salinity gradient and, the complex biogeochemical processes occur in the low salinity (0 - 10) (RAGUENEAU *et al.*, 2002). During periods of high riverine discharges estuarine water column is expected to be highly stratified, this trend was not observed in the Paraíba do Sul Estuary. The main reasons for the water column homogeneity are probably the low depths of the estuary (maximum depth of the estuary channel is 6.5m) and the adjacent continental shelf; The low tidal amplitude (spring tide average variation is 0.65 m) and the presence of sand banks in front of the estuary mouth. Therefore, according to SCHETTINI (2001) although dominated by fluvial waters the friction forces on the PSR estuary are

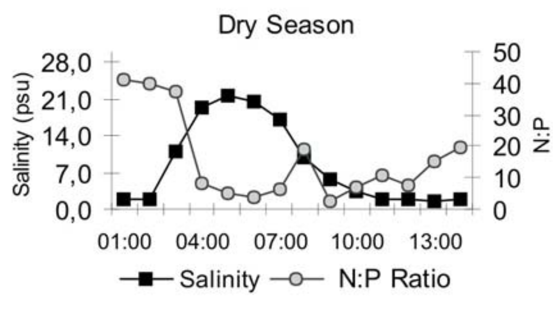

Figure 5. N:P ratio distribution during the dry season spring tide.

Table 2. *P values obtained with the T-test for nutrients, DOC and Clorophyll a. P 0,05 in bold represent significant correlation at 5% confidence level between dry and rainy periods.*

T- Test	
DOC	**0,006**
P-PO_4	**0,0000**
DOP	0,130
N-NO_3	**0,00003**
N-NO_2	**0,00033**
DON	0,108
N-NH_4	**0,0005**
Si $(OH)_4$	**0,0000**
Chl-a	**0,0000**

sufficient to maintain the homogeneity of the water column practically all the time.

Nutrient Dynamic in Dry Season

According to several authors (SILVA, 2000; TIAN *et al.,* 1993; KRESS *et al.*, 2002) during the dry period the primary productivity tend to be enhanced mainly due to a lower turbidity of the system, causing a raise of the Chl-a and dissolved oxygen concentrations in the water column.

During this period the DON was predominant nitrogen from in the PSR estuary, probably reflecting the raise in the activities of sugarcane and alcohol factories, enhancing the effluent discharges with high organic matter content to the riverbed. In addition the lower water level decreases the dilution effect (FIGUEIREDO, 1999). The interference of the salt wedge on the DON concentrations were better observed during the spring tide (25/10/00) when the values drop from 50.65 μM to 16.41μM three hours after the beginning of the ebb tide. The dilution effect observed for DON is indicating a conservative behavior, the same pattern was observed for NO_3, which decreased its concentrations from 16.84 μM when the salinity was 2.0 psu to 0.46μM when the salinity reaches 20.34 psu. CARNEIRO (1998) also observed the same behavior in the Paraíba do Sul Estuary in March and July 1995. PAKULSKI *et al*. (2000), based in the DIN and DON distribution, suggested that the increment of DON in relation to the DIN in intermediate salinities is probably associated with the transformation of the nitrate in DON mediated by the phytoplankton assimilation. The average NO_3 concentrations obtained in this study were higher than the values observed for other tropical estuaries during the dry period as the Moresby River in Australia (EYRE, 1994) and the Nicoya Gulf in Costa Rica (KRESS *et al.*, 2002), both under environmental stress. Concerning the NH_4 distribution the low observed concentrations followed the same pattern described for the Nicoya Gulf, which presented negligible values (KRESS *et al.*, 2002). A tendency of increasing concentrations following the salinity gradient was observed for NO_2 and NH_4 (Figure 5), is probably due to the release of interstitial waters from the estuarine sediments that are enriched in these elements (Turner, 1990) was also observed by CARNEIRO (1998) in the Paraíba do Sul Estuary.

Phosphate concentrations presented a slightly increase in low salinity (2 - 5 psu) decreasing its concentrations in higher salinities. The mechanisms that include the PO_4 dynamics and its other chemical forms in the Paraíba do Sul estuary seems to be more related to chemical processes, considering the salinity gradient and the pH changes. Many authors suggested that a buffer mechanism is probably regulating the PO_4 concentrations between 0.6 1.4 μM in estuarine systems. This mechanism is based in the adsorption/desorption of the PO_4 from the suspended particulate matter and sediments when the concentrations are low. The process is reversible and mainly controlled by the pH variation (below 7.8 the PO_4 removal is intensified), followed by other factors as the SPM and sediments concentration, biological activity and residence time

(EYRE, 1994; FOX *et al.*, 1986, FANG, 2000; RAGUENEAU *et al.,* 2002). Concerning the PO^4 adsorption on iron hydroxides, assumed to be the most important inorganic phosphorous removal process between salinities of 5 15 psu (FOX, 1990; FANG, 2000) the absence of the iron concentrations data do not allowed any speculations about it. Although the presence of iron enriched soils in the PSR drainage basin may contribute to the iron input for the estuary, probably becoming an important factor in the phosphate removal process (CARVALHO *et al.*, 2002). The dissolved organic fraction (DOP) is probably associated with the raise of the organic matter during this period of the year, as indicated by the COD distribution. The other possible DOP source to the estuary is probably the primary production, also higher during the dry period (FANG, 2000, CARNEIRO, 1998). Finally the increasing DIP concentration in the water column is probably reflecting the sediment ressuspension and the ortophosphate desorption, once the DOP values are low and a possible conversion of DOP into DIP seems to be improbable due to the small importance of the organic fraction in the total dissolved phosphorous. The phosphorous values measured in the present study are in the same range of other studies developed in tropical estuarine systems of Brazil and other tropical countries (FANG, 2000; KRESS *et al*., 2002), STERZA, 2002; PEREIRA-FILHO *et al.*, 2001 and SIERRA *et al.*, 2002).

The COD that generally present a conservative behavior in the PSR estuary present a clear tendency to raise its concentrations with the ebb tide (3,15 $mg.l^{-1}$ when the salinity was 5,8 psu increasing to 4,0 $mg.l^{-1}$ when the salinity reaches 1,7 psu). The COD behavior, as well as the concentration range follows other studies previously developed in the PSR Estuary (CALASANS *et al.*, 1995 and CARNEIRO, 1998)

Although high Chl-a concentrations were measured, the Si concentrations were lower than the observed during the rainy period, probably indicating that the main Si source for the estuary are the intemperism processes, as soil lixiviation and the flood of marginal inundated soils, that generally occurs during high river discharge periods (KRESS *et al*., 2002; SILVA, 2000).

Nutrient Dynamic in Rainy Season

With the beginning of the rainy season and the raise of the river discharge, the river became the most important source of nutrients for the estuary. During the rainy season the mixing of the distinct water masses play a secondary role as source of the studied nutrient, mainly due to the low tidal amplitude and the homogeneity of the water column.

The Chl-a distribution followed a distinct pattern when compared with the dry period. Peaks of high Chl-a concentrations were observed just after the peak of the flood tide. This behavior have already been observed by PEREIRA-FILHO *et al.* (2001) for the Camburiú River Estuary (SC, Brazil), and the probable explanation for this behavior is the occurrence of a very high productive zone near the estuarine mouth. During the flood tide part of this phytoplankton enriched water is probably entering the main estuarine channel causing the increment of the Chl-a after the flood tide.

The NO3 became the main nitrogen form present in the estuary, been basically related to the input from the surface runoff for the riverine system. According to YIN *et al.* (1995) and HERNANDEZ-AYON *et al.* (1993), that studied estuaries in Canada and in the USA, when the high river discharge period started no physical or biological processes (e.g. mineralization and the phytoplankton activity) are capable to alter the NO_3 concentration in estuarine waters. According to CARNEIRO (1998) the NO_3 in the PSR estuary is quickly transported trough the estuary not being available to the reactions and transformations along the mixing zone. The same situation could probably be applied for DON and NH_4 that most of the time presented a conservative behavior, with moments of gain and lost without a clear trend. In addition, the low Chl-a concentrations did not support the hypothesis of a significant release of this nitrogen forms from primary producers, to the water column. Concerning the NO_2 and NH_4 distribution, peaks of these elements were observed in the end of the flood tide, and are directly correlated with the decrease in the dissolved oxygen concentrations, probably suggesting the reduction of the NO_3 associated with the bottom sediments (ZHANG *et al.*, 1999).

Higher PO_4 concentrations are generally expected in the rainy season mainly due to the input caused by the surface runoff along the drainage basin as well as by the flood of the plain river margins, where cattle farming and agriculture are developed, enhancing the transport of the material accumulated during the dry season to the river bed (SILVA, 2000). In the rainy season a significant correlation between PO_4 and pH was observed (0.43), this correlation is probably indicating that the PO4 removal mediated by the pH that was described for the dry period is also occurring. The dissolved organic form (DOP) presented peaks of concentration during the flood tide, this fact in addition to the Chl-a data is probably indicating that a small fraction of the fluvial PO_4 is being transformed in DOP by the assimilation and transformation caused by the primary producers (PAKULSKI *et al.*, 2000).

Althought DOC concentration were expected to be higher during the rainy season (CARNEIRO, 1998; FIGUEIREDO, 1999), in the present study the values were a little bit higher during the dry season. This trend was probably due to the more intense penetration of the salt wedge in 24/02 (spring tide), when the DOC concentrations decreased during the flood tide, from 2.5 $mg.L^{-1}$ to 1.5 $mg.L^{-1}$. Besides that, the PSR discharge during this sampling was lower than the historical average for the rainy season. Therefore a statistical difference was expected between dry and rainy season, althoght not with lower concentrations during the rainy season.

BESSA and PAREDES (1990) studing the São Francisco River already observed lower DOC concentrations during the dry season. These authors attributed this behavior to the intense evaporation of the river waters, and consequently increase of the organic matter, as well as the decomposition of the ressuspended particulate organic matter.

The silica values were inside the range already observed for some estuarine systems (CABEÇADAS *et al.*, 1999; TIAN *et al.*, 1993) and higher than other estuaries (HASSEN, 2001; HERNANDEZ-AYON *et al.*, 1993; PAKULSKI *et al.*, 2000; PEREIRA-FILHO *et al.,* 2001 and CORBETT *et al.*, 2002). Although Si presented a conservative behavior, a significative correlation with NO_3 (0.61) is probably indicating that part of the silica concentration is being removed by the biological assimilation (EYRE, 1994).

Concenning the tidal influence, Si concentrations tend to decrease with increasing salinity (CORBETT *et al.*, 2002; PEREIRA-FILHO *et al.*, 2001; RAGUENEAU *et al.*, 2002).

Finally, according to Zhang (1999), the Si/N ratio that could interfere in the primary production (= 0,5 1), variate between 5 and 7 during all samplings, suggesting that silica is not a limiting nutrient for the system. According to previous studies, the N:P ratio for the Paraíba do Sul river (62 to 496) was much higher than the PSR estuary where uit variates between 9 and 23 (CARNEIRO, 1998). In the estuarine zone under the influence of the mixing waters the observed ratio was lower (Figure 5), mainly due to the strong phosphorous desorption when compared with the DIN. The values observed in this study are inside of the range reported for others estuaries like the Vitória Bay (ES), 10 21 (STERZA, 2002), Camburiú River Estuary (SC) 12 149 (PEREIRA-FILHO *et al.*, 2001) and the Danubio River Estuary, 40 100 (RAGUENEAU *et al.,* 2002), all of them with relative antropogenic influence (domestic sewage, fertilizers, etc.).

CONCLUSION

The elements concentrations showed that the rain events are the main regulators of the nutrient, Chl-a and DOC dynamic in the PSR estuary. With exception of the PO_4, NO_2 and Nh_4 the majority of the studied elements presented a conservative behavior, being the decrease of its concentrations attributed to behavior, being the decrease of its concentrations attributed to the dillution effect caused by the mixture of marine and fluvial waters. The presented data showed that the freshwater end-member composition are comparable with other Brazilian and world rivers. The nutrient ratios could be considered as low for a polluted river, and they did not seems to increase the estuarine primary production. Independently from the river discharge, during the spring tides higher amplitudes between maximum and minimum nutrient concentrations were observed (with exception of DOC and NH_4). An influence of the tides in the primary productivity was also observed, with higher variation of the Chl-a concentrations also observed during the spring tides.

In the period of lower fluvial discharge the estuary presented the highest concentratiosn of Chl-a and the organic nutrient forms. When the discharge incresed the river became the main source of nutrients for the estuary. In this period the photosintetic activity also decreased and a consequently decrease in the dissolved oxygen was also observed. Finnaly, during the rainy period the decrease in the DON concentrations are probably associated with the mineralization processes indicated by the increase of the NH4 cocentrations during this period.

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